

## EXPERIMENTAL AND THEORETICAL ELECTROCHEMISTRY

### Textbook of Electrochemistry

By Prof. G. Kortüm and J. O'M. Bockris. Vol. 1, pp. xvi+351; 50s. Vol. 2, pp. xiii+353-882; 70s. (New York and Amsterdam: Elsevier Publishing Co., Inc.; London: Cleaver-Hume Press, Ltd., 1951.)

THE period following the theoretical and experimental establishment of the interionic attraction theory has seen the appearance of a number of treatises on electrochemistry and related subjects. The earliest of these was the German book by Falkenhagen (later translated into English); but apart from this the subject has been mainly written about by British or American authors. However, during the Second World War, Prof. G. Kortüm published "Elektrolytlösungen" (1941) and more recently "Lehrbuch der Elektrochemie" (1947), neither of which has received much attention in English-speaking countries. These books naturally follow to a considerable extent well-established lines; but they have several less usual features, notably the attention given to optical properties of electrolytes, electrolytic conduction in solids, melts and gases, and irreversible processes in electrolytes. These points, together with the good general exposition of Prof. Kortüm's writings, provide justification for making them more available to the English-speaking reader.

The volumes under review represent a translation and revision of the second edition of "Lehrbuch der Elektrochemie", together with enough additional material to produce a book approximately twice as large. Unfortunately, it must be said that the English edition does scant justice to the original, especially in some of the revisions and additions. The English is often clumsy by an exact adherence to the German (in phrases such as "the considered ion"), while in some instances the translation badly distorts the author's meaning. Outstanding examples of the latter are the rendering of "Größen" as "volumes" in the second paragraph of p. 160, producing a meaningless sentence, and the translation of "lockernen Einfluss" as "attractive influence" at the bottom of p. 350, which exactly reverses the meaning and contradicts the rest of the paragraph. The chapter on thermodynamics has been largely rewritten, with unfortunate results. No clear account is given of the fundamentals of thermodynamics (for example, the definition of temperature is not mentioned), and there are many individual errors and ambiguities. Thus, after drawing a clear distinction between "volume work" ( $p\Delta v$ ) and "specialized work", a statement is made (p. 52) implying that in the reversible expansion of a gas only volume work is done, the specialized work being zero. Similarly, the treatment of partial molar quantities (p. 58) does not distinguish between the amounts and concentrations of the components, and the account given of standard states and reference states (p. 82) is very likely to confuse even the most clear-headed reader.

The next four chapters follow the original fairly closely, but Chapter 7, on electromotive force, has been considerably modified. The chief criticism of this section (applying in part to the German edition also) is the emphasis given to individual electrode

potentials and the activities of individual ionic species. The impression is given that our ignorance of these quantities arises only from experimental difficulties, and no mention is made of the fact that many authorities regard them as undefinable in principle and without practical value. Chapters 10 and 11, dealing with electrical phenomena at interfaces and irreversible electrode processes, have been considerably revised and expanded. It is in this latter field that Dr. J. O'M. Bockris's own contributions to electrochemistry have been chiefly made, and it is useful to have an up-to-date account of this difficult and growing branch of the subject. The variety of mechanisms proposed by different authors is well brought out, and the need for more experimental work of high quality is made clear.

The last 340 pages of the book represent material not contained in the German edition. There is a chapter on experimental methods in electrochemistry (by Roger Parsons), which is clearly written and contains much of value, though it may be doubted whether it is worth while to attempt a brief treatment of borderline techniques such as calorimetry and optical measurements. There follows a section of 160 pages devoted to tables of numerical data, compiled by B. E. Conway. It is not always easy to see the principles which have governed the choice of these data (for example, five pages are devoted to the densities of mixtures of fused salts); but many of the tables and the accompanying references should be useful. It is, of course, imperative that any such compilation shall have a high standard of accuracy, and this can only be judged by continued use. A few points I have noticed give evidence of some lack of care. The data in Table III, 3, are described as the parameters of the Debye-Hückel theory, but actually refer to the extended theory given by Robinson and Stokes. The data given in Table III, 48, for the transport numbers of sodium chloride and potassium chloride are listed under aqueous solutions, but actually refer to methanol-water mixtures. In Table III, 59, the values of  $pK$  for *N*-methylaniline and *N*-ethylaniline are described as "in alcoholic solution", though they refer to water, being extrapolated from measurements in alcohol-water mixtures of varying composition; conversely, the  $pK$  quoted for acridine was measured in 50 per cent alcohol, though this is not mentioned in the table. It is to be hoped that these samples are not representative of the reliability of the tables as a whole.

Volume 2 concludes with a collection of 120 numerical exercises (compiled by Roger Parsons and others), together with answers and hints for solution. These appear to have been well selected, and should be useful to students and teachers alike.

The work as a whole is attractively produced and easy to read, though it is marred by a large number of misprints; more than fifty were noticed in one reading of the first volume.

To sum up, these volumes contain a good deal of material which is of value; but their claim to be (to quote the dust-cover) "a solid and comprehensive summary of modern electrochemistry" is vitiated by a large number of blemishes, only a few examples of which have been given in this review. The impression is received that not nearly enough time and care have been devoted to the preparation of the English edition. Failing this, it would have been wiser to produce a smaller (and less expensive) work adhering more closely to Prof. Kortüm's original book.

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