BOOK REVIEWS

Chemical Thermodynamics. By I. PRIGOGINE, Professor in the Université Libre de Bruxelles (Faculty of Science), and R. DEFAY, Professor in the Université Libre de Bruxelles (Faculty of Applied Sciences). Translated by D. H. EVERETT, Leverhulme Professor of Inorganic and Physical Chemistry, University of Bristol; formerly Professor of Chemistry at University College, Dundee, in the University of St. Andrews. Longmans, Green and Co., Inc., 55 Fifth Avenue, New York 3, N. Y. 1954. xxxii + 543 pp. 16.5 × 24 cm. Price, $12.50.

During the last 30 years Théophile De Donder and his disciples at Brussels have developed for systems in process of chemical reaction an elegant thermodynamic formalism whose starting point is the calculation of the entropy production of such systems. The De Donder formalism in turn fits perfectly into the theory based on Onsager's profound discovery of 1931, according to which thermodynamics may be systematically and fruitfully applied to irreversible processes in general, in so far as these occur close to equilibrium. In the United States the last five years have witnessed a widening appreciation of the Onsager theory, brought about in large part by the books of De Groot and of Denbigh, and this, finally, has produced a growing interest in the contributions of the De Donder school. This interest, however, most of us have found difficult to gratify, because prior to the book under review the only account in English of De Donder's work, the "Affinity" published by De Donder and Van Rysselberghe in 1936, is very concentrated and formal in character. This barrier is now happily removed by the present book which is the principal part of what will be a comprehensive exposition. The book is a translation of Volume I of a projected work in three volumes, authored by Profs. Prigogine and Defay, and entitled (in translation) "Treatise on Thermodynamics Based on the Methods of Gibbs and De Donder." Volume I of the French original has already had two editions, of which the first consisted of two volumes of the years 1944 and 1946, respectively, and the second of a single volume of the year 1951. The translation is based on the second edition revised to include work up to the end of 1951, and contains an appendix dealing briefly with further published work up to the end of 1953. Volume II of the projected "Treatise," entitled "Surface Tension and Adsorption," has had one French edition and is due to appear in translation shortly. Volume III, entitled "Irreversible Phenomena," has not yet been published. In preparing the present translation, Prof. Everett has had the full coöperation of the authors. In order to make the work more readily assimilable by his intended readers, he has extensively modified the notation of the French original to conform with established conventions. The translation strikes me as excellent for its clarity and smoothness. Printing and proofreading are likewise exemplary. The number of misprints not covered by the short list of errata included next to p. 1 is extremely small.

The bulk of the work consists of 29 chapters with the following titles: I, Thermodynamic variables; II, Principle of the conservation of energy; III, Principle of the creation of entropy; IV, Affinity; V, Average values of the affinity; VI, Chemical potential; VII, Ideal systems and reference systems; VIII, Standard affinities; IX, The Nernst heat theorem; X, Perfect gases; XI, Real gases; XII, Condensed phases; XIII, Gibbs' phase rule and Duhem's theorem; XIV, Phase changes; XV, Thermodynamic stability; XVI, Stability and critical phenomena; XVII, Theorems of moderation; XVIII, Displacements along an equilibrium line; XIX, Equilibrium processes, relaxation phenomena and transformations of second order; XX, Solutions; XXI, Solution–vapor equilibrium; XXII, Solution–crystal equilibrium: eutectics; XXIII, Solution–crystal equilibrium: mixed crystals and addition compounds; XXIV, The thermodynamic excess functions; XXV, Regular solutions and athermal solutions; XXVI, Associated solutions; XXVII, Electrolyte solutions; XXVIII, Azeotropy; XXIX, Indifferent states.

This list bears out the title in showing that the book is far more than a résumé of the original contributions of the Brussels school. While including many of these contributions it is in fact a reworking of a major part of chemical thermodynamics from the special point of view of that school. The authors have brought together from widely scattered sources, and presented in a unified and up-to-date fashion, a great deal of highly valuable material, particularly in regard to the finer details of heterogeneous equilibrium. References to the non-Belgian literature are numerous. Many of the conclusions are illustrated by experimental data. At a number of points the discussion is deepened by brief excursions into statistical mechanics. The treatment is on the whole satisfyingly lucid. Qualified readers will, I think, find the book immensely informative, stimulating, and distinguished by a pleasant verve rare in scientific treatises. It would be good as the text for an advanced course, provided one accepts the De Donder view of chemical thermodynamics. For specialists, whether or not they accept this view, I regard the book as a "must."

The book, however, avoids almost totally the discussion of fundamental concepts. Many of these, such as state, process, equilibrium and component are taken entirely for granted. Reversibility is discussed but briefly. The Zeroth Law is not mentioned. Energy, heat, work, entropy and absolute temperature are introduced by merely postulating the relations $dU = dQ + dW$ and $dS \geq dQ/T$. That for systems undergoing irreversible processes the entropy becomes ill defined is briefly considered, but that the same is true for the temperature is not mentioned. These remarks are intended not as criticism, but only to say that proper use of the book requires a previous study of the fundamentals.

Now I must make two criticisms. The first concerns the following statement, which occurs in the "Introduction" (p. xviii): ". . . the domain of validity of the thermodynamic treatment of irreversible phenomena . . . can be determined only by a comparison of the results of the thermodynamic treatment with those obtained by the use of statistical mechanics." I hold that the only criterion for the validity of any scientific theory outside of pure mathematics is agreement with empirical experience. Unless the latter is assured, exploration of the possibility of including the theory in another more general one seems worse than pointless. Secondly, certain important aspects of physical meaning associated with the use of that hallmark of the De Donder method, the "extent of reaction" ξ, as an independent variable, are never mentioned, and so the unsuspecting reader, charmed into a false sense of understanding by the simplicity and smoothness of the mathematics, is very likely to overlook them. Consider a homogeneous closed system in which a single chemical reaction is going on. As independent variables fixing the state we may take, as on p. 21, T, V, ξ. Now consider any partial derivative at constant ξ say $(\partial U/\partial V)_{T,\xi}$. At first sight this appears to mean that, holding T and ξ constant, we are to impose upon the system a volume change ΔV, to measure the resulting change ΔU of its energy (of course as heat plus work received), and to proceed to the limit. But then we notice that any change requiring a finite time Δt cannot in fact be carried out at constant ξ, because the reaction proceeds inexorably. The meaning of the derivative is therefore not what at first sight appears, but rather something either pretty fictitious or pretty complicated, which I cannot consider here. Now suppose that $\rho \geq 2$ chemical reactions are going on in the system simultaneously. Then we are told, as on pp. 57–58, that we may take as independent variables two "physical variables" such as S, V or T, P, and the variables $\xi_1 \cdots \xi_\rho$. But what does this mean physically? Thus, how can we vary one of the ξ's while holding all the others fast; etc.? Again, the answer is complicated. The authors do not even raise the question.

In conclusion, a few words about the De Donder view. This consists in taking *ab initio* the field of systems in which net chemical reactions are going on as the proper domain of thermodynamics, then constructing the appropriate theory, and finally treating equilibrium as a special case within this theory. From the fact that temperature and

entropy are exactly defined only for the equilibrium case, it is then clear that the De Donder theory is an inexact theory which includes an exact one as a special case. If one loves generality enough to purchase it at such a price, one has afterwards to contend with the fact that it is by no means always obvious whether a given result obtained within the exposition of the general theory belongs to the inexact or the exact category. This is particularly true of the theory of stability as expounded in Chapter XV, most of the results of which are deducible without ever attributing temperature and entropy to systems not in equilibrium. The alternative to De Donder's procedure is first to develop the exact theory of equilibrium in full, and then, as an annex, the less exact one of irreversible processes in general, in which the De Donder method would have the place of honor when it comes to chemical reactions. I may add that in the book under review almost all of the experimental illustrations pertain to equilibrium, and that this is still perfectly representative of the present relation of theory to data in thermodynamics. We are thus far from having in this book or anywhere else a proof of the intrinsic superiority of the De Donder view. Which view is better bids fair to remain for some time a matter of taste.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIF. FREDERICK O. KOENIG

Ciba Foundation Symposium on Chemistry and Biology of Pteridines. By G. E. W. WOLSTENHOLME, O.B.E., M.A., M.B., B.Ch., and MARGARET P. CAMERON, M.A., A.B.L.S. Editors for the Ciba Foundation for the Promotion of International Co-operation in Medical and Chemical Research, 41 Portland Place, London, W. 1, England. Little, Brown and Company, Publishers, Boston 6, Massachusetts. 1954. xiv + 425 pp. 14.5 × 21 cm. Price, $8.00.

The papers presented at the Ciba Foundation sponsored international conference on the chemistry and biological aspects of pteridines are combined into a single volume with transcriptions of the general discussions of the conference. The discussions in a free conversational manner are very stimulating and allow more insight and speculation into the problems and difficulties of pteridine research than would be possible in formal papers.

The initial part of the symposium was devoted to chemistry of pteridines and includes topics concerning various reactions of pteridines (ring-opening, E. C. Taylor, Jr.; alkylation, H. C. S. Wood; reduction and reoxidation, G. B. Elion), synthesis of pteridines (monosubstituted pteridines, D. J. Brown; use of *o*-aminonitroso compounds in pteridine synthesis, G. M. Timmis, D. G. I. Felton and T. S. Osdene; recent developments, E. C. Taylor, Jr., J. A. Carbon, R. B. Garland, D. R. Hoff, C. F. Howell and W. R. Sherman; sulfonamide derivatives of pteridines, M. J. Fahrenbach, K. H. Collins, M. E. Hultquist and J. M. Smith, Jr.; pyrimidopteridines, E. A. Falco and G. H. Hitchings), isolation and constitution of pteridines (urothione, R. Tschesche; pteridines of *Drosophila melanogaster*, H. S. Forrest and H. K. Mitchell; fluorescyanine, F. Korte; fluorescyanine B, M. Polonovski, R.-G. Busnel, H. Jérome and M. Martinet; structural studies on pyrimidopteridines, E. C. Taylor, Jr., C. K. Cain and H. M. Loux), physical properties (ultraviolet absorption spectra, S. F. Mason; chromatographic and electrophoretic studies, M. Polonovski, H. Jérome and P. Gonnard) and some unresolved problems (A. Albert). These excellent papers on chemistry of pteridines will assist rapidly developing research in this very important class of compounds which includes pigments of many insects and fish, vitamins and growth factors, growth-regulating agents and other biologically active substances.

The second part of the symposium was devoted to biological aspects which include topics such as the biological functions and activities of essential metabolites related to pteridines (metabolic relations between *p*-aminobenzoic acid and folic acid, D. D. Woods; function of folic acid in purine and pyrimidine biosynthesis, R. H. Nimmo-Smith; activity of folic acid and substituted pteridines for *Tetrahymena*, G. W. Kidder), clinical aspects of folic acid and related compounds (disordered folic acid metabolism in man, R. H. Girdwood, hepatic fibrosis in children with acute leukemia treated with folic acid antagonists, J. Colsky), folic acid analogs (effect on growth and cell-division of microörganisms, M. Webb; effect on embryonic development, R. Bellairs; mode of action of folic acid antagonists and the function of the *Leuconostoc citrovorum* factor, W. Jacobson), antimetabolites related to folic acid (certain 2,4-diaminopteridines, H. O. J. Collier; derivatives of condensed pyrimidine systems, G. H. Hitchings, G. B. Elion and S. Singer), pteridine metabolism (D. J. Hutchison and J. H. Burchenal), and the yellow pigment of the argentaffine cells of mammalian gastro-intestinal tract (W. Jacobson).

The papers presented contain some original work as well as reviews of previously published material. This book will be of great value to all investigators interested in pteridine chemistry and biochemistry from the various disciplines, organic chemistry, biological chemistry, cell physiology, microbiology, pharmacology, insect physiology and leukemia research, and contains authoritative viewpoints of the history and future of pteridine research. A debt of gratitude is due the Ciba Foundation for making this symposium and its record possible.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS WILLIAM SHIVE
AUSTIN 12, TEXAS

Ionography. Electrophoresis in Stabilized Media. By HUGH J. MCDONALD, D.Sc., Professor of Biochemistry, Stritch School of Medicine of Loyola University, Chicago, Ill. In collaboration with ROBERT J. LAPPE, M.S., Research Assistant, Department of Biochemistry, Loyola University, EDWARD P. MARBACH, Ph.D., Associate Chemist, American Meat Institute Foundation and Research Associate (Instructor), Department of Biochemistry, University of Chicago, ROBERT H. SPITZER, M.S., Research Assistant, Department of Biochemistry, Loyola University, and MATTHEW C. URBIN, Ph.D., Associate Chemist, Chemical Division, Corn Products Refining Company, Argo, Ill. The Year Book Publishers, Inc., 200 East Illinois Street, Chicago 11, Illinois. 1955. x + 268 pp. 14.5 × 22 cm. Price, $6.50.

The subject of this book is electrophoresis under conditions where the solvent is stabilized, *i.e.*, supported in some sort of solid medium for the purpose of preventing convection. The word *ionography* is not the universally accepted term for this kind of electrophoresis. Since filter paper is the commonest supporting medium in use, the term *paper electrophoresis* is frequently employed; Tiselius and coworkers have used the term *zone electrophoresis*; and several other terms with essentially the same meaning are in the literature. One of the purposes of the authors of this book is undoubtedly to establish the term *ionography* and several pages are devoted to its defense.

The contents of the book may be divided into three parts, as follows: (1) Description of apparatus and experimental methods. This section includes a discussion of the various ways which have been used to suspend filter paper strips with particular emphasis on the authors' own method, in which the paper strips are held in a taut horizontal position in a controlled atmosphere.

(2) Determination of mobilities and their relation to mobilities measured by the moving boundary method. In this section much of the space is devoted to theory, *e.g.*, to the effect of electroösmosis. There is lengthy criticism of the "tortuous path" theory of Kunkel and Tiselius, and a preference for the authors' own "barrier" theory.

(3) A survey of the recorded applications of the method, divided into chapters on proteins, peptides and amino acids; carbohydrates and related compounds; lipoproteins and related substances; enzymes, hormones and vitamins; inorganic substances; miscellaneous applications. The survey of the literature is very complete: the bibliography comprises 865 papers, of which only 93 are dated earlier than 1950.

The book can be criticized on a number of counts. Especially, the "barrier" theory is of dubious validity, as is evident from the summary on page 88 which states that ". . . the paper can be thought of as interposing obstacles or barriers in the migration path of the migrant. As a con-