Potentiometry and Potentiometric Titrations

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PREFACE

This work was undertaken in response to a request for a book that would replace the classic Kolthoff–Furman *Potentiometric Titrations* published in 1931. In recent years there has been a resurgence of interest in the applications of potentiometry to analysis as a result of the development of ion selective and associated membrane electrodes. The literature covering the theory and application of these electrodes is now large, and there are a number of good texts devoted exclusively to this aspect of potentiometry. At the same time there has also been a steady, though less spectacular, development in the applications of electrodes and techniques that were already established in 1931. These include the applications of potentiometry both to titrimetric analysis and to the investigation of the solution equilibria upon which these analyses are based. It was felt necessary, therefore, that this book should survey the endeavors in all three areas and, accordingly, it is divided into three parts. The first part deals with cells, electrodes, and the basic procedures of direct potentiometry together with a description of electrodes and techniques used for equivalence point detection in titrimetric analysis. The second part deals with the applications of potentiometry to the determination of solution equilibrium data, concentrating mainly upon the determination of ionization constants of acids and bases in aqueous and nonaqueous solution, and also upon the determination of stability constants. The third part is devoted to titrimetric analysis and covers the four main branches; acid-base, complexometric, oxidation–reduction, and precipitation titrations. The main thrust of the literature search into these topics was concentrated upon the two decades from 1958 to 1978, although some reference is made to important work prior to and subsequent to this period.

Within the three subdivisions mentioned, the measurement of a cell potential can be performed to fulfill different requirements ranging from measurements having thermodynamic significance performed at "zero current" in carefully calibrated cells without liquid junction to the monitoring of a potential between two electrode immersed in a titrant solution through which a current is deliberately impressed during the course of a titration. In the first case the object of the measurement of potential is to interpret it in terms of the activity of an electroactive electrolyte present in

the cell solution by means of the thermodynamically derived Nernst equation. In the second case the monitoring of the potential is performed only to establish that point in the titration at which it is hoped a large change in potential can be interpreted as signifying the point of completion of the titration reaction. The volume (or weight) of titrant required to reach this point is of prime interest to the analyst, and the actual values of the potentials have no thermodynamic or even quasi-thermodynamic significance. It is difficult, therefore, to preserve the integrity of the word "potentiometry" if both these applications are described equally as potentiometric. To distinguish unequivocally between these two types of applications, the use of the term "potentiometry" in this book is taken to mean the measurement of a cell potential E_{cell} which can be interpolated in terms of activity or concentration by means of a form of the Nernst equation written as

$$E_{cell} = \text{constant} \pm \text{slope} \log a_x$$

where a_x is the activity of an electroactive electrolyte, or a single electroactive species such as an ion. In contradistinction to this, the term "potentiotitrimetry" is used to describe a traditional method of locating the equivalence volume of a titration by the monitoring of cell potentials during the course of the reaction. Following upon these definitions, a "*potentiometric titration*" is one in which the measured potentials are used to obtain the activity of an electrolyte or a species at particular points during a titration. To this end the cell must be carefully calibrated before the titration. The determination of an ionization constant by *p*H titration is an example of a potentiometric titration, and so is the titrimetric application when computer-generated curves are used to fit experimental data to theoretical curves in order to determine the equivalence volume.

There are now many fields of scientific endeavor in which either direct potentiometry or potentiotitrimetry make a useful contribution as a powerful analytical tool. It is not always evident, however, that workers without formal training in the analytical chemistry of these techniques fully appreciate the theoretical basis for their application, and their limitations. It has been the aim of the author, therefore, to present the necessary basic theory in a form which is assimilable to those with only an elementary knowledge of chemistry, and this theory is then developed further at appropriate points in the book to provide a basis for the understanding of the practical applications of the techniques. The emphasis has been towards these applications, and to this end much practical information is contained in over 60

tables presented in the book. Some detailed practical instructions are included in the text but, unfortunately, these inclusions have had to be curtailed in order to present a comprehensive treatment of the subject as a whole in the space available. It is hoped this deficiency is remedied to a degree by the inclusion of many references to the original work. Detailed descriptions of general purpose apparatus is not a feature of the book since these are available from the manufacturers, and only passing references are made to the important field of automation. It is worth noting that some books devoted to ion selective electrodes give details of automation techniques and, of course, Svehla's *Automatic Potentiometric Titrations* fulfills a need in this direction.

It is hoped that this book will be useful also in formulating courses in potentiometry and in titrimetry at the undergraduate and the beginning graduate level. Indeed, parts of it have been derived from or have formed a basis for undergraduate courses given to chemistry majors at the second and third-year levels. Thus parts of Chapter 1 were derived from a 12-lecture course given to second-year students as part of a topic dealing with electrochemistry and thermodynamics. This was backed by a practical course that included some of the $p(a_{H}\gamma_{Cl})$ measurements described in Chapter 6. Parts of Chapters 3 and 4 have formed the basis for a course in potentiometry given to students in second and third-year analytical chemistry courses. However, the primary purpose of the book is to provide a source of reference for practicing analytical chemists and those engaged in allied fields.

The guidance and patience of Dr. P. J. Elving, University of Michigan, who suggested the project, and the comments of his editorial colleague, Dr. J. D. Winefordner, University of Florida, have been particularly appreciated over the years taken in compiling this book. The author gratefully acknowledges the help given by his wife, Joan, in processing many of the thousands of abstracts collected during the literature search, and also thanks Dr. R. G. Bates, Emeritus Professor, University of Florida, for reading Chapter 4 while it was still in the handwritten state. Dr. D. D. Perrin, Professorial Fellow, Australian National University, is thanked for his useful comments on Chapter 8, and Dr. A. Albert, Emeritus Professor, Australian National University, and Research Professor, State University of New York, Stonybrook, is thanked for his encouragement and for reading Chapters 6 and 7. The use of library facilities and the help given by the staffs of the Chemistry Department and Health Center libraries in the University of Florida and the John Curtin School of Medical Research and Research School of Chemistry libraries in the Australian National University are also acknowledged with gratitude. The staffs of the Bridges Library,

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E. P. SERJEANT

Duntroon, Australian Capital Territory
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E. P. S.

CONTENTS

PART

1

CELLS, ELECTRODES, AND BASIC PROCEDURES