

chromatography for reaction kinetics studies (pp. 378-381), the two most important basic references^{3,4} are missing.

When discussing the flame ionization detector, the presentation of some basic plots (*e.g.*, response *vs.* H₂/O₂ ratio, etc.) is recommended. It is true that the authors refer to some publications where such plots can be found, but they belong to the basic discussion of this type of detector and the visualization of these correlations is a great help for the average reader.

I disagree with the present place of the chapter on "capillary" columns (pp. 267-284) (they should be discussed right after the performance of packed columns) and with the use of the term "capillary columns." These particular columns are not restricted at all to capillary diameters; on the other hand, their theoretical treatment (discussed in this chapter) is not valid for packed capillary columns, which are also described recently in the literature. Thus, the authors have to use once (p. 267) the absurd expression of "capillary capillary column." The correct term is "open tubular columns" which can be prepared in a wide variety of diameters from capillary dimensions up. For sake of historical accuracy, I want to mention that in my opinion, Dr. Martin's "prediction" (p. 267) did not refer to *open tubular* columns.

I do not understand why Golay's expression⁵ for the possible minimum HETP of open tubular columns

$$\text{HETP}_{\min} = r \sqrt{\frac{1 + 6k + 11k^2}{3(1 + k)^2}}$$

(where r is the column radius and k the partition (capacity) ratio) is not mentioned during the discussion of the theory of these columns. It describes excellently the influence of the open tube's radius and of the peak's relative position, and it is also very useful when studying actual column performances in comparison with the possible ideal values.

The chapter on the separation of high boiling compounds (pp. 285-299) is evidently an earlier part of the manuscript. Today, such a detailed chapter would not be necessary, since most of the new commercial chromatographs can be used up to 3-400°; thus, only the differences in the applicable liquid phases deserve a brief discussion. This could, however, be done as well during the general discussion of the liquid phases.

The chapter on trace analysis (pp. 300-318) is very useful, and particularly the discussion of the correlation of sensitivity and column resolution, since most people like to think *only* of the detector when dealing with trace analysis. The sensitivity of the ionization detectors (p. 307) would deserve a little more detailed discussion, and the possibilities of increasing the sensitivity of such GC systems by increasing the flow rate should be mentioned; the ionization detectors namely differ in this fact from the TC cells. The references on low temperature trapping (pp. 310-311) and on the use of precolumns (pp. 311-313) and the discussion of some techniques are somewhat mixed-up. One reference⁶ belongs to low temperature trapping and has nothing to do with the subtraction technique; on the other hand, the latter method⁷⁻¹⁰ was aimed rather for sample component identification than for application in trace analysis. Further, when quoting the work of Krejčí, *et al.* (p. 313), the explanation is incorrect because, argon and oxygen *can* be resolved on a Molecular Sieve 5A column if it is sufficiently long and is used at low temperatures.

As mentioned, these remarks do not intend to reduce the value of the book. I want to repeat my opinion that the present book is very valuable for the practice and is highly recommended to the practical gas chromatographers.

(3) R. J. Kokes, H. Tobin, Jr., and P. H. Emmett, *J. Am. Chem. Soc.*, **77**, 5860 (1955).

(4) W. K. Hall and P. H. Emmett, *ibid.*, **79**, 2091 (1957).

(5) M. J. E. Golay, in "Gas Chromatography 1958," ed. by D. H. Desty, Butterworths, London, 1958, pp. 36-55.

(6) N. Brenner and L. S. Ettre, *Anal. Chem.*, **31**, 1815 (1959).

(7) N. Brenner and V. J. Coates, *Nature*, **182**, 1401 (1958).

(8) B. T. Whitham, *ibid.*, **182**, 391 (1958).

(9) N. Brenner, E. Cieplinski, L. S. Ettre and V. J. Coates, *J. Chromatography*, **3**, 230 (1960).

(10) L. S. Ettre and N. Brenner, *ibid.*, **3**, 235 (1960).

GC INSTRUMENT APPLICATIONS
THE PERKIN-ELMER CORPORATION
NORWALK, CONNECTICUT

L. S. ETTRE

Gas Chromatography. By JOHN H. KNOX, Lecturer in Chemistry in the University of Edinburgh. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1962. viii + 126 pp. 12.5 × 19 cm. Price, \$3.25.

The number of textbooks on gas chromatography is growing, but most of them are general textbooks. The present small booklet intends to serve as a *short compilation* of the subject.

The book is divided into seven chapters. After a brief introduction, the theory of gas chromatographic separation is discussed in a separate chapter followed by information on columns

and column packings, detectors, ancillary equipment and special gas chromatographic methods. The book is concluded by a short description of the most important GC books and a good subject index.

As mentioned in the preface of the book, its purpose is to give an adequate coverage to the new aspects (capillary columns and ionization detectors), and to present at the same time the basic principles of gas chromatography with sufficient details on apparatus construction in order to allow the reader the fabrication of his own instrument. In my opinion, the most objectionable part of the book is exactly this intention. I do not believe that the very brief descriptions on the construction of different instrumental parts are sufficient for somebody who actually wants to build his own instrument; at the same time, the philosophy that it is very easy to build a gas chromatograph results in some oversimplification. For example, when mentioning temperature programming (pp. 106-110), the author is forced to the very objectionable remark that precise control of the programming is really not required because otherwise he could not recommend simplified solutions for a home-made instrument. My feeling is that the usefulness of the book could be improved if more emphasis would be taken on the operation of the instruments and on the practical interpretation of the theories, and less on the possibilities of instrument building.

Besides this general problem, the book is a very useful brief discussion of the subject, and it can easily be read. In some details, however, I do not agree fully with the author's remarks.

It is not true that the katharometer detector was introduced in gas chromatography by Ray (p. 4). The first gas (solid) chromatographs consisting of a sampling device, a column and a katharometer detector were built by Cremer, Prior and Müller in the second part of the forties, and they even exhibited a primitive breadboard model at the 1952ACHEMA exhibition in Frankfurt.

It is not fully understood what the author means under the "same speed" of packed and open tubular ("capillary") columns (p. 7). If it means the column performance, I am in disagreement, because Golay proved that an open tubular column has fundamentally a better performance. I also have to repeat my remark made in the previous review on the name "capillary columns": This expression is incorrect and the term "open tubular columns" should rather be used.

The discussion of the support materials (pp. 45-47) is somewhat restricted; a very detailed method is given on how to silver plate or coat with polymer the Firebrick, but at the same time, the different kinds of diatomaceous earth-type supports (*e.g.*, the Chromosorb series) are not mentioned at all (except Celite) although they belong in a practical handbook. The very important method of silane-treatment (which is much more important than the silver plating) of the support is missing, although it should at least be mentioned.

The given temperature limits of the liquid phases are sometimes too conservative; *e.g.*, polypropylene glycols can be used up to at least 150° and not only up to 120° (p. 50). Some given values are contradictory to each other: *e.g.*, dimethyl sulfolane can be used at room temperature (p. 53) and not only up to 0° (p. 50).

When discussing the flame ionization detector (p. 74), it is incorrect that a H₂/N₂ mixture is used as carrier gas; the hydrogen is usually mixed only with the column effluent. Besides this one question, however, the author was very successful in the short compilation of the detectors, and particularly of the ionization detectors; this is the best part of the book. I just want to correct on p. 69 the reference to Fig. 4.1 which is a printing error: It should read, Fig. 4.2.

I could not understand why a T-shape construction is recommended for the sample splitter with the open tubular columns (p. 95 and Fig. 5.8): It has been proved in the literature and practice that this construction of the splitting device gives usually a non-linear splitting.

Finally, I would like to make two general remarks. The first refers to the symbols used in the book. It is very unfortunate that many of them not only differ from the recommended I.U.P.A.C. nomenclature, but some are even used in a quite different meaning. The most disturbing is the use of K as the capacity coefficient (ratio) while in most other publications, as well as in the I.U.P.A.C. nomenclature, K is reserved for the partition coefficient and k is used for the capacity ratio. At the same time, the book is using α as the partition coefficient (instead of K), although in other publications, α is usually the symbol for the relative retention. It would be most welcome if the different publications would agree on generally accepted symbols.

My second remark concerns the references. I understand and accept the intentions of the author not to give a detailed literature survey but only a few references after each chapter as selected literature (there are altogether only 43 references in the whole book). However, even so, some other publications should definitely be quoted: for example, those of Giddings in the theoretical part or the results of Bayer at the discussion of preparative columns. Besides this, it is interesting to note that although

the preface of the author is dated September, 1961, all references except one (which is from the January, 1961, issue of *Analytical Chemistry*) refer to publications through 1960, and this cannot be accidental. My impression is that the manuscript was compiled late in 1960 or early in 1961, and it took more than one year until it was published. In this respect, I would like to refer again to my earlier remarks in the previous book review: If fast publication is necessary in a general textbook, it is even more important in a short handbook.

Despite certain limitations, the book of Dr. Knox contains much valuable information and gives a good compilation of difficult questions, the knowledge of which is necessary in the everyday work; therefore, the book belongs in the library of the practical gas chromatographer.

GC INSTRUMENT APPLICATIONS
THE PERKIN-ELMER CORPORATION
NORWALK, CONNECTICUT

L. S. ETTRE

Biochemical Mechanisms. By LLOYD L. INGRAHAM, Department of Biochemistry and Biophysics, University of California, Davis, California. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1962. x + 108 pp. 15.5 × 23.5 cm. Price, \$5.75.

This book represents a birds eye view of biochemical mechanisms, albeit from a considerable height. The first part of the book consists of a review of atomic orbitals, bonding, conjugated systems, ligand field theory, transition states, ionic reactions, displacement reactions, concerted reactions, metals as acid catalysts, charge transfer complexes and "high energy" bonds in the course of 30 pages, presumably to enable the reader to grasp the second part, which consists of a more detailed discussion of specific mechanisms of different types of reaction. The usefulness of the first part for the average biochemist is open to question, especially in the case of more recent developments. Thus, for example, the treatment of charge transfer complexes occupies less than one page.

The reaction mechanisms put forward are lucidly explained and alternate possibilities are pointed out, although for an introductory treatment of this type perhaps too many of the proposed schemes are of a speculative nature. It is interesting to consider how even within a single year after publication, some of the proposed mechanisms have been disproved and others confirmed. Thus the mechanisms for rearrangements catalyzed by vitamin B₁₂ discussed on pp. 100, 101, and 102 cannot be correct since it has now been shown that these reactions are not accompanied by deuterium uptake from a D₂O medium (Barker, *Fed. Proc.* 20, 956 (1961), and Overath, *et al.*, *Biochem. Z.*, 335, 500 (1962)). Similarly, on p. 63 the view is expressed that the decarboxylation of prephenic acid, if concerted, would require a *trans* configuration for the COOH and OH groups. Plieninger (*Z. Naturforsch.*, 16b, 81(1961)) has now shown, however, that the stereochemical relationship between these two groups in prephenic acid is *cis*. On the other hand, Lindberg, *et al.* (*Biochemistry*, 1, 182 (1962)) have confirmed the mechanism of the decarboxylation of mevalonic acid 5-pyrophosphate described in the same section.

It is also regrettable that there are a considerable number of what are presumably printing errors in the labeling of formulas and in the equations; *e.g.*, on p. 69 the equation contains 2 Fe on one side and 3 on the other, and on p. 71, the second reaction is obviously meant to lead to the formation of a ferryl ion and not FeO⁺.

Perhaps the most valuable part of this presentation are the references, quoted in connection with each reaction mechanism, which will lead the conscientious student to a more thorough contemplation of the subject.

DEPARTMENT OF BIOCHEMISTRY
COLLEGE OF PHYSICIANS AND SURGEONS
COLUMBIA UNIVERSITY
NEW YORK, NEW YORK

REINHOLD BENESCH
MILON SPRECHER

L'oxydation des métaux. Tome I. Processus fondamentaux. Sous la direction de JACQUES BÉNARD, Professeur à la Faculté des Sciences de Paris. Avec la collaboration de JEAN BARDOLE, FLORENT BOUILLON, MICHEL CAGNET, JEAN MOREAU et GABRIEL VALENSI. Gauthier-Villars et Cie., 55, Quai des Grands-Augustins, Paris 6, France. 1962. 465 pp. 16.5 × 24.5 cm. Price, NF. 55.

The rapid development of ideas and theories in the field of oxidation of metals has led to the publication, in 1962, of two important books dealing with this subject matter: the one under review and a second, thoroughly revised edition of Kubaschewski's and Hopkins' standard monography. The reviewer has read both with infinite pleasure and found them to be complementary. Both should be consulted frequently by any one interested in the mechanism of gas-solid reactions.

The book edited by Prof. Bénard, whose fundamental work on many aspects of oxidation is universally appreciated, is the result of the coöperation of many authors. But they have clearly worked as a team, comparing results and exchanging ideas, so that there is little duplication and the unavoidable heterogeneity of a collective enterprise has been reduced to a minimum.

This is not an encyclopedia, a work of compilation, and the book should complement rather than replace older ones.

The classical theories of Wagner, Mott and Cabrera, and others are adequately summarized but more stress is laid on recently discovered facts and on new ideas. Each author dealing with his own subject puts forward his own views resulting from first-hand knowledge acquired by carrying out extensive experimental research. The authors have steered a midway course, avoiding two common pitfalls: they have resisted the temptation of considering only too simplified models, and they have not restricted themselves to purely descriptive statements. One finds in every chapter a sound and constructive criticism of experimental methods, a number of reliable data, which are classified and interpreted and a fresh and original outlook on many well known facts.

Every single chapter has its merits, but the reviewer has been particularly struck by the following ones.

Chapters II to V dealing with the adsorption of oxygen (by J. Bénard): The influence of chemisorption of oxygen on the surface structure of metals, and the importance of adsorption as a first step in the formation of an oxide layer, is clearly shown. This aspect has never been treated so exhaustively.

Chapter VI. Nucleation in oxide films (by J. Bénard): Nucleation is interpreted as resulting from the local crystallization of a primary film. Nucleation is shown to be a very general phenomenon, representing an intermediate stage between the formation of thin continuous layers at low temperatures, and thick ones, kinetically controlled by diffusion, at high temperatures.

Chapter VIII. Orientation of reaction products at the surface of a metal (by J. Bardolle): This orientation results from a superposition of *lines* rather than *planes* of maximum atomic or ionic density.

Chapter XI. Quantitative theory of the kinetics of metal oxidation (by G. Valensi): Thermodynamics of irreversible processes are applied far more thoroughly and rigorously than is usual in this field, so that this chapter should be invaluable to many readers.

Chapter XV. Various modes of oxidation of alloys (by J. Bénard and J. Moreau) and *Chapter XVI. Internal oxidation of alloys* (by J. Moreau): The importance of dissolved oxygen is discussed, and certain conclusions might be extended to the oxidation of pure metals.

Chapter XVII. The real structure of oxidation layers (by M. Cagnet): The importance of the mechanical properties of the oxide layer and of their variation with temperature is pointed out.

Finally it must be stressed that process of oxidation is followed in a logical sequence: adsorption, nucleation, thin films, thick films, oxidation of alloys, so that the book should be read from cover to cover. It is well worthy of an English translation.

As is frequently the case with French books, the printing and binding might be better, but illustrations, including microphotographs, are reasonably good, and there are few misprints.

FACULTÉ DES SCIENCES U.L.B.
50 AV. F.-D. ROOSEVELT
BRUXELLES 5, BELG.

LUCIA DE BROUCKÈRE

Physical Organic Chemistry. Second Edition. By JACK HINE, Professor of Chemistry, Georgia Institute of Technology. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1962. x + 552 pp. 16 × 23.5 cm. Price, \$11.50.

The appearance of a new edition of this well-known and widely-used textbook is an event to be welcomed. I still believe it is the best available general introduction to organic reaction mechanisms. Its judicious tone and its excellent balance between rigor and clarity inform the student without prejudicing him, and without teaching him blatant oversimplifications that he must unlearn later. This is not to say that all experts will agree with everything in the book, but all will certainly agree that Dr. Hine tries his best to be fair in controversial matters. There are times when he is a bit too reticent about expressing an opinion. I wondered, for example, just what views he does hold on hyperconjugation and on mechanisms of borderline displacement reactions.

Among the new features of this edition are the problems at the end of each chapter. Though obviously intended to meet the competition, they are by no means perfunctory, and offer ample intellectual stimulus even to the experienced worker. Another improvement is more extended coverage of kinetics and catalysis. Especially to be commended is Chapter 4 on "Quantitative Correlations of Reaction Rates and Equilibria." There is an ex-