ELECTROCHEMISTRY

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PRENTICE-HALL, INC.
Englewood Cliffs, N. J. 07632

Library of Congress Cataloging-in-Publication Data

RIEGER, PHILIP HENRI, date
Electrochemistry.

Includes bibliographies and index.
1. Electrochemistry. I. Title.
QD553.R53 1987 541.3′7 87-2229
ISBN 0-13-248907-4

Cover design: Edsal Enterprises
Manufacturing buyer: Harry Baisley

A Division of Simon & Schuster,
Englewood Cliffs, New Jersey 07632

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ISBN 0-13-248907-4 01

Prentice-Hall International (UK) Limited, *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall Canada Inc., *Toronto*
Prentice-Hall Hispanoamericana, S.A., *Mexico*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Prentice-Hall of Southeast Asia Pte. Ltd., *Singapore*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*
Whitehall Books Limited, *Wellington, New Zealand*

Dedicated to the memory of those who
inspired my interest in electrochemistry:

Arthur F. Scott

William H. Reinmuth

Donald E. Smith

PREFACE

It has been fashionable to describe electrochemistry as a discipline which interfaces with many other sciences. A perusal of the table of contents will affirm that view. Electrochemistry finds applications in all branchs of chemistry as well as in biology, biochemistry, and engineering; electrochemistry gives us batteries and fuel cells, electroplating and electrosynthesis, and a host of industrial and technological applications which are barely touched on in this book. However, I will maintain that electrochemistry is really a branch of physical chemistry. Electrochemistry grew out of the same tradition which gave physics the study of electricity and magnetism. The reputed founders of physical chemistry—Arrhenius, Ostwald, and van't Hoff—made many of their contributions in areas which would now be regarded as electrochemistry. With the post–World War II capture of physical chemistry by chemical physicists, electrochemists have tended to retreat into analytical chemistry, thus defining themselves out of a great tradition. G. N. Lewis defined physical chemistry as "the study of that which is interesting." I hope that the readers of this book will find that electrochemistry qualifies.

While I have tried to touch on all the important areas of electrochemistry, there are some which have had short shrift. For example, there is virtually nothing on spectroelectrochemistry or the use of dedicated microcomputers in electrochemical instrumentation, and there is rather little on ion–selective electrodes and chemically modified electrodes. The selection of topics has been far harder than I anticipated, a reflection of my ignorance of some important areas when I started. On the other hand, there may be a few topics which may appear to have received too much attention. I confess that my interest in electrochemistry is primarily in mechanistic studies, particularly with organometallic systems. This orientation may be all too apparent for some readers.

Since this is a textbook with the aim of introducing electrochemistry to the previously uninitiated, breadth has been sought at the expense of depth. I have tried, however, to provide numerous entries into the review literature so that a particular topic of interest can be followed up with a minimum of effort. References in the text are of four types. Some are primarily of historical interest; when I have traced ideas to their origins, I have tried to give the original reference, fully aware that only a science history buff is likely to read them but equally aware that such references can be hard to find. A second class of references is to specific results from the recent literature, and a third class leads to the review literature. These references are collected at the end of each chapter. A fourth class of references includes the books and monographs which are collected in a classified Bibliography, Appendix 1.

SI units have been employed throughout the book. References to older units are given in footnotes where appropriate. In most cases, the use of SI units eliminates unit conversion problems and greatly simplifies numerical calculations. The major remaining source of units ambiguity comes from concentrations. When a concentration is used as an approximation to an activity, molar units (mol L^{-1}) must be used to conform to the customary standard state. But when a concentration acts as a mechanical variable, *e.g.*, in a diffusion problem, the SI unit, mol m^{-3}, should be used. The mol m^{-3} concentration unit is equivalent to mmol L^{-1} and, in a sense, is a more practical concentration scale since voltammetric experiments often employ substrate concentrations in the millimolar range.

This book has had a long, slow evolution. It began as chapters on electrochemistry and transport processes in a textbook on biophysical chemistry, a joint project with J. H. Gibbs and J. M. Steim which unfortunately came to naught. There is a slightly biological flavor in parts of Chapters 1 and 2 which reflects this origin. It then evolved into a set of lecture notes for a short course in electrochemistry for seniors and graduate students at Brown; the emphasis in the course was organometallic applications and again that flavor remains, particularly in Chapters 4 and 5. Chapters and sections were added over the years until about 200 pages had accumulated. In the spring of 1983, the chemistry editor at Prentice-Hall, Elizabeth Perry, expressed interest in the book and the lecture notes started on a painful journey toward a book. Progress was slow until the summer of 1984, by which time Chapters 1–3 had attained nearly their present form, and Ms. Perry's successor, Nancy Forsyth, formalized the nascent book with a contract. Chapters 4 and 5 grew during 1984 and early 1985, and Chapter 6 was largely written during the spring of 1985 while I enjoyed a sabbatical leave at the University of Vermont. Ms. Forsyth was succeeded at Prentice-Hall by Curtis Yehnert in 1985 and by Dan Joraanstad in 1986, and they shepherded the book into final form.

Many people have helped along the way. I am particularly grateful to my wife, Anne L. Rieger, for her patience in listening to my problems and for her encouragement in times of discouragement.

David Gosser has listened to my ideas and offered many helpful suggestions; the cyclic voltammogram simulations of Chapters 4 and 5 are his work. I have benefitted from the advice and encouragement of many of my colleagues at Brown, most particularly Joe Steim, John Edwards, Dwight Sweigart, and Ed Mason. In addition to providing a stimulating atmosphere at the University of Vermont, Bill Geiger offered some timely advice on electroanalytical chemistry. I am particularly grateful to James Anderson of the University of Georgia, to Arthur Diaz of IBM, San Jose, to Harry Finklea of Virginia Polytechnic Institute, and to Franklin Schultz of Florida Atlantic University for their careful reading of the manuscript and numerous helpful suggestions; the book has been much improved through their efforts. I am also grateful to Catherine Schwab, who contributed several problems; to Nancy Stone, whose careful reading turned up some errors; to Bertha Hansen, Carol White, and Patricia Fay, who typed early versions of Chapters 1–3; and to Barbara Tellier, who helped with the assembly of the figures.

Since late 1984, I have been linked to Brown's mainframe computer, and Chapters 4–6 have been written and edited directly at a terminal. The book has been produced using the IBM Waterloo SCRIPT word-processing system and a Xerox 9700 laser printer equipped with Century Schoolbook roman, italic, bold, bold italic, greek, and mathematics fonts. The help of Richard Damon and Allen Renear, of the Brown Computer Center, and Virginia Huebner, production editor at Prentice-Hall, has been essential to the completion of a book which at least approachs professional standards. All the figures have been produced using TOPDRAW software (SLAC Computation Group, Stanford, CA) and a Calcomp plotter. TOPDRAW was never intended for line drawings and some of the figures turned out to be *tours de force*. Multiple drafts were often required to get a figure just right; the patience of the Computer Center staff has been appreciated.

Philip H. Rieger

December 1986

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1

ELECTROCHEMICAL POTENTIALS

1.1 INTRODUCTION

Origins of Electrode Potentials

When a piece of metal is immersed in an electrolyte solution, an electric potential difference is developed between the metal and the solution. This phenomenon is not unique to a metal and electrolyte; in general whenever two dissimilar conducting phases are brought into contact, an electric potential is developed across the interface. In order to understand this effect, let us consider first the related case of two dissimilar metals in contact.

When individual atoms condense to form a solid, the various atomic orbital energy levels broaden and merge, generally forming two bands of allowed energy levels. The band of levels corresponding to the bonding molecular orbitals in a small molecule is called the *valence band* and usually is completely filled. The band of levels corresponding to nonbonding molecular orbitals is called the *conduction band.* This band is partially filled in a metal and is responsible for the electrical conductivity. As shown in Figure 1.1, electrons fill the conduction band up to an energy called the *Fermi level.* The energy of the Fermi level, relative to the zero defined by ionization, depends on the atomic orbital

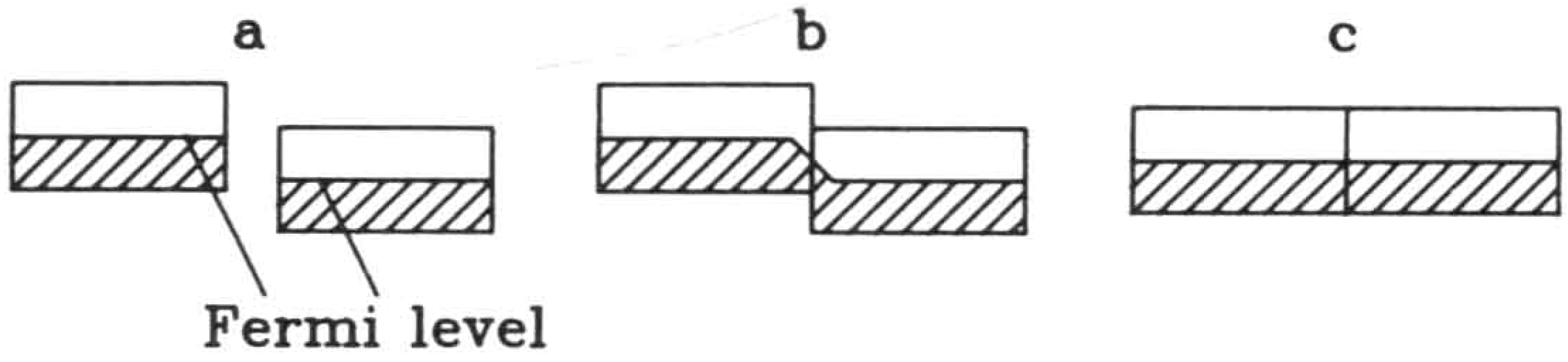

Figure 1.1 The conduction bands of two dissimilar metals (a) when the metals are not in contact; (b) at the instant of contact; and (c) at equilibrium.

energies of the metal and on the number of electrons occupying the band and thus varies from one metal to another. Now consider two dissimilar metals. Since the Fermi levels are at different energies, when the two metals are brought into contact, electrons flow from the metal with the higher Fermi level into the metal with the lower Fermi level. This electron transfer results in a separation of charge and an electric potential difference across the phase boundary. The effect of the electric potential difference is to raise the energy of the conduction band of the second metal and to lower the energy of the conduction band of the first until the Fermi levels are equal in energy; when the Fermi levels are equal, no further electron transfer takes place. In other words, the intrinsically lower energy of the second metal's conduction band is exactly compensated by the electrical work required to move an electron from the first metal to the second against the electric potential difference.

A very similar process occurs when a metal, say a piece of copper, is placed in a solution of copper sulfate. Some of the copper ions may deposit on the copper metal, accepting electrons from the metal conduction band and leaving the metal with a small positive charge and the solution with a small negative charge. With a more active metal, it may be the other way around: a few atoms leave the metal surface as ions, giving the metal a small negative charge and the solution a small positive charge. The direction of charge transfer depends on the metal, but in general charge separation occurs and an electric potential difference is developed between the metal and the solution.

When two dissimilar electrolyte solutions are brought into contact, there is generally a charge separation at the phase boundary owing to the different rates of diffusion of the various ions. The resulting electric potential difference, called a *liquid junction potential*, is discussed in Section 3.4.