
 BOOK REVIEWS

The Principles of Chemical Equilibrium, with Applications in Chemistry and Chemical Engineering. By KENNETH DENBIGH, M.A., D.Sc., Professor of Chemical Technology in the University of Edinburgh and of Chemical Engineering in the Heriot-Watt College, formerly University Lecturer in the Department of Chemical Engineering, Cambridge. Cambridge University Press (American Branch), 32 East 57th Street, New York 22, N. Y. 1955. xxi + 491 pp. 15 × 22 cm. Price, \$7.50.

In his preface the author states "Thermodynamics is a subject which needs to be studied not once but several times over at advancing levels. In the first round . . . a good deal of attention is given to calorimetry, before going forward to the second law. In the second or third round—such as I am concerned with in this book—it is assumed that the student is already familiar with the concepts of temperature and heat, but it is useful once again to go over the basis of the first and second laws, this time in a more logical sequence."

This is one of the best of the recent crop of texts on chemical thermodynamics. About 110 pages are devoted to a discussion of "The Principles of Thermodynamics," 220 pages to "Reaction and Phase Equilibria," and 125 pages to "Thermodynamics in Relation to the Existence of Molecules." Many problems together with answers are given. In comparison with most American texts at the same level somewhat more emphasis is given to problems of the discussion and derivation type. The numerical problems and illustrative examples worked out in the text are, to a considerable extent, related to industrial processes.

The first two sections of the text are well adapted for a one-term senior course in chemical thermodynamics for chemistry majors who have taken a sound one-year course in physical chemistry. The small amount of statistical mechanics introduced in these sections is presented as supplementary material and is not woven into the thermodynamic argument. The text is not sufficiently advanced for a graduate course for chemists, and it does not have sufficient material on the flow of fluids for a course given to chemical engineers.

The fundamental theory is well presented. The reviewer has noted a few errors and several places where the presentation could be changed. Among these we shall mention the following. The discussion of work on pp. 14 and 23 is somewhat puzzling. The author seems to believe that slowness of change is a sufficient and necessary condition for reversibility. The proof on p. 37 contains a fallacy: it is not the given system but the composite system consisting of the given system plus the Carnot engine that is connected to a single heat reservoir. The footnote on p. 37 is thus an integral part of the text and then we see that

$$\oint dw (\text{system}) + dw (\text{Carnot engine}) \neq 0.$$

And again in eq. (2.15) and (2.16) on p. 64 the work w includes the work of the Carnot engine if the temperature of the system changes in the process. The discussion at the top of p. 45 should be deleted: all we need to say about the use of the equation $dU = TdS - pdV$ for a change in state in a closed system is that it must be integrated along some reversible path connecting the initial and final states of the system. The author does not make it clear, par. 2.7, p. 74, that when the chemical potentials are defined the variations of the differentials dn_1, dn_2, \dots, dn_k must be independent. He does state that when we use the first and second law equations these differentials need not be independent. But this requires proof that the chemical potential of a constituent when considered as a component equals its potential when considered as a species. In the definition of heat capacity, p. 92, a path is not stated nor does one seem to be implied.

The section on the application of thermodynamics to various systems is, on the whole, well done. The author should consider writing a change in state rather than writing simply a chemical reaction, for, although a reaction may

have an equilibrium constant at each temperature, a free energy increase is not defined until the initial and the final states of the system are specified. There are a number of changes that a teacher using the book as a text will make, but these are usually small matters that do not detract from the effectiveness of the presentation. Figures (20), (32) and perhaps (33) should be redrawn. On p. 320 the author should warn the student against calculating ΔS and ΔC_p from half-cell changes in state. In fact there does not seem to be a discussion of the entropy of ions although their free energies and heat contents are treated.

In the section on statistical mechanics the topics treated are: statistical analogues of thermodynamic functions, the perfect gas, perfect crystals and the third law, regular solutions and adsorption, and chemical kinetics. There is a misprint in eq. (13.29), p. 401.

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Actions Chimiques et Biologiques des Radiations. First Series. By M. HAÏSSINSKY (Editor). I. Aspects Physiques de la Radiobiologie. By L. H. GRAY. II. Chimie des Radiations des Solutions Aqueuses, Aspects Actuels des Résultats Expérimentaux. By M. LEFORT. III. Modern Trends in Radiation Biochemistry. By W. M. DALE. Masson et Cie, Éditeurs, Libraires de l'Académie de Médecine, 120 Boulevard Saint-Germain, Paris VI, France. 1955. viii + 252 pp. 16.5 × 24 cm. Price, 2,800 Fr.

Chemical and biological actions induced by ionizing radiations have been extensively studied in the past decade. Great have been the strides in research in radiation chemistry and biology since Lea's monumental volume on the "Actions of Radiations on Living Cells." Consequently the present book by three authorities active in research on the physical, chemical and biological actions of radiations is a timely addition to this field.

Part I by Dr. L. H. Gray, consisting of 91 pages in French, deals with the modes of interaction of radiation with matter, physical methods of measuring dosage, localization of dissipated energy by light and heavy particle radiation and the individual transfer of energy of the particle in the absorbing medium. These important problems are competently discussed and many curves, useful in dosimetry problems, are presented.

Part II by Dr. M. Lefort, 110 pages in French, provides a complete resumé of experimental work on the radiation chemistry of aqueous solutions. No attempt has been made to furnish the reader with a critical analysis or interpretation of the results. American radiation chemists will welcome this part of the book since the important French contributions are succinctly summarized and discussed. The entire field of radiation chemistry in aqueous solutions from experimental techniques to the oxidation of simple organic compounds and compounds of biological interest is encompassed. An index and appendix of G values for X-ray, γ -ray and α -particles is also given.

Part III by Dr. W. M. Dale consists of 37 pages in English. Dr. Dale has given an account of recent experimental work concerned with the chemical, biochemical and physicochemical effects of ionizing radiations. The sections on dilution-effect, sensitization, deamination and radiation effects on sulfur-containing compounds and nucleic acids will be of particular interest to chemists and biochemists.

This book is recommended for chemists established in the field of radiation chemistry and for those anticipating research in this field.

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