

Electrochemical Systems



SECOND EDITION

Electrochemical Systems

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Preface

to the Second Edition

A major theme of *Electrochemical Systems* is the simultaneous treatment of many complex, interacting phenomena. The wide acceptance and overall impact of the first edition have been gratifying, and most of its features have been retained in the second edition. New chapters have been added on porous electrodes and semiconductor electrodes. In addition, over 70 new problems are based on actual course examinations.

Immediately after the introduction in Chapter 1, some may prefer to study Chapter 11 on transport in dilute solutions and Chapter 12 on concentrated solutions before entering the complexities of Chapter 2. Chapter 6 provides a less intense, less rigorous approach to the potentials of cells at open circuit. Though the subjects found in Chapters 5, 9, 10, 13, 14, and 15 may not be covered formally in a one-semester course, they provide breadth and a basis for future reference.

The concept of the electric potential is central to the understanding of the electrochemical systems. To aid in comprehension of the difference between the potential of a reference electrode immersed in the solution of interest and the electrostatic potential, the quasi-electrostatic potential, or the cavity potential—since the composition dependence is quite different—problem 6.12 and Figure 12.1 have been added to the new edition. The reader will also benefit by the understanding of the potential as it is used in semiconductor electrodes.

Preface

to the First Edition

Electrochemistry is involved to a significant extent in the present-day industrial economy. Examples are found in primary and secondary batteries and fuel cells; in the production of chlorine, caustic soda, aluminum, and other chemicals; in electroplating, electromachining, and electrorefining; and in corrosion. In addition, electrolytic solutions are encountered in desalting water and in biology. The decreasing relative cost of electric power has stimulated a growing role for electrochemistry. The electrochemical industry in the United States amounts to 1.6 percent of all U.S. manufacturing and is about one third as large as the industrial chemicals industry.¹

The goal of this book is to treat the behavior of electrochemical systems from a practical point of view. The approach is therefore macroscopic rather than microscopic or molecular. An encyclopedic treatment of many specific systems is, however, not attempted. Instead, the emphasis is placed on fundamentals, so as to provide a basis for the design of new systems or processes as they become economically important.

Thermodynamics, electrode kinetics, and transport phenomena are the three fundamental areas which underlie the treatment, and the attempt is made to illuminate these in the first three parts of the book. These areas are interrelated to a considerable extent, and consequently the choice of the proper sequence of material is a problem. In this circumstance, we have

¹ G. M. Wenglowksi, "An Economic Study of the Electrochemical Industry in the United States," J. O'M. Bockris, ed., *Modern Aspects of Electrochemistry*, no. 4 (London: Butterworths, 1966), pp. 251-306.

pursued each subject in turn, notwithstanding the necessity of calling upon material which is developed in detail only at a later point. For example, the open-circuit potentials of electrochemical cells belong, logically and historically, with equilibrium thermodynamics, but a complete discussion requires the consideration of the effect of irreversible diffusion processes.

The fascination of electrochemical systems comes in great measure from the complex phenomena which can occur and the diverse disciplines which find application. Consequences of this complexity are the continual rediscovery of old ideas, the persistence of misconceptions among the uninitiated, and the development of involved programs to answer unanswerable or poorly conceived questions. We have tried, then, to follow a straightforward course. Although this tends to be unimaginative, it *does* provide a basis for effective instruction.

The treatment of these fundamental aspects is followed by a fourth part, on applications, in which thermodynamics, electrode kinetics, and transport phenomena may all enter into the determination of the behavior of electrochemical systems. These four main parts are preceded by an introductory chapter in which are discussed, mostly in a qualitative fashion, some of the pertinent factors which will come into play later in the book. These concepts are illustrated with rotating cylinders, a system which is moderately simple from the point of view of the distribution of current.

The book is directed toward seniors and graduate students in science and engineering and toward practitioners engaged in the development of electrochemical systems. A background in calculus and classical physical chemistry is assumed.

William H. Smyrl, currently of the University of Minnesota, prepared the first draft of chapter 2, and Wa-She Wong, formerly at the General Motors Science Center, prepared the first draft of chapter 5. The author acknowledges with gratitude the support of his research endeavors by the United States Atomic Energy Commission, through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory, and subsequently by the United States Department of Energy, through the Materials Sciences Division of the Lawrence Berkeley Laboratory.

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Introduction

1

Since the fundamental aspects of electrochemistry are to be developed, in order, in Parts A, B, and C, this chapter has been designed to introduce important concepts related to the flow of fluids, mass transfer, interfacial phenomena, and electrochemical thermodynamics. For accomplishing this purpose, it seems appropriate to begin with a superficial consideration of the behavior of a particular electrochemical system. In this way the reader can see how these factors act, and interact with each other, to determine system behavior. He can then proceed with an overall view of the ultimate utility and application of the detailed material as it is presented subsequently. Since essentially all the material in Chapter 1 will be repeated later with a more thorough development, reference to original work and collateral reading will be postponed.

1.1 THERMODYNAMICS, ELECTRODE KINETICS, AND TRANSPORT PROCESSES

The analysis of electrochemical systems draws primarily on three fundamental areas of electrochemistry.

Thermodynamics provides the framework for describing the properties of electrolytic solutions and their dependence on composition, temperature, and pressure. This is a macroscopic science and hence provides an appropriate basis for our studies, since the system behavior need not be correlated with microscopic or molecular concepts. Thermodynamics also provides a

framework for describing reaction equilibria and thermal effects, which manifest themselves most directly in equilibrium cell potentials. Furthermore, the driving forces for irreversible processes are conveniently expressed in thermodynamic terms.

Departures from equilibrium conditions are inherent in the application of electrochemical systems. *Electrode kinetics* concerns the nonequilibrium driving force, or *surface overpotential*, necessary to make heterogeneous electrode reactions proceed at appreciable rates. Here again, we seek to express relationships among macroscopically measurable quantities as they will affect system behavior.

Of equal importance are irreversibilities associated with *transport* in electrolytic solutions. These are responsible for ohmic losses and heating in the solutions, and for limited rates of transfer of reactants to electrodes and products away from electrodes.

1.2 ROTATING CYLINDERS

To illustrate the applications of these fundamental areas of thermodynamics, electrode kinetics, and transport phenomena. Chapter 1 will consider their use in the analysis of a simple electrochemical system; namely, two concentric, cylindrical electrodes with an electrolytic solution in the annulus between the two, as shown in Figure 1.1. The application of an

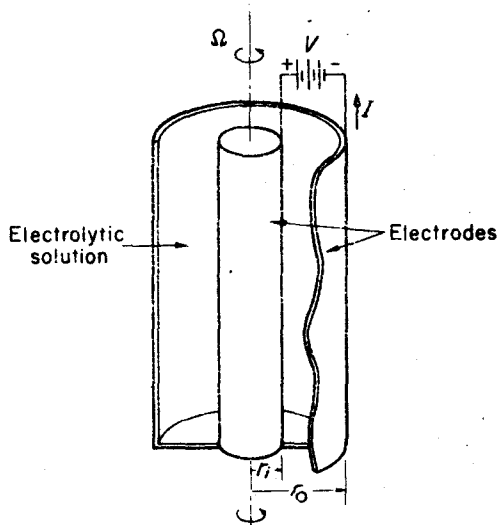


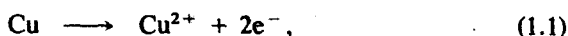
Figure 1.1 System of cylindrical electrodes, the inner of which can rotate.

electric potential difference between these electrodes leads to the passage of current and the occurrence of electrode reactions. We include the possibility of rotating one or both of the electrodes about the axis to stir the solution.

This electrode system is not utilized extensively in any commercial application nor as a routine research tool, although the latter possibility has perhaps been overlooked. It is used here because it can illustrate a variety of complex behavior, and, at the same time, it is simple enough to permit some definite descriptions of this behavior.

1.3 ELECTROLYTIC CONDUCTION

Suppose that the solution placed between the electrodes is an aqueous solution of cupric sulfate and that the electrodes are copper. The process consists of the dissolution of copper at the positive electrode, the anode;



the passage of cupric ions through the solution; and the deposition of copper at the negative electrode, the cathode.

In the solution, cupric sulfate will dissociate into charged cupric ions Cu^{2+} and sulfate ions SO_4^{2-} , which are driven through the solution by the electric field; the cupric ions are driven toward the negative electrode, and the sulfate ions toward the positive electrode. The velocity of migration of an ion is proportional to the charge on the ion and the electric field, the negative of the gradient of electric potential

$$v_i = -z_i u_i F \frac{d\Phi}{dr}. \quad (1.2)$$

Here Φ is the potential; r is the radial distance from the axis; z_i is the charge number of the ion; and F is Faraday's constant, equal to 96,487 C/equiv. Thus $z_i F$ is the charge per mole. The proportionality factor u_i is called the *mobility* of the ion and has units of $\text{cm}^2 \cdot \text{mol} / \text{J} \cdot \text{s}$.

The current density i is the sum of the currents carried by the two kinds of ions and has the units of A/cm^2 . It is obtained by multiplying the ionic velocities by the concentrations and the charges and adding:

$$i = z_+ c_+ F v_+ + z_- c_- F v_-. \quad (1.3)$$

Since the solution is electrically neutral, that is, the charges on the cations are balanced by the charges on the anions, the ionic concentrations are related by

$$z_+ c_+ + z_- c_- = 0. \quad (1.4)$$