July, 1933

New Books

In a tiny but accurate dilatometer the change of volume with temperature was studied. The volume divided by the volume at 4° is given at several even temperatures in Table II, while the individual measure-

TABLE II t 5 10 15 20 25 30 35 40 V_4^t 0.99987 0.99948 0.99958 1.00016 1.00111 1.00243 1.00415 1.00605

ments (corrected for the expansion of Pyrex glass according to Buffington and Latimer [THIS JOURNAL, **48**, 2305 (1926)]) are shown in the figure. Like common water there is a temperature of maximum density which for H^2H^2O is about 11.6° .

In the various respects in which water is said to be an abnormal liquid $H^{2}H^{2}O$ seems to be more abnormal, but the differences between the two become smaller with rising temperature.

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NEW BOOKS

Qualitative Chemical Analysis. Certain Principles and Methods Used in Identifying Inorganic Substances together with a Systematic Survey of the Chemistry of these Materials. Based upon the Text by A. B. Prescott and O. C. Johnson. By Rov K. MCALPINE AND BYRON A. SOULE, University of Michigan. D. Van Nostrand Company, Inc., 250 Fourth Ave., New York, 1933. xii + 696 pp. 15.5 × 23.5 cm. Price, \$4.50.

"The remarkable vitality of the older book," to quote the authors, is well illustrated by the ruinous condition of the copy accessible to the classes of the undersigned. In the present revision, the sections dealing with properties, reactions and detection of elements and compounds have been modernized, and amplified so as to include practically all the atomic types as well as many of the less common anions. Inert gases, only, are omitted. Systematic and detailed directions are now given for separation and detection of twenty-three common cations and about the same number of anions. Although it would not at first be clear how to extend this scheme so as to analyze any imaginable mixture, the student could at once detect the rarer cations or anions occurring alone or in the presence of a very few others. Thereafter his resourcefulness would increase with his grasp of the data supplied. To this extent the discipline of the older book, which often left the analyst to invent his own procedure, is preserved.

A hundred and forty pages now recount principles and theories underlying qualitative analysis. Recent interpretations are duly mentioned, but the classical point of view predominates. This section is clear and helpful. More emphasis might well be laid, in so extended a discussion, upon dispersion and coagulation. New Books

The reference list is full, well chosen, and up-to-date, presenting both sides of controversial matters. Numerous tables give solubilities, dissociation constants, delicacy of tests, and so on. At the end there is a summarized index in a novel form.

Supplying, as it does, sound and pertinent data upon all aspects of the subject, as well as detailed suggestions for applications, this book will prove highly valuable in professional as well as educational laboratories.

G. S. Forbes

The Sorption of Gases and Vapours by Solids. By JAMES WILLIAM MCBAIN, F.R.S., Professor of Chemistry at Stanford University, California. George Routledge and Sons, Ltd., Broadway House, 68-74 Carter Lane, London, E. C. 4, 1932. xii + 577 pp. 151 figs. 14 × 22 cm. Price, 25/0 net.

This book consists of three parts. Part I gives an historical survey of the subject, a general description of the phenomena involved and of methods for the measurement of sorption. Part II, which constitutes the bulk of the volume, presents the experimental data. Separate chapters are devoted to sorption by charcoal, zeolites, silica gel, etc., glass, impermeable crystalline substances and metals. There are also chapters in this part dealing with the thickness of adsorbed films, mobility within such films, heat of sorption, etc. Part III discusses in some six chapters the various hypotheses and theories of sorption.

The author has been successful in his presentation of the subject in two important respects. In the first place, he has made a surprisingly complete collection of the literature of this very extensive field. While of course the more recent items of this literature receive the most consideration, the author has not neglected the older exploratory researches and thus has maintained a same perspective. The text is replete with tables where the data of many investigators are presented on a common basis, and there must be at least a thousand footnote references to the literature.

In the second place, the author's presentation is discriminating and critical; the book is not a mere compilation. The diction is lively and reflects the patent enthusiasm of the author for his subject; it is also terse and to the point, for the author evidently does not wish to waste either his time or that of his readers.

All told, the volume is a valuable contribution to the literature of physical chemistry and is indispensable to anyone particularly concerned with the phenomena it discusses. It should not only stimulate research by calling attention, as it does, to so many unsolved problems, but by its full presentation of previous work should save investigators from many false starts.

Arthur B. Lamb

Über den Mechanismus intra- und intermolekularer Reaktionen. Theorie des Ringtausches. (On the Mechanism of Intra and Inter Molecular Reactions. The Theory of Ring Fission.) By JOHANNES SIELISCH AND EVA GRUND. Verlag Walter Blank, Derfflingerstrasse 15, Berlin W 35, Germany, 1932. 121 pp. 15.5 × 23 cm.

The monograph represents an attempt by the authors to provide a uniform conception of reaction mechanism in the form of a "theory of simple and more complex substitution" by the aid of which "so-called abnormal reactions . . . and in particular the formation of by-products may be predicted."

The theory, in brief, assumes that "a reaction can only take place when all of the related participating atoms are able to approach one another so that an interaction takes place as a result of interchange of valency unions." In this way there ensues ring formation of the active atoms in question.

The authors, in other words, postulate as a principle in all organic reactions, the primary formation of a more or less unstable ring through the agency of an interchange of valency forces, which ring is then capable of undergoing "ring fission" to yield the new products.

The idea is not new, as admitted by the authors [Ann., 316, 53 (1901); see also THIS JOURNAL, 45, 740 (1923); 51, 1509 (1929)] but hitherto the hypothetical rings in question have been regarded as possessing in general, a five- or six-membered ring structure.

By assuming the intermediate formation of a much wider variety of homo- and heterocyclic unstable ring compounds, they are able to bring a very wide group of organic reactions under a general scheme of classification.

While the assumptions made as to the actual existence of these intermediate rings belong, in general, to the realm of speculation, it would seem highly probable that they are actually formed in many cases. In any event the authors have assembled a large and interesting group of highly diverse organic chemical reactions under a general scheme of primary ring formation followed by ring fission. The book can be recommended to all interested in the mechanism of organic reactions.

HAROLD HIBBERT

Drehung der Polarisationsebene des Lichtes. (Rotation of the Plane of Polarization of Light.) By W. KUHN AND K. FREUDENBERG. Vol. III, Part III of "Handund Jahresbuch der chemische Physik." Edited by Prof. Dr. A. EUCKEN AND Prof. Dr. K. L. WOLF. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany, 1932. ii + 142 pp. 37 figs. 17.5 × 25.5 cm. Price, M. 12.80.

This monograph is practically identical with the chapter written by Kuhn for "Stereochemie" edited by K. Freudenberg. Werner Kuhn has rendered a great service to chemistry and particularly to organic chemistry by presenting the general theories of Born, Oseen and others in a simplified form. The fundamental idea of Kuhn's theory is the generally accepted conception that optical rotation of a molecule similarly to its refraction is an additive function of the frequencies (Eigenschwinkungen) of the absorption bands. The contribution of a given band to the molecular rotation differs from the contribution to the refraction principally by one factor, which is termed by Kuhn the factor of anisotropy. This represents the relative difference between the absorption within a given band for the levo and dextro circularly polarized light: $g_k = (\epsilon_e - \epsilon_d)/\epsilon_k$.

The origin of anisotropy in the band Kuhn explains on the basis of a simple visual model in which the vibrations of two resonators are coupled, the resonators being at a finite distance from each other and the directions of vibration perpendicular to each other. This system is affected differently by levo or dextro circularly polarized light, thus giving rise to anisotropy. In the case of a system composed of only two coupled bands, the factors of anisotropy are of opposite sign. Kuhn later extends the consideration of the system of two bands to one consisting of a higher number of coupled absorption bands.

The theory further states that for each band the product $f_k g_k$ (strength of band by the factor of anisotropy) is of the same order of magnitude. On the basis of this consideration and of the further consideration that the sum of $f_k g_k / v_k = 0$, Kuhn reaches the conclusion that the anisotropy of the bands nearest to the visible furnishes the principal contribution for the rotation in the visible part of the spectrum. New Books

The anisotropy of each band resulting from the coupling with other bands Kuhn refers to as *induced* anisotropy and the inducing function of the neighboring groups is referred to as the *vicinal* function. Thus, when the attention is centered on the contribution furnished by a given absorption band, Kuhn speaks of the induced anisotropy of this band and when he considers the influence of the same band on the anisotropy of the neighboring band, he speaks of its vicinal effect.

Of the one hundred and forty odd pages of the monograph, forty are devoted to recapitulation of the fundamentals of the stereochemical concepts. Fifty pages are devoted to the mathematical treatment of the theory arrived at on the basis of the mechanical model of Kuhn. The treatment is very rigorous. The remaining fifty pages are devoted in the main to the application of the concepts developed in the theoretical part to the interpretation of older observations relating to chemical structure and optical activity, principally to a more rational interpretation of the empirical rules connecting molecular configuration with optical rotation. The treatment of the material of this part of the monograph is less rigorous and less objective.

As has been already stated, the monograph represents only one chapter of the larger book, "Stereochemie," edited by K. Freudenberg. The latter publication contains an additional chapter written by Freudenberg devoted to a more extensive discussion of the bearing of the theory on the problems of organic chemistry.

In the present state of knowledge, it is difficult to state whether the model of Kuhn will be capable of explaining all the complexities which arise even in the simplest molecules containing one asymmetric center only. Be this as it may, Kuhn has rendered a great service to chemistry by stressing the importance of the analysis of the effect of structure not on the rotation of the molecule as a whole, but on the anisotropy of as many component parts as are accessible to analysis. Much of the older work on rotatory dispersion will have to be re-investigated in accordance with the new concepts. The monograph of Kuhn will be indispensable to all those interested in stereochemistry who do not possess the larger book, the "Stereochemie" edited by K. Freudenberg.

P. A. LEVENE

Lehrbuch der organischen Chemie. (Textbook of Organic Chemistry.) By PAUL KARRER, Professor at the University of Zurich. Third, revised and enlarged edition. Georg Thieme Verlag, Antonstrasse 15/19, Leipzig C 1, Germany, 1933. xxiii + 922 pp. 8 figs. 17 × 25 cm. Price, RM. 34; bound, RM. 36.

In the preface to the third edition of his highly successful textbook Professor Karrer comments on the surprising number of fundamental questions on which the point of view has changed in the brief time since the publication of the last edition. Naturally these changes have been greatest in the case of those classes of organic compounds which have been most actively investigated—the carotinoids, vitamines, hormones, chlorophylls, and other natural products. Here the changes have been sufficiently significant to necessitate extensive revision and expansion of the text.

Professor Karrer has not confined his attention to these special topics. Minor revisions and insertions—like the structural formula of glutathione, the stereochemistry of N-phenylpyrroles, and the polymerization of chloroprene—show that the entire text has been carefully reëxamined and, wherever necessary, altered to meet our present knowledge. The third edition can therefore be recommended as heartily as was the second.

E. P. Kohler