

## BOOK REVIEW

*OXIDATION-REDUCTION POTENTIALS OF ORGANIC SYSTEMS.*  
By W. Mansfield Clark. Pp. xi + 584 (including Index). Baillière, Tindall & Cox Ltd., London, 1960. 108s.

In his book Dr. Mansfield Clark critically examines the methods used in oxidation-reduction measurements and discusses the results obtained from different organic oxidation-reduction systems in terms of thermodynamic principles.

The author introduces the electrochemistry of oxidation and reduction historically, clearing up some misconceptions in the interpretation of results of early work. This chapter could have been much reduced in content, the practising chemist being familiar with the points the author mentions at great length. This chapter is followed by the thermodynamic principles of electrochemistry; to many this section will serve as a useful revision of the theoretical treatment pertinent to the subject. It is an essential part of the book and will be helpful to the organic and biological chemist. Mention is then made of definitions, conventions and some special terms used in this field of chemistry. This completes the first quarter of the book; the remainder is devoted in a masterly way to a large number of general and specific systems which have been investigated in organic chemistry.

Complexities arising in organic oxidation-reduction systems, for example, dimerisation of the quinhydrone type, aggregation of molecules of dyes, preferential adsorption of a component, free radicals of the triphenylmethane and also the pyocyanine types necessitate the construction of equations to account for the deviations of these systems from the more simple ones. This is done most comprehensively in chapters 6, 7 and 8, which are devoted to the modifications of basic equations to deal with the special cases, both real and hypothetical.

In a short chapter on liquid junction potentials the author brings a fresh approach to the meaning of electrostatic potential between solutions which are in liquid junction and he discusses the cause of this potential in terms of thermodynamical aspects of diffusion. An important chapter on the standardisation of potentials by the standard hydrogen half-cell and pH values of buffer solutions follows. The many results from recent experimental work justifies a revision of pH values of certain buffer solutions. This the author has attempted and in doing so has suggested the preparation of a few important buffer solutions.

The accumulated experience of Dr. Mansfield Clark has produced a very clear and full account in chapter 11 of the methods which are used in obtaining potentiometric measurements. In chapter 12, criteria by which the reliability of redox potentials may be judged is discussed.

In the remainder of the book the author deals admirably with a large number of results from important organic redox systems; he discusses the chemical reactions taking place and interpretation of the results obtained therefrom. This section is also a valuable source of references. The book ends with a glossary of symbols and a useful bibliography.

Some topics such as polarography have been treated sparsely and irreversible systems, of which there are many, are not dealt with at all. However, the book is costly enough and any extension would have made the price prohibitive to most readers. The reviewer thinks the author could have economised in his

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use of words and quotations when introducing topics and producing argument, in this respect he has tried too hard to make the book "readable." Nevertheless, Dr. Mansfield Clark has made a valuable contribution to the chemistry of redox potentials of organic systems. His wide experience and critical faculties have been invaluable in emphasising the important aspects of the technique and the necessity of interpreting the method in terms of sound theoretical relationships.

Although the subject is a specialised one, the book is suitable for organic, physical and biochemists.

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