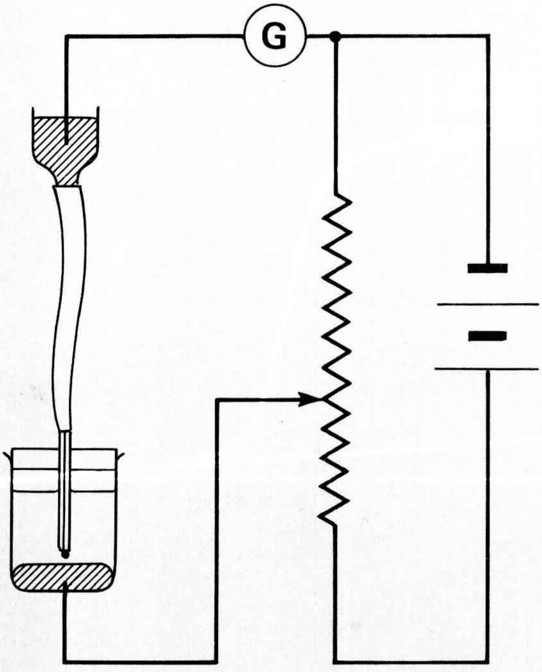
D.R. CROW



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Principles and Applications of Electrochemistry

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D. R. CROW
Professor of Electrochemistry
The Polytechnic, Wolverhampton

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Preface to the first edition

The purpose of this book is to present in a simple and concise way the basic principles of electrochemistry and some of its applications.

In a volume of this size it has not been possible to give an exhaustive treatment of the subject and careful selection of material has been necessary. Despite this constraint, I have attempted to cover, in a logically developing sequence, the essential electrochemistry that students require.

Deeper insight into the subject and extended theory may be obtained from the further reading lists given at the end of each chapter. I wish to acknowledge the help that these texts and articles have been to me.

My colleagues and students have helped me greatly while writing this book; the former by their constructive criticism and advice, the later through their questions and discussion of their problems. I cannot adequately express my gratitude to my wife for her help in typing and checking and for her encouragement and moral support.

D. R. C.
London
April 1973

Preface to the third edition

It is gratifying to have seen this book pass through two editions and several reprintings. Its nature is such that, being largely concerned with basic principles, and therefore not too amenable to expansion, the inclusion of newer developments with each edition presents some problems if the size is not to become excessive. Were this to happen, the original purpose would have been set aside and I am concerned that this be avoided. However, the opportunity has been taken in the present instance not only to correct persistent errors but to add some small new sections. It is to be hoped that these, within the framework of some minor restructuring, will serve at least to direct the reader to some of the rapidly expanding applications of electrochemistry. To aid this process further, the reading lists have been extended and updated; no apologies, however, are given for retaining rather older cited texts which remain part of the foundation fabric of the subject.

A major change is the inclusion at the end of each chapter of a small range of numerical examples with outline solutions and answers. These cover the main types of calculation that the undergraduate may encounter during a course of electrochemistry.

I am grateful to my many colleagues and students who, having used the book in its previous editions, have been helpful in correcting errors or clarifying obscurities; any of the latter which remain are my responsibility alone. In particular, I am indebted to Dr S. C. Wallwork and Dr M. R. Willis of the Department of Chemistry, University of Nottingham, for their meticulous work in commenting on the manuscript for this new edition.

As ever, the major inspiration and encouragement comes from my wife, Margaret, and she cannot be thanked adequately.

D. R. C.
Wolverhampton
September 1987

Principles and Applications of Electrochemistry
Third Edition
D.R. Crow

Electrochemistry, although formally a branch of physical chemistry, has wide ranging applications in physics, the biological sciences, medicine and engineering – for example, in the development of new batteries, electroplating, corrosion control and laboratory analysis of the water supply, foods and body fluids. This book deals with the fundamental principles on which such applications are based and with some of the applications themselves.

Principles and Applications of Electrochemistry is a comprehensive introduction to the subject for undergraduates in chemistry and related fields, but will also serve as an excellent revision text for more advanced students. Many students find electrochemistry 'difficult', but the emphasis here is on a simple presentation of the basic material and every effort has been made to ease passage over the traditional stumbling blocks. In this 3rd edition, a wide range of numerical problems has been added to each chapter, together with outline solutions and answers, to cover almost all situations a student may encounter. Also, the discussion of electrode processes has been enhanced by a new emphasis on electrochemical sensors and discussions of some of the newer power cells and aspects of electrocatalysis and electrosynthesis.

SI units are used throughout, but adequate account is taken of the continued use by many of older systems of units.

The author is Professor of Electrochemistry at Wolverhampton Polytechnic. He is author of *Polarography* (with J.V. Westwood) and of *Polarography of Metal Complexes.*

Also available

NMR and Chemistry
J.W. Akitt
2nd edition, 1983, paperback (0 412 240203), 263 pages

Mathematics for Chemists
P.G. Francis
1984, hardback (0 412 24980 4) and paperback (0 412 24990 1), 204 pages

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11 New Fetter Lane, London EC4P 4EE
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Contents

1

The structure of electrochemistry

Electrochemistry is a large and important area of physical chemistry. It is, however, difficult to define precisely the limits of this area, not simply on account of its size but because of its influence in so many areas in chemistry as well as in biology and physics. Many concepts, accepted universally now as fundamental to chemistry, originated in electrochemistry. On the other hand it is now realized that future developments in many fields, and we may at random quote such widely differing ones as corrosion prevention, power supply and biochemistry and cellular biology, are dependent in no small way upon the exploitation of electrochemical principles.

In the short sections which follow an attempt is made to indicate the more important contributions that electrochemistry has made to chemistry as a whole and the important place which the subject occupies in science at the present time.

1.1 Faraday's Laws

Implicit in the demonstration and implementation of these laws are the concepts of atomic structure and the nature of ions and electrons. It is apparent that charges which are transferred through solution and across electrode/solution interfaces are 'atomic' in nature. The two laws are simply expressed as follows:

1. In electrolytic processes the amount of chemical decomposition is proportional to the quantity of electricity passed.
2. The masses of different species deposited at or dissolved from electrodes by the same quantity of electricity are in direct proportion to M_r/z (or A_r/z). M_r, A_r refer to relative molecular or atomic masses while z is the change in charge number which occurs in the electrode reaction. Thus, when a given current is passed for a given time through a series of electrolyte solutions, the extent of decomposition is always the same when expressed in terms of $1/z$ moles. In this statement lies the definition of the Faraday

constant (F) which is the amount of electricity required to deposit $1/z$ mole of any species from solution and has the value $9{\cdot}6487 \times 10^4$ C mol^{-1}. The units emphasize that $9{\cdot}6487 \times 10^4$ coulombs is the amount of electricity associated with '1 mole of unit charges'.

1.2 Ion interactions in solution

It was appreciated very early on that in systems of oppositely charged ions in solution, independent movement of ions could not be expected except under the extreme condition of infinite dilution. Therefore, independent contribution to bulk properties such as conductance or osmotic pressure cannot occur. Electrostatics demands that considerable attractive and repulsive forces be exerted between unlike and like charges respectively. In such interactions lies, to a very large extent, the demonstrable non-ideal behaviour of electrolyte solutions.

Debye and Hückel rationalized the way in which the conductivities of strong electrolyte solutions were observed to vary with their concentration by proposing models of the ion distribution and applying to them well-established relationships of thermodynamics and electrostatics. The concept of ion atmospheres, formed by the preferential distribution of ions about a given central ion carrying charge of opposite sign, when developed in this way, provided experimentally verifiable expressions for the mean ion activity coefficients of electrolytes. These expressions make possible the determination of thermodynamic equilibrium constants in electrolyte systems and the interpretation of ionic reaction rates in solution.

1.3 Acid-base theory

The classical theory of electrolytic dissociation put forward by Arrhenius is successful in explaining to a large extent the behaviour of weak acids and bases in aqueous solution. It led to the concept of pH and pH scale of acidity for aqueous solutions. The realization that the solvent plays a vital role in ionic equilibria led to the development of a general theory of acids and bases applicable to all solvents.

1.4 Thermodynamics

Much of conventional thermodynamics developed from electrochemical work. The detailed investigation of the behaviour of reversible electrochemical cells and the reactions occurring within them contributed to the appreciation of the concept of standard free energy and led to the accurate determination of thermodynamic constants for cell reactions. Early work on the temperature dependence of reversible cell e.m.f.'s contributed considerably to the formulation of the Third Law of Thermodynamics.

It is, in fact, with the use and understanding of reversible electrochemical cells that many people see for the first time the significance and applicability of thermodynamic principles. Here thermodynamics may be seen to apply to tangible practical situations.

So many modern analytical techniques are based upon electrochemistry. Quite apart from methods based on the direct measurement of a current, voltage or resistance, classical 'wet' analysis stands on the electrochemical foundation of equilibria and electrode potentials.

1.5 Interfacial phenomena

The interfacial region between a solid electrode surface and a solution with which it is in contact is of great significance. An understanding of the structure of this region is necessary to explain the mechanisms and rates of oxidation–reduction processes occurring at the electrode. The theory of this 'double-layer' region lies at the heart of the physical chemistry of colloid systems and the interpretation of colloid stability, membrane behaviour and ion-exchange processes lie within the realm of interfacial electrochemistry.

1.6 Electrode processes

Studies grouped under this general heading are concerned with the kinetics and mechanisms of electrode reactions. They are to be distinguished from thermodynamic studies, based upon reversible cells and electrode potentials in which, by definition, systems at equilibrium are investigated.

Detailed knowledge of the energetics and kinetics of electrode processes and the factors which affect them, is essential for the efficient running of the electroplating, electroforming and electromachining industries. Corrosion mechanisms and the control of corrosion can only be interpreted quantitatively in terms of electrode kinetics. The development of understanding of electrode processes is reflected in the increased utilization of electrochemical processes as sources of energy – both in storage and power generating devices. Such utilization is likely to increase dramatically over the next few decades with the increasing demand for non-polluting energy production.

1.7 The domains of electrochemistry

It can be seen from the previous sections what a range of chemical disciplines have their roots in electrochemistry. This emphasizes the necessity for every chemist to have a sound grasp of electrochemical principles. Indeed, many modern developments in molecular biology stress the electrochemical basis of many natural processes, e.g. nerve response by conduction of electricity, the pH dependence of amino acid and protein equilibria, cell membrane equilibria and ion-body fluid redox equilibria. It is becoming more apparent that an electrochemical background is essential for biologists.

It is hardly surprising that, since electrochemistry makes incursions into so much of chemistry, opinions as to what constitutes the subject are numerous. While the classification of such areas as electroplating, storage batteries and fuel cells as 'electrochemistry' would be almost universally accepted, the position of some other areas could call forth considerable disagreement.

If the widest view is taken of the material considered above, and this is only generally expressed and not exhaustive, it is apparent that there are essentially three domains of electrochemistry which may be expressed in tabular form.

Ionics	*Interfacial phenomena*	*Electrodes*
Behaviour of ions in solution and in fused state	Double layer theory Adsorption	Kinetics and mechanisms of electrode reactions
Ionic equilibria	Electrokinetic phenomena	Electron transfer reactions
Transport processes	Colloidal systems	Electro-catalytic processes
Potential-determining ion reactions (reversible electrode potentials)	Ion exchange processes	

Strictly, it is necessary to include a further domain which takes its place to the right of electrodics above. This is the solid state physics of the electrode materials used and is concerned essentially with the structure of the materials used as electrodes and the energy levels of electrons and atoms within them.

Owing to the size of the subject, it has proved necessary in the following chapters, to be selective in the choice of material presented. Earlier chapters are concerned with ionics and its applications. Here are considered ion interactions in solution, acid–base equilibria, transport phenomena, and the concept of reversible electrode potential. This last named leads to the development of reversible cells and their exploitation. Here one is dealing with electrochemical thermodynamics – with the rapid attainment of equilibrium between species at an electrode surface and charged species in solution.

Chapter 7, devoted to interfacial phenomena, deals with the theory of the double layer at electrode/solution interfaces but develops the concept in the treatment of electrokinetic phenomena, colloidal systems and membrane equilibria. It forms a bridge between the earlier part of the book and the final two chapters, concerned with the theory and applications of electrodics.

2

Ionic interaction

2.1 The nature of electrolytes

Electrolytes are species giving rise to ions to a greater or lesser extent, strong electrolytes being completely ionized even in the solid and fused states. In the latter case, and also when dissolved in a solvent, the ions become free to move and the highly ordered lattice structure characteristic of crystals is almost entirely destroyed. Weak electrolytes, on the other hand, are ionized to only a small extent in solution, ionization increasing with dilution according to the well-known Ostwald Law.

Very many salts are known to dissolve readily in solvents with heats of solution that are usually fairly small in magnitude and which may be exothermic or endothermic. At first sight this is a phenomenon rather difficult to account for, since crystal structures have high lattice energies. A lattice energy is the large-scale analogue of the dissociation energy of an individual ionic 'molecule'. In a crystal, the energies of a large number of component ion-pairs contribute to the total lattice energy which is effectively the energy evolved when the lattice is built up from free ions. Since such energies are large, we are led to suppose that a large amount of energy is required to break down the ordered structure and liberate free ions. A way in which the observed easy dissolution can be explained is by the simultaneous occurrence of another process which produces sufficient energy to compensate for that lost in the rupture of the lattice bonds. Exothermic reactions of individual ions with the solvent – giving rise to the heat of solvation – provide the necessary energy. From the First Law of Thermodynamics, the algebraic sum of the lattice and solvation energies is the heat of solution. This explains both why the heats of solution are usually fairly small and why they may be endothermic or exothermic – depending upon whether the lattice energy or the solvation energy is the greater quantity.

A great difficulty when dealing with electrolytes is to ascribe individual properties to individual ions. Individual thermodynamic properties cannot be determined, only mean ion quantities being measurable. Interionic and ion-solvent interactions are so numerous and important in solution that, except in the most dilute cases, no ion may be regarded as behaving independently of others. On the other hand, there is no doubt that certain dynamic properties such as ion conductances, mobilities and transport numbers may be determined, although values for such properties are not absolute but vary with ion environment.

2.2 Ion activity

Since the properties of one ion species are affected by the presence of other ions with which it interacts electrostatically, except at infinite dilution, the concentration of a species is an unsatisfactory parameter to use in attempting to predict its contribution to the bulk properties of a solution. What is rather required is a parameter similar to, and indeed related to, concentration, i.e. the actual number of ions present, but which expresses the availability of the species to determine properties, to take part in a chemical reaction or to influence the position of an equilibrium. This parameter is known as activity (a) and is related to concentration (c) by the simple relationship

$$a_{\mathrm{i}} = \gamma_{\mathrm{i}} c_{\mathrm{i}} \tag{2.1}$$

γ_{i} is known as an activity coefficient which may take different forms depending on the way in which concentrations for a given system are expressed, i.e. as molarity, molality or mole fraction. For instance, the chemical potential (μ_{i}) of a species i may be expressed in the forms

$$\mu_{\mathrm{i}} = (\mu_{\mathrm{i}}^{\ominus})_x + RT \ln x_{\mathrm{i}} \gamma_x \tag{2.2a}$$

$$\mu_{\mathrm{i}} = (\mu_{\mathrm{i}}^{\ominus})_c + RT \ln c_{\mathrm{i}} \gamma_c \tag{2.2b}$$

$$\mu_{\mathrm{i}} = (\mu_{\mathrm{i}}^{\ominus})_m + RT \ln m_{\mathrm{i}} \gamma_m \tag{2.2c}$$

x_{i}, c_{i} and m_{i} are the mole fraction, molar concentration and molal concentration respectively. γ_x is known as the rational activity coefficient while γ_c, γ_m are practical activity coefficients. (Often, the symbols f_x, f_c are used for molar and molal activity coefficients, but to avoid confusion γ will be used throughout with an appropriate suffix to indicate the concentration units.)

Until about 1923 activity coefficients were purely empirical quantities in that when concentrations were modified by their use, correct results could be predicted for the properties of a system. We shall see that, on the basis of the Debye–Hückel theory, to be discussed shortly, activity coefficients become rationalized and theoretically predictable quantities.

For the purposes of deriving relationships in which activity coefficients occur it is very convenient to make use of the idea of individual ion activities and activity coefficients. However, as already stressed, such quantities are incapable of measurement and so are meaningless in a practical sense. One ion species, deriving from a dissolved electrolyte, cannot on its own determine properties of a system; it will always do so in concert with an equivalent number of oppositely charged ions. It is therefore only possible to use a form of activity or activity coefficient which takes account of both types of ions characteristic of an electrolyte. Such forms are known as mean ion activities ($a_{\pm}$) and mean ion activity coefficients ($\gamma_{\pm}$) and are defined by

$$(a_{\pm})^{\nu} = a_{+}^{\nu_{+}} \times a_{-}^{\nu_{-}} \tag{2.3}$$

and

$$(\gamma_{\pm})^{\nu} = \gamma_{+}^{\nu_{+}} \times \gamma_{-}^{\nu_{-}} \tag{2.4}$$

where $\nu = \nu_{+} + \nu_{-}$, the latter being the number of cations and anions respectively deriving from each formula unit of the electrolyte.

2.3 Ion–ion and ion–solvent interactions

Although strong electrolytes are completely ionized, their ions are not entirely free to move independently of one another through the body of a solution, except when this is infinitely dilute. A fairly realistic picture of the situation in a solution containing the oppositely charged ions of an electrolyte is as follows. Ions will move randomly with respect to one another due to fairly violent thermal motion. Even in this condition, however, coulombic forces will exert their influence to some extent with the result that each cation and anion is surrounded on a time average by an 'ion atmosphere' containing a relatively higher proportion of ions carrying charge of an opposite sign to that on the central ion.

Movement of ions under the influence of an applied field will be very slow and subject to disruption by the thermal motion. Under the influence of such a field, movement of the atmosphere occurs in a direction opposite to that of the central ion, resulting in the continuous breakdown and re-formation of the atmosphere as the ion moves in one direction through the solution. The time-lag between the restructuring of the atmosphere and the movement of the central ion causes the atmosphere to be asymmetrically distributed around the central ion causing some attraction of the latter in a direction opposite to that of its motion. This is known as the asymmetry, or relaxation effect. In addition, central ions experience increased viscous hindrance to their motion on account of solvated atmosphere ions which, on account of the latter's movement in the opposite direction to the central ion, produce movement of solvent in this opposing direction as well. This is known as the electrophoretic effect.

Such interactions must obviously increase in significance with increasing concentration of the electrolyte. In the extreme condition of infinite dilution, all interionic effects are eliminated, ions move without the above restrictions, current may pass freely and consequently conductivity reaches a maximum value – a result, as we shall see shortly, in accordance with experience. In another extreme situation, interionic attraction may become so great that the formation of discrete ion-pairs may be regarded as occurring. The most