

out and interesting to follow, a major point of criticism is that the criterion for equilibrium is taken as the homogeneity of temperature, pressure, and composition, rather than of temperature, pressure, and chemical potential. One might also criticize the uneven level of presentation. If the author wrote this book for the beginning student, then he should have included, for example, a more thorough discussion of the concept of temperature (p. 4), a definition of *heat capacity* (p. 20), and an explanation of the sign convention for changes in mass (p. 22). On the other hand, if this book is intended for the more advanced reader, then the elaborate discussion of the concept of a semipermeable membrane (pp. 48-49) and the definition of the boiling point of a liquid (p. 63) are unnecessary. For either class of reader, the last two chapters are too sketchy to be of value.

In summary, because of its original approach to the second law, this book should be of interest to those concerned with the foundations of thermodynamics and those involved with teaching advanced courses in this subject. It is unlikely, however, that the beginning student would be able to follow and appreciate the lengthy arguments.

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Determination of pH. Theory and Practice. By ROGER G. BATES, National Bureau of Standards. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1964. 435 pp. 15.5 × 23.5 cm. Price, \$13.00.

The most striking impression that one receives on reading this monograph is the large number of references to work that has been done in the decade since the publication of Dr. Bates' "Electrometric pH Determinations." The author's description of the present volume as a "revised and enlarged version" of that published in 1954 is both modest and conservative. Much of the new material reflects the continuing interest in acid-base equilibria in mixed solvents and nonaqueous media. Both the theoretical work on proton activities as computed with modifications of the Born-Haber cycle and comparisons of the indicator and electrometric methods for the definition of pH scales are reviewed critically. Moreover, much of the experimental work is that of the author and his collaborators. With the aid of cells with, and without, liquid junction and with indicators of at least two different charge types, he and Schwarzenbach have compared the acidity functions of three buffer systems in seven water-ethanol mixtures. When referred to an aqueous standard state, these functions diverge by as much as 4 pH units in the transition from water to ethanol. This is but a small portion of the experimental evidence assembled by the author in his survey of the formidable problems associated with the establishment of a universal scale of acidity.

An essential and useful feature is the description of the preparation and properties of standard buffers. Those recommended as primary standards cover the pH range from 3.5 to 9.5 and from 0 to 95°. In the temperature interval from 10 to 40° the internal consistency of these standards is quite remarkable, i.e., a pH cell with a glass or hydrogen electrode that has been calibrated with one of these standards measures the pH of any other within a very few thousandths of a unit. Secondary standards are also recommended and include the extremes of pH where some glass electrodes exhibit salt errors and the liquid junction potential becomes increasingly uncertain.

Of the many electrodes responsive to pH, the hydrogen electrode remains the standard, but for routine measurements the glass electrode is now used almost universally. It is appropriate, therefore, that one chapter is devoted exclusively to this electrode whereas the preceding chapter deals with other pH electrodes and the reference electrodes that, together with the KCl bridge, complete the galvanic cell. Many electrode glasses are now available and from the author's thorough and comprehensive review of their properties a user should have no difficulty in selecting the one best suited to his needs. The closing chapters describe the measurement of the e.m.f. of pH cells and their adaptation to automatic control, including the electronic instrumentation that permits the use of circuit elements having the extremely high resistance of most glass electrodes.

To paraphrase King Gama in *Princess Ida*, "Isn't a review extremely flat with nothing whatever to grumble at?" A very

minor question is concerned with the author's treatment of the suspension effect. As Overbeek has suggested, is this not an example of sedimentation equilibrium in which gravity immobilizes the colloidal particles with ion-exchange properties just as effectively as would a semipermeable membrane at the suspension-supernate interface? The resulting potential difference across this interface can be described as a Donnan effect with considerable justification. Moreover, if identical calomel half-cells and saturated KCl bridges are used to make contact with the suspension and supernate, respectively, and the resultant cell potential is more than a few millivolts, the bulk of this potential is to be assigned to the interface rather than the KCl-suspension junction. Although an isolated Donnan system is in true equilibrium, and hence incapable of serving as a source of free energy, constraints maintaining that equilibrium are removed when the system is incorporated into the foregoing galvanic cell.

This is a most welcome monograph. Prepared by one who has had experience at first hand with almost every aspect of the subject it bears the unmistakable stamp of authority and can be recommended without reservation to anyone concerned with the measurement of pH.

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Azeotropy and Polyazeotropy. By WOJCIECH SWIETOSLAWSKI, Professor of Physical Chemistry, University of Warsaw. Edited by K. RIDGWAY, University College, London. The Macmillan Co., 60 Fifth Ave., New York, N. Y. 1964. 226 pp. 17 × 25 cm. Price, \$10.00.

Like Lecat in Belgium before him, Swietoslawski in Poland has devoted much of a lifetime to azeotropy. Now 83 and a director of the Polish Academy of Sciences, he continues to participate enthusiastically in research. The present book is based upon his Polish monograph of 1957. It includes some 200 cited references through 1959, another 100 supplemental references through 1958, and a bibliography of 30 more that stops at 1955. The extensive Polish literature is well covered, but few of the papers appear that were published elsewhere during the past decade.

An odd sequence of topics contributes to the bewildering complexity of the subject. Binary mixtures above (homo) and below (hetero) the critical solution temperature may (azeotropic) or may not (zeotropic) vaporize below (positive) or above (negative) the boiling points of the components. Ternary homo- or heteroazeotropes may be tripositive, bipositive-negative (saddle), binegative-positive (miscalled saddle), or trinegative. Quaternary azeotropes, as exemplified by the benzene-naphtha-ethanol-water system that so intrigues the author, are not classified, although five types should exist. As pressure is changed, most azeotropes fade into "tangent" azeotropes and thence into zeotropes, whereas some continue all the way to the critical temperature, and others perhaps merge somehow into eutectics. Polyazeotropy is the name the author gives to the further dimensions of homologous series of azeotrope substances.

Beautifully drawn figures compete for attention with little errors: pyrocatechol (Table IV 1), 2,5-dimethylbutane (Table IV 3), 52.5° instead of 57.5° (Fig. X 6), point A instead of point AH₃ (Fig. X 22), mislabeled axes (Fig. XIV 3), and so on. A few figures founder for want of assistance from the text. The statement is repeatedly made that no paraffin or naphthene boils at 101-102°, whereas methylcyclohexane boils at 101.2°. The names of several U. S. authors are misspelled and several volume numbers are incorrect. Slightly imperfect letters "e" and "s" give the pages a peculiar "face." My copy is coming apart between pages 14 and 15.

Swietoslawski's book is interpretive, in contrast to either Lecat's annotated lists of 1918 and 1949, or particularly Horsley's compendia of 1952 and 1962. It thus supplements these sources, but follows too closely the interests of the Polish school to become the definitive book on azeotropy. The author points out a dozen aspects in need of further study, but his main emphasis is upon polyazeotropy, the direct if not rapid approach to learning more details about azeotropes. So there is still nowhere to turn for an understanding of the subject.

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