Electroanalytical Chemistry

Basil H. Vassos
Galen W. Ewing

ELECTROANALYTICAL CHEMISTRY

Basil H. Vassos

Professor
Department of Chemistry
University of Puerto Rico

Galen W. Ewing

Professor Emeritus
Seton Hall University
Adjunct Professor
New Mexico Highlands University

A Wiley-Interscience Publication

JOHN WILEY & SONS

New York Chichester Brisbane Toronto Singapore

Library of Congress Cataloging in Publication Data

Vassos, Basil H.
Electroanalytical chemistry.

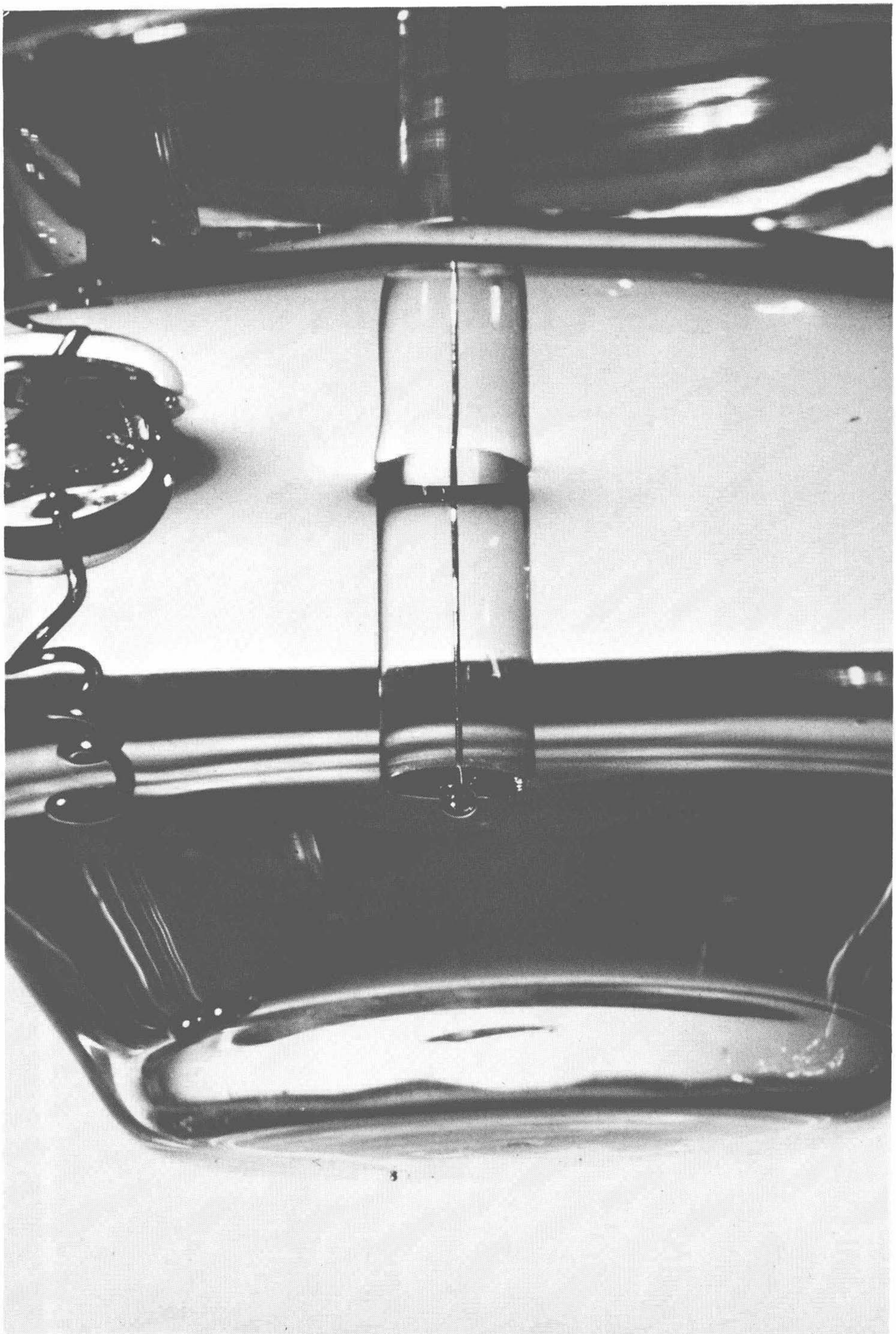
"A Wiley-Interscience publication."
Includes bibliographical references and index.
1. Electrochemical analysis. I. Ewing, Galen Wood, 1914- . II. Title.

QD115.V28 1983 543'.0871 82-17400
ISBN 0-471-09028-X

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ELECTROANALYTICAL CHEMISTRY



Dropping mercury electrode and silver chloride reference electrode (Courtesy IBM Instruments).

PREFACE

In this book we have attempted to include those aspects of electrochemistry, both theoretical and practical, that we feel a graduate student specializing in analytical chemistry should master. The early chapters contain an abbreviated review of material that should be familiar from prior courses, leading directly into more specialized advanced topics. Subsequent chapters then treat the several subdisciplines in detail.

Principles of quantitation *per se* are treated in some detail in Chapter 15, with emphasis on titrimetric and standard addition methods. The intent is to tie together many of the techniques from earlier chapters, showing their relations to each other in a way that will reinforce the individual treatments.

Similarly, Chapter 16 serves to unify the theoretical aspects of the various dynamic electroanalytical methods with a more extensive treatment of diffusion phenomena. The fractional calculus is given a brief elementary exposition.

The final chapter is a short description of the electronic instrumentation used in modern electroanalytical apparatus. This material can, of course, be omitted if the student has sufficient background in this area.

We have included literature references, partly to indicate the sources for statements or quotations, and more importantly, to suggest to the inquiring student where to find further material on a particular subject.

The book is suitable for upper-class undergraduate and first-year graduate students in chemistry and allied fields such as biology and physics. A working knowledge of calculus is assumed.

We wish to thank Professor Peter E. Sturrock for a careful and critical reading of the manuscript and for many useful suggestions. We are grateful to Mr. Stanley P. Dodd of Sargent-Welch Scientific Company for the loan of a Sargent-Welch Polarograph with which a number of the illustrations were prepared. Professor Ronald D. Clark of New Mexico Highlands University kindly permitted our use of their facilities. Our thanks also go to Gayle Foss Ewing, who typed the manuscript with the aid of a word-processing computer, and Myrtle King who assisted in reading proof.

BASIL H. VASSOS
GALEN W. EWING

Rio Piedras, Puerto Rico
Las Vegas, New Mexico
August 1983

ELECTROANALYTICAL CHEMISTRY

CONTENTS

Chapter 1. INTRODUCTION 1

What Is Electrochemistry? 1
Electroanalytical Measurements 4
    Potentiometry 4
    Galvanostatic Measurements 6
    Potentiostatic Measurements 7
Electrochemical Conventions 8
References 11

Chapter 2. ELECTROCHEMICAL MEASUREMENTS 12

Voltage measurements 12
    Voltage Measurements with Finite Current 15
Impedance Measurements 16
The Electrical Double Layer 20
Electrocapillarity 23
Current Measurements 25
Diffusion Transport 33
References 35

Chapter 3. POTENTIOMETRY 37

Electrode Potentials 37
    Liquid Junction Potentials 39
    The Indicator Electrode 41
Classification of Electrodes 42
The Glass Electrode 44
Ion-Selective Electrodes 48
    Classification of Ion-Selective Electrodes 50
Instrumentation 58
References 58

Chapter 4. VOLTAMMETRY: I. POLAROGRAPHY 60

Introduction 60
Voltammetry 60
Polarography 62
  The Basic Experiment 63
Theoretical Considerations 70
  The Ilkovič Equation 70
  The Heyrovský-Ilkovič Equation 73
  Irreversible Systems 74
  Anodic Oxidations 76
  Polarographic Maxima 78
Instrumentation 78
  Sampling 79
  Resistance Compensation 80
  Charging-Current Compensation 80
  Cell Design 80
  The Capillary System 83
Experimental Methodology 83
  Supporting Electrolytes and Half-Wave-Potentials 83
  Resolution 84
  Precision, Accuracy, and Sensitivity 86
  Scope of Applicability 86
  Organic Applications 87
References 88

Chapter 5. VOLTAMMETRY: II. PULSE AND SQUARE-WAVE POLAROGRAPHY 90

A Basic Experiment 90
Classification of Step Methods 92
The Fundamental Process 94
Instrumentation 100
References 101

Chapter 6. VOLTAMMETRY: III. AC POLAROGRAPHY 102

The Basic Experiment 102
Theoretical Considerations 104
Instrumentation 108
  Second-Harmonic AC Polarography 109

Methods Related to AC Polarography 113
AC-Pulse Polarography 114
References 115

Chapter 7. VOLTAMMETRY: IV. LINEAR SWEEP 116

The Basic Experiment 116
Theoretical Considerations 119
Irreversible Processes 126
Coupled Chemical Reactions 127
Staircase LSV 128
AC and Pulse LSV 128
References 129

Chapter 8. VOLTAMMETRY: V. FINITE DIFFUSION 130

Thin-Layer Cells 130
Electrochemistry with Immobilized Reagents 135
Membrane Electrodes 136
Ultramicroelectrodes 138
References 138

Chapter 9. CONTROLLED-CURRENT METHODS 140

Chronopotentiometry 140
The Basic Experiment 140
Theoretical Considerations 142
Instrumentation 146
AC Chronopotentiometry 146
Chronopotentiometry with Increasing Current 147
Coulostatic Analysis 149
References 150

Chapter 10. METHODS WITH CONVECTION: I. ELECTRODEPOSITION AND COULOMETRY 152

Electrodeposition 152
The Basic Experiment 152
Theoretical Considerations 153
Coulometry 155
Controlled-Potential Coulometry 156

Constant-Current Coulometric Titration 157
Instrumentation 158
References 161

Chapter 11. METHODS WITH CONVECTION: II. HYDRODYNAMIC VOLTAMMETRY 162

Classification of Methods 162
Interface Renewal 162
Flow-through Systems 163
Continuously Stirred Systems 163
Disk Electrodes 163
A Basic Experiment 163
Theoretical Considerations 165
Flow-Through Electrodes 167
Experimental Techniques 169
Applications 171
References 174

Chapter 12. STRIPPING ANALYSIS 176

The Basic Experiment 176
Theoretical Considerations 177
Preconcentration (Plating) 177
Stripping 178
Instrumentation 179
Electrodes 180
References 183

Chapter 13. CONDUCTOMETRY 184

The Experimental Basis 184
With Electrodes 184
Without Electrodes 187
Magnetic Induction 187
Theoretical Considerations 189
Instrumentation 189
The Four-Electrode Cell 189
The Two-Electrode Cell 190
Electrodeless Cells 193
References 194

Chapter 14. OPTICAL–ELECTROCHEMICAL METHODS 195

Spectroelectrochemistry 195
Electrochemical Photochemistry 199
Photoelectrochemistry 201
Electrochemiluminescence (ECL) 202
Surface-Enhanced Raman Spectroscopy (SERS) 203
References 203

Chapter 15. TECHNIQUES OF MEASUREMENT 205

Comparison with Standards 205
Standard Addition or Subtraction 207
Titrimetry 208
    Endpoint Detection 209
    Constant-Potential Titrimetry 214
Coulometric Titration 215
References 217

Chapter 16. SOME ASPECTS OF DIFFUSION PHENOMENA 218

Diffusion Transport 218
    The General Equation 222
Semi-Integral and Semidifferential Techniques 225
    Measurement of μ and ϵ 227
References 228

Chapter 17. ELECTRONIC INSTRUMENTATION 229

Electrical Quantities 229
Components 230
Operational Amplifiers 231
Analog Modules 236
Digital Modules 236
Noise 237
    Modulation 239
    AC Filters 240
Phase Relations 242
Microprocessors 244
References 244

Appendix 1. SYMBOLS AND ABBREVIATIONS 245

Appendix 2. STANDARD ELECTRODE POTENTIALS 249

INDEX 251

Chapter 1

INTRODUCTION

WHAT IS ELECTROCHEMISTRY?

In the chemical reactions known as *redox*, the fundamental step is the exchange of one or more electrons between two species, 1 and 2:

$$OX_1 + ne^- \longrightarrow RED_1 \qquad (1\text{-}1a)$$

$$RED_2 \longrightarrow OX_2 + ne^- \qquad (1\text{-}1b)$$

$$OX_1 + RED_2 \longrightarrow OX_2 + RED_1 \qquad (1\text{-}1)$$

where OX and RED represent the oxidized and reduced forms, respectively. Frequently, this fundamental process is complicated by other chemical changes. For example, when bromate ions and arsenic(III) atoms are involved in a redox reaction, the process is:

$$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O \qquad (1\text{-}2a)$$

$$3As(III) \longrightarrow 3As(V) + 6e^- \qquad (1\text{-}2b)$$

$$BrO_3^- + 3As(III) + 6H^+ \longrightarrow Br^- + 3As(V) + 3H_2O \qquad (1\text{-}2)$$

Even with the complications of the protons and water molecules, the basic process is simply the transfer of electrons from arsenic to bromate ions.

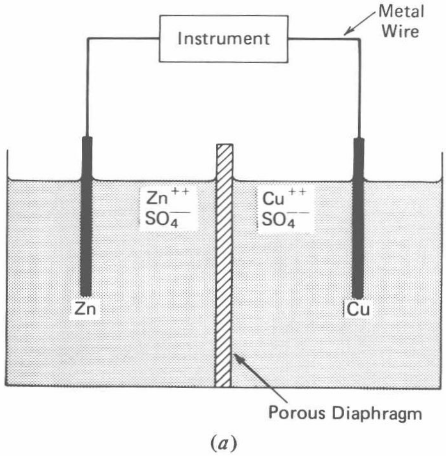
The importance of a redox reaction, in the present context, lies in the fact that the transfer of electrons from reductant to oxidant can be made to take place at a pair of electrodes connected through external circuitry. At one electrode (the anode), the reductant transfers one or more electrons to the metal electrode [as Eqs. (1-1b) and (1-2b)], while to maintain overall electrical balance, an equal number of electrons must leave that electrode and pass through the external wiring. Simultaneously, the cathode yields up a like number of electrons to the oxidant [Eqs. (1-1a) and (1-2a)]. This constitutes a complete electrical circuit, and the extent of the redox process can be monitored or controlled by electronic operations on the external portion of the circuit. It is this ability to control the extent and direction of a reaction by electrical means that constitutes the unique importance of electrochemistry.

Analytical electrochemistry is concerned with small currents (seldom greater than a few milliamperes) at low voltages (up to perhaps 2 volts). This is precisely the magnitude easily handled by modern integrated-circuit electronics, allowing the vast body of electronic techniques of measurement and control to be utilized directly. This explains the facility with which electroanalytical chemistry has developed into a highly sophisticated group of instrumental techniques.

An electrochemical cell can be simulated by resistors and capacitors (R, C) combined in a network that will possess nearly identical electrical behavior. Such a network, designated an *equivalent circuit*, is often useful in theoretical studies, to assist in elucidating the properties of a cell. Similarly, the actual RC-network can be used as a *dummy cell* to substitute for the real one in testing the operation of an electrochemical instrument.

In order to achieve control of the reaction, it is necessary to prevent the oxidant and reductant from coming into direct contact with each other. For this purpose, a special container provided with a membrane or barrier is generally required. An example is shown in Figure 1-1, where the redox process is $Zn + Cu^{++} \longrightarrow Cu + Zn^{++}$. In this case the zinc electrode generates an excess of electrons that will flow along the wire, pass through an external instrument, and return to the copper electrode. The electrical circuit is then completed by ions moving through the solution between the two electrodes. The "porous diaphragm" is a barrier, such as fritted glass, to prevent the mixing of the two solutions, while permitting the transport of ions.

The electrode where oxidation takes place, in this case the zinc, is the *anode*, and the electrode where reduction occurs is the *cathode*. It is convenient to speak of



(*a*)

$Zn|Zn^{++}||Cu^{++}|Cu$

(*b*)

Figure 1-1. (*a*) Electrochemical cell; (*b*) Symbolic representation. The anode is conventionally shown on the left.

anodic and cathodic half-reactions, while in terms of charge transport, we define corresponding anodic and cathodic currents. In practice, the direction of the reaction, and hence which electrode acts as the anode and which the cathode, depends on the nature of the external instrument. If the instrument is passive, in that it merely either allows or prevents the electron flow, the cell will show a spontaneous anode and cathode, as described above. In contrast, in many electroanalytical experiments, active instrumentation is used to control the electron flow. In this case, the electrons can be forced to move in either the spontaneous or the opposite direction; they can even be made to move rapidly in alternating directions, so that anode and cathode are periodically interchanged.†

If the cell is left without an external controlling instrument, it will exhibit a difference of potential, E, between its electrodes, indicating the tendency of the electrons to circulate outside the cell. This potential, in turn, is a measure of the free energy, ΔG, of the reaction:

$$E = -\frac{\Delta G}{nF} \tag{1-3}$$

where the negative sign indicates that, for a spontaneous reaction, ΔG is negative. The potential of an electrochemical cell is always taken as positive, and is the physically measurable difference of potential between the electrodes.‡

In Eq. (1-3), the factor n is the number of electrons exchanged, and F is the Faraday constant (estimated to be 96486.332 coulombs/mole). Equation (1-3) is strictly valid only if there is no current passing through the cell. This is because the passage of current causes not only changes of concentration, but also voltage drops and heat effects. Fortunately, with the very small currents needed by modern measuring devices, the error is usually negligible, and one can measure E, and thus ΔG, with great accuracy.

For electric current to pass through the cell, redox (faradaic) processes must occur at both electrodes, to the extent of one mole for each nF coulombs. It can thus be written:

$$\begin{matrix}\text{Number of}\\ \text{Moles reacted}\end{matrix} = \frac{Q}{nF} = \frac{1}{nF}\int I\,dt \tag{1-4}$$

where Q is the number of coulombs passed, which, in turn, is equal to the time-integral of the current, I.

†Sometimes a distinction is drawn between *galvanic cells*, in which the reaction takes place spontaneously, and *electrolytic cells*, in which the direction of the reaction is reversed. This is not a particularly helpful classification, at least for us, because a given cell can be equally well operated either way.

‡On the other hand, if the potential is defined thermodynamically rather than experimentally, it is necessary to allow the reversal of the sign of E with the reversal of ΔG. Thus, if the chemical reaction is written backwards, the free energy of reaction changes sign, and it would complicate the algebra if E could not follow this change [1].

According to Eq. (1-3), in reversible systems, for every value of ΔG there is a corresponding value of the potential E of the cell. This relationship also is valid in the reverse sense, so that if one forces a potential E upon a cell, the free energy of the reaction will change by the necessary amount so that the relation $\Delta G = -nFE$ continues to hold for negligible currents. A more negative value of ΔG will cause the reaction to go forward, while a positive value will reverse the direction. The system will proceed on a path leading to the equilibrium condition.† This process is effected by changes in activities (and thus in concentrations), since ΔG depends on activities through the relation:

$$\Delta G = \Delta G^\circ + \sum_i RT \ln a_i \tag{1-5}$$

in which ΔG° is a constant depending on the reference state, while the variables symbolized by a_i are the activities of the various species involved.

Upon changing the potential, the activities in Eq. (1-5) will begin to change until ΔG goes to zero. This occurs by means of redox processes, which alter the relative concentrations. Eventually, a form of equilibrium is attained where no further change takes place. This is not a true chemical equilibrium in the conventional sense, since upon removing the applied potential, the reactions will occur again. Chemical and electrochemical equilibria have the same properties, including reversibility, for as long as the potential is applied.

The control of ΔG by electrical means, as outlined above, is unique in chemistry. Otherwise chemists have little or no control over the free energy of a reaction once they have mixed their reagents.

ELECTROANALYTICAL MEASUREMENTS

Electrochemical processes are involved in many areas such as industrial synthesis, corrosion studies, physiological experimentation, and battery research, in addition to analytical measurements. This book is limited to those applications that can give analytical information. In other words, the emphasis is on measurements that ultimately lead to either the quantity or the concentration of chemical species.

In this context, there are three principal types of electrochemical experiments and three kinds of controlling or measuring devices to implement them. The three classes of experiments are: potentiometric, galvanostatic, and potentiostatic. We will consider them in turn.

Potentiometry

This is a type of measurement in which the function of the controlling device is primarily to ensure that no significant current is drawn from the cell. Voltage is

†The rate at which the equilibrium is approached varies from system to system, and for some it may be practically zero.