Contents

Preface *xxi*
Major Symbols and Abbreviations *xxv*
About the Companion Website *liii*

1 Overview of Electrode Processes *1*
1.1 Basic Ideas *2*
1.1.1 Electrochemical Cells and Reactions *2*
1.1.2 Interfacial Potential Differences and Cell Potential *4*
1.1.3 Reference Electrodes and Control of Potential at a Working Electrode *5*
1.1.4 Potential as an Expression of Electron Energy *6*
1.1.5 Current as an Expression of Reaction Rate *6*
1.1.6 Magnitudes in Electrochemical Systems *8*
1.1.7 Current–Potential Curves *9*
1.1.8 Control of Current *vs.* Control of Potential *16*
1.1.9 Faradaic and Nonfaradaic Processes *17*
1.2 Faradaic Processes and Factors Affecting Rates of Electrode Reactions *17*
1.2.1 Electrochemical Cells—Types and Definitions *17*
1.2.2 The Electrochemical Experiment and Variables in Electrochemical Cells *18*
1.2.3 Factors Affecting Electrode Reaction Rate and Current *21*
1.3 Mass-Transfer-Controlled Reactions *23*
1.3.1 Modes of Mass Transfer *24*
1.3.2 Semiempirical Treatment of Steady-State Mass Transfer *25*
1.4 Semiempirical Treatment of Nernstian Reactions with Coupled Chemical Reactions *31*
1.4.1 Coupled Reversible Reactions *31*
1.4.2 Coupled Irreversible Chemical Reactions *32*
1.5 Cell Resistance and the Measurement of Potential *34*
1.5.1 Components of the Applied Voltage When Current Flows *35*
1.5.2 Two-Electrode Cells *37*
1.5.3 Three-Electrode Cells *37*
1.5.4 Uncompensated Resistance *38*
1.6 The Electrode/Solution Interface and Charging Current *41*
1.6.1 The Ideally Polarizable Electrode *41*
1.6.2 Capacitance and Charge at an Electrode *41*
1.6.3 Brief Description of the Electrical Double Layer *42*
1.6.4 Double-Layer Capacitance and Charging Current *44*

1.7 Organization of this Book *51*
1.8 The Literature of Electrochemistry *52*
1.8.1 Reference Sources *52*
1.8.2 Sources on Laboratory Techniques *53*
1.8.3 Review Series *53*
1.9 Lab Note: Potentiostats and Cell Behavior *54*
1.9.1 Potentiostats *54*
1.9.2 Background Processes in Actual Cells *55*
1.9.3 Further Work with Simple RC Networks *56*
1.10 References *57*
1.11 Problems *57*

2 Potentials and Thermodynamics of Cells *61*
2.1 Basic Electrochemical Thermodynamics *61*
2.1.1 Reversibility *61*
2.1.2 Reversibility and Gibbs Free Energy *64*
2.1.3 Free Energy and Cell emf *64*
2.1.4 Half-Reactions and Standard Electrode Potentials *66*
2.1.5 Standard States and Activity *67*
2.1.6 emf and Concentration *69*
2.1.7 Formal Potentials *71*
2.1.8 Reference Electrodes *72*
2.1.9 Potential–pH Diagrams and Thermodynamic Predictions *76*
2.2 A More Detailed View of Interfacial Potential Differences *80*
2.2.1 The Physics of Phase Potentials *80*
2.2.2 Interactions Between Conducting Phases *82*
2.2.3 Measurement of Potential Differences *84*
2.2.4 Electrochemical Potentials *85*
2.2.5 Fermi Energy and Absolute Potential *88*
2.3 Liquid Junction Potentials *91*
2.3.1 Potential Differences at an Electrolyte–Electrolyte Boundary *91*
2.3.2 Types of Liquid Junctions *91*
2.3.3 Conductance, Transference Numbers, and Mobility *92*
2.3.4 Calculation of Liquid Junction Potentials *96*
2.3.5 Minimizing Liquid Junction Potentials *100*
2.3.6 Junctions of Two Immiscible Liquids *101*
2.4 Ion-Selective Electrodes *101*
2.4.1 Selective Interfaces *101*
2.4.2 Glass Electrodes *102*
2.4.3 Other Ion-Selective Electrodes *106*
2.4.4 Gas-Sensing ISEs *111*
2.5 Lab Note: Practical Use of Reference Electrodes *112*
2.5.1 Leakage at the Reference Tip *112*
2.5.2 Quasireference Electrodes *112*
2.6 References *113*
2.7 Problems *116*

3 Basic Kinetics of Electrode Reactions *121*
3.1 Review of Homogeneous Kinetics *121*
3.1.1 Dynamic Equilibrium *121*
3.1.2 The Arrhenius Equation and Potential Energy Surfaces *122*
3.1.3 Transition State Theory *123*
3.2 Essentials of Electrode Reactions *125*
3.3 Butler–Volmer Model of Electrode Kinetics *126*
3.3.1 Effects of Potential on Energy Barriers *127*
3.3.2 One-Step, One-Electron Process *127*
3.3.3 The Standard Rate Constant *130*
3.3.4 The Transfer Coefficient *131*
3.4 Implications of the Butler–Volmer Model for the One-Step, One-Electron Process *132*
3.4.1 Equilibrium Conditions and the Exchange Current *133*
3.4.2 The Current–Overpotential Equation *133*
3.4.3 Approximate Forms of the i–η Equation *135*
3.4.4 Exchange Current Plots *139*
3.4.5 Very Facile Kinetics and Reversible Behavior *139*
3.4.6 Effects of Mass Transfer *140*
3.4.7 Limits of Basic Butler–Volmer Equations *141*
3.5 Microscopic Theories of Charge Transfer *142*
3.5.1 Inner-Sphere and Outer-Sphere Electrode Reactions *142*
3.5.2 Extended Charge Transfer and Adiabaticity *143*
3.5.3 The Marcus Microscopic Model *146*
3.5.4 Implications of the Marcus Theory *152*
3.5.5 A Model Based on Distributions of Energy States *162*
3.6 Open-Circuit Potential and Multiple Half-Reactions at an Electrode *168*
3.6.1 Open-Circuit Potential in Multicomponent Systems *169*
3.6.2 Establishment or Loss of Nernstian Behavior at an Electrode *170*
3.6.3 Multiple Half-Reaction Currents in i–E Curves *171*
3.7 Multistep Mechanisms *171*
3.7.1 The Primacy of One-Electron Transfers *172*
3.7.2 Rate-Determining, Outer-Sphere Electron Transfer *173*
3.7.3 Multistep Processes at Equilibrium *173*
3.7.4 Nernstian Multistep Processes *174*
3.7.5 Quasireversible and Irreversible Multistep Processes *174*
3.8 References *177*
3.9 Problems *180*

4 Mass Transfer by Migration and Diffusion *183*
4.1 General Mass-Transfer Equations *183*
4.2 Migration in Bulk Solution *186*
4.3 Mixed Migration and Diffusion Near an Active Electrode *187*
4.3.1 Balance Sheets for Mass Transfer During Electrolysis *188*
4.3.2 Utility of a Supporting Electrolyte *192*
4.4 Diffusion *193*

4.4.1 A Microscopic View *193*
4.4.2 Fick's Laws of Diffusion *196*
4.4.3 Flux of an Electroreactant at an Electrode Surface *199*
4.5 Formulation and Solution of Mass-Transfer Problems *199*
4.5.1 Initial and Boundary Conditions in Electrochemical Problems *200*
4.5.2 General Formulation of a Linear Diffusion Problem *201*
4.5.3 Systems Involving Migration or Convection *202*
4.5.4 Practical Means for Reaching Solutions *202*
4.6 References *204*
4.7 Problems *205*

5 Steady-State Voltammetry at Ultramicroelectrodes *207*
5.1 Steady-State Voltammetry at a Spherical UME *207*
5.1.1 Steady-State Diffusion *208*
5.1.2 Steady-State Current *211*
5.1.3 Convergence on the Steady State *211*
5.1.4 Steady-State Voltammetry *212*
5.2 Shapes and Properties of Ultramicroelectrodes *214*
5.2.1 Spherical or Hemispherical UME *215*
5.2.2 Disk UME *215*
5.2.3 Cylindrical UME *221*
5.2.4 Band UME *221*
5.2.5 Summary of Steady-State Behavior at UMEs *222*
5.3 Reversible Electrode Reactions *224*
5.3.1 Shape of the Wave *224*
5.3.2 Applications of Reversible *i–E* Curves *226*
5.4 Quasireversible and Irreversible Electrode Reactions *230*
5.4.1 Effect of Electrode Kinetics on Steady-State Responses *230*
5.4.2 Total Irreversibility *232*
5.4.3 Kinetic Regimes *234*
5.4.4 Influence of Electrode Shape *234*
5.4.5 Applications of Irreversible *i–E* Curves *235*
5.4.6 Evaluation of Kinetic Parameters by Varying Mass-Transfer Rates *237*
5.5 Multicomponent Systems and Multistep Charge Transfers *239*
5.6 Additional Attributes of Ultramicroelectrodes *241*
5.6.1 Uncompensated Resistance at a UME *241*
5.6.2 Effects of Conductivity on Voltammetry at a UME *242*
5.6.3 Applications Based on Spatial Resolution *243*
5.7 Migration in Steady-State Voltammetry *245*
5.7.1 Mathematical Approach to Problems Involving Migration *245*
5.7.2 Concentration Profiles in the Diffusion–Migration Layer *246*
5.7.3 Wave Shape at Low Electrolyte Concentration *248*
5.7.4 Effects of Migration on Wave Height in SSV *248*
5.8 Analysis at High Analyte Concentrations *251*
5.9 Lab Note: Preparation of Ultramicroelectrodes *253*
5.9.1 Preparation and Characterization of UMEs *254*
5.9.2 Testing the Integrity of a UME *254*
5.9.3 Estimating the Size of a UME *256*
5.10 References *257*
5.11 Problems *258*

6 Transient Methods Based on Potential Steps *261*
6.1 Chronoamperometry Under Diffusion Control *261*
6.1.1 Linear Diffusion at a Plane *262*
6.1.2 Response at a Spherical Electrode *265*
6.1.3 Transients at Other Ultramicroelectrodes *267*
6.1.4 Information from Chronoamperometric Results *270*
6.1.5 Microscopic and Geometric Areas *271*
6.2 Sampled-Transient Voltammetry for Reversible Electrode Reactions *275*
6.2.1 A Step to an Arbitrary Potential *276*
6.2.2 Shape of the Voltammogram *277*
6.2.3 Concentration Profiles When R Is Initially Absent *278*
6.2.4 Simplified Current–Concentration Relationships *279*
6.2.5 Applications of Reversible *i–E* Curves *279*
6.3 Sampled-Transient Voltammetry for Quasireversible and Irreversible Electrode Reactions *279*
6.3.1 Effect of Electrode Kinetics on Transient Behavior *280*
6.3.2 Sampled-Transient Voltammetry for Reduction of O *282*
6.3.3 Sampled Transient Voltammetry for Oxidation of R *284*
6.3.4 Totally Irreversible Reactions *285*
6.3.5 Kinetic Regimes *287*
6.3.6 Applications of Irreversible *i–E* Curves *287*
6.4 Multicomponent Systems and Multistep Charge Transfers *289*
6.5 Chronoamperometric Reversal Techniques *290*
6.5.1 Approaches to the Problem *292*
6.5.2 Current–Time Responses *293*
6.6 Chronocoulometry *294*
6.6.1 Large-Amplitude Potential Step *295*
6.6.2 Reversal Experiments Under Diffusion Control *296*
6.6.3 Effects of Heterogeneous Kinetics *299*
6.7 Cell Time Constants at Microelectrodes *300*
6.8 Lab Note: Practical Concerns with Potential Step Methods *303*
6.8.1 Preparation of the Electrode Surface at a Microelectrode *303*
6.8.2 Interference from Charging Current *305*
6.9 References *306*
6.10 Problems *307*

7 Linear Sweep and Cyclic Voltammetry *311*
7.1 Transient Responses to a Potential Sweep *311*
7.2 Nernstian (Reversible) Systems *313*
7.2.1 Linear Sweep Voltammetry *313*
7.2.2 Cyclic Voltammetry *321*
7.3 Quasireversible Systems *325*
7.3.1 Linear Sweep Voltammetry *326*
7.3.2 Cyclic Voltammetry *326*
7.4 Totally Irreversible Systems *329*
7.4.1 Linear Sweep Voltammetry *329*
7.4.2 Cyclic Voltammetry *332*
7.5 Multicomponent Systems and Multistep Charge Transfers *332*
7.5.1 Multicomponent Systems *332*
7.5.2 Multistep Charge Transfers *333*

7.6 Fast Cyclic Voltammetry *334*
7.7 Convolutive Transformation *336*
7.8 Voltammetry at Liquid–Liquid Interfaces *339*
7.8.1 Experimental Approach to Voltammetry *340*
7.8.2 Effect of Interfacial Potential on Composition *341*
7.8.3 Voltammetric Behavior *341*
7.9 Lab Note: Practical Aspects of Cyclic Voltammetry *344*
7.9.1 Basic Experimental Conditions *344*
7.9.2 Choice of Initial and Final Potentials *345*
7.9.3 Deaeration *347*
7.10 References *347*
7.11 Problems *349*

8 Polarography, Pulse Voltammetry, and Square-Wave Voltammetry *355*
8.1 Polarography *355*
8.1.1 The Dropping Mercury Electrode *355*
8.1.2 The Ilkovič Equation *356*
8.1.3 Polarographic Waves *357*
8.1.4 Practical Advantages of the DME *358*
8.1.5 Polarographic Analysis *358*
8.1.6 Residual Current and Detection Limits *359*
8.2 Normal Pulse Voltammetry *361*
8.2.1 Implementation *362*
8.2.2 Renewal at Stationary Electrodes *363*
8.2.3 Normal Pulse Polarography *364*
8.2.4 Practical Application *366*
8.3 Reverse Pulse Voltammetry *367*
8.4 Differential Pulse Voltammetry *369*
8.4.1 Concept of the Method *370*
8.4.2 Theory *371*
8.4.3 Renewal *vs.* Pre-Electrolysis *374*
8.4.4 Residual Currents *375*
8.4.5 Differential Pulse Polarography *375*
8.5 Square-Wave Voltammetry *376*
8.5.1 Experimental Concept and Practice *376*
8.5.2 Theoretical Prediction of Response *377*
8.5.3 Background Currents *380*
8.5.4 Applications *381*
8.6 Analysis by Pulse Voltammetry *383*
8.7 References *385*
8.8 Problems *386*

9 Controlled-Current Techniques *389*
9.1 Introduction to Chronopotentiometry *389*
9.2 Theory of Controlled-Current Methods *391*
9.2.1 General Treatment for Linear Diffusion *391*
9.2.2 Constant-Current Electrolysis—The Sand Equation *392*
9.2.3 Programmed Current Chronopotentiometry *394*

9.3 Potential–Time Curves in Constant-Current Electrolysis *394*
9.3.1 Reversible (Nernstian) Waves *394*
9.3.2 Totally Irreversible Waves *394*
9.3.3 Quasireversible Waves *395*
9.3.4 Practical Issues in the Measurement of Transition Time *396*
9.4 Reversal Techniques *398*
9.4.1 Response Function Principle *398*
9.4.2 Current Reversal *398*
9.5 Multicomponent Systems and Multistep Reactions *400*
9.6 The Galvanostatic Double Pulse Method *401*
9.7 Charge Step (Coulostatic) Methods *403*
9.7.1 Small Excursions *404*
9.7.2 Large Excursions *405*
9.7.3 Coulostatic Perturbation by Temperature Jump *405*
9.8 References *406*
9.9 Problems *407*

10 Methods Involving Forced Convection—Hydrodynamic Methods *411*
10.1 Theory of Convective Systems *411*
10.1.1 The Convective-Diffusion Equation *412*
10.1.2 Determination of the Velocity Profile *412*
10.2 Rotating Disk Electrode *414*
10.2.1 The Velocity Profile at a Rotating Disk *414*
10.2.2 Solution of the Convective-Diffusion Equation *416*
10.2.3 Concentration Profile *418*
10.2.4 General *i–E* Curves at the RDE *419*
10.2.5 The Koutecký–Levich Method *420*
10.2.6 Current Distribution at the RDE *423*
10.2.7 Practical Considerations for Application of the RDE *426*
10.3 Rotating Ring and Ring-Disk Electrodes *426*
10.3.1 Rotating Ring Electrode *427*
10.3.2 The Rotating Ring-Disk Electrode *428*
10.4 Transient Currents *432*
10.4.1 Transients at the RDE *432*
10.4.2 Transients at the RRDE *433*
10.5 Modulation of the RDE *435*
10.6 Electrohydrodynamic Phenomena *436*
10.7 References *439*
10.8 Problems *440*

11 Electrochemical Impedance Spectroscopy and ac Voltammetry *443*
11.1 A Simple Measurement of Cell Impedance *444*
11.2 Brief Review of ac Circuits *446*
11.3 Equivalent Circuits of a Cell *450*
11.3.1 The Randles Equivalent Circuit *451*
11.3.2 Interpretation of the Faradaic Impedance *452*
11.3.3 Behavior and Uses of the Faradaic Impedance *455*
11.4 Electrochemical Impedance Spectroscopy *458*

11.4.1 Conditions of Measurement *458*
11.4.2 A System with Simple Faradaic Kinetics *460*
11.4.3 Measurement of Resistance and Capacitance *465*
11.4.4 A Confined Electroactive Domain *466*
11.4.5 Other Applications *470*
11.5 ac Voltammetry *470*
11.5.1 Reversible Systems *470*
11.5.2 Quasireversible and Irreversible Systems *473*
11.5.3 Cyclic ac Voltammetry *477*
11.6 Nonlinear Responses *477*
11.6.1 Second Harmonic ac Voltammetry *478*
11.6.2 Large Amplitude ac Voltammetry *479*
11.7 Chemical Analysis by ac Voltammetry *481*
11.8 Instrumentation for Electrochemical Impedance Methods *482*
11.8.1 Frequency-Domain Instruments *482*
11.8.2 Time-Domain Instruments *483*
11.9 Analysis of Data in the Laplace Plane *485*
11.10 References *485*
11.11 Problems *487*

12 Bulk Electrolysis *489*
12.1 General Considerations *490*
12.1.1 Completeness of an Electrode Process *490*
12.1.2 Current Efficiency *491*
12.1.3 Experimental Concerns *491*
12.2 Controlled-Potential Methods *495*
12.2.1 Current–Time Behavior *495*
12.2.2 Practical Aspects *497*
12.2.3 Coulometry *498*
12.2.4 Electrogravimetry *500*
12.2.5 Electroseparations *501*
12.3 Controlled-Current Methods *501*
12.3.1 Characteristics of Controlled-Current Electrolysis *501*
12.3.2 Coulometric Titrations *503*
12.3.3 Practical Aspects of Constant-Current Electrolysis *506*
12.4 Electrometric End-Point Detection *507*
12.4.1 Current–Potential Curves During Titration *507*
12.4.2 Potentiometric Methods *508*
12.4.3 Amperometric Methods *509*
12.5 Flow Electrolysis *510*
12.5.1 Mathematical Treatment *510*
12.5.2 Dual-Electrode Flow Cells *515*
12.5.3 Microfluidic Flow Cells *516*
12.6 Thin-Layer Electrochemistry *521*
12.6.1 Chronoamperometry and Coulometry *521*
12.6.2 Potential Sweep in a Nernstian System *524*
12.6.3 Dual-Electrode Thin-Layer Cells *526*
12.6.4 Applications of the Thin-Layer Concept *526*

12.7 Stripping Analysis *527*
12.7.1 Introduction *527*
12.7.2 Principles and Theory *528*
12.7.3 Applications and Variations *529*
12.8 References *531*
12.9 Problems *534*

13 Electrode Reactions with Coupled Homogeneous Chemical Reactions *539*
13.1 Classification of Reactions *539*
13.1.1 Reactions with One E-Step *541*
13.1.2 Reactions with Two or More E-Steps *542*
13.2 Impact of Coupled Reactions on Cyclic Voltammetry *545*
13.2.1 Diagnostic Criteria *545*
13.2.2 Characteristic Times *547*
13.2.3 An Example *547*
13.2.4 Including Kinetics in Theory *548*
13.2.5 Comparative Simulation *551*
13.3 Survey of Behavior *552*
13.3.1 Following Reaction—Case E_rC_i *552*
13.3.2 Effect of Electrode Kinetics in EC_i Systems *556*
13.3.3 Bidirectional Following Reaction *558*
13.3.4 Catalytic Reaction—Case E_rC_i' *561*
13.3.5 Preceding Reaction—Case C_rE_r *564*
13.3.6 Multistep Electron Transfers *569*
13.3.7 ECE/DISP Reactions *576*
13.3.8 Concerted *vs.* Stepwise Reaction *584*
13.3.9 Elaboration of Reaction Schemes *590*
13.4 Behavior with Other Electrochemical Methods *591*
13.5 References *593*
13.6 Problems *595*

14 Double-Layer Structure and Adsorption *599*
14.1 Thermodynamics of the Double Layer *599*
14.1.1 The Gibbs Adsorption Isotherm *599*
14.1.2 The Electrocapillary Equation *601*
14.1.3 Relative Surface Excesses *601*
14.2 Experimental Evaluations *602*
14.2.1 Electrocapillarity *602*
14.2.2 Excess Charge and Capacitance *603*
14.2.3 Relative Surface Excesses *606*
14.3 Models for Double-Layer Structure *606*
14.3.1 The Helmholtz Model *607*
14.3.2 The Gouy–Chapman Theory *609*
14.3.3 Stern's Modification *614*
14.3.4 Specific Adsorption *617*
14.4 Studies at Solid Electrodes *619*
14.4.1 Well-Defined Single-Crystal Electrode Surfaces *620*
14.4.2 The Double Layer at Solids *623*

14.5 Extent and Rate of Specific Adsorption *627*
14.5.1 Nature and Extent of Specific Adsorption *628*
14.5.2 Electrosorption Valency *629*
14.5.3 Adsorption Isotherms *630*
14.5.4 Rate of Adsorption *633*
14.6 Practical Aspects of Adsorption *634*
14.7 Double-Layer Effects on Electrode Reaction Rates *636*
14.7.1 Introduction and Principles *636*
14.7.2 Double-Layer Effects Without Specific Adsorption of Electrolyte *638*
14.7.3 Double-Layer Effects with Specific Adsorption *639*
14.7.4 Diffuse Double-Layer Effects on Mass Transport *640*
14.8 References *645*
14.9 Problems *648*

15 Inner-Sphere Electrode Reactions and Electrocatalysis *653*
15.1 Inner-Sphere Heterogenous Electron-Transfer Reactions *653*
15.1.1 The Role of the Electrode Surface *653*
15.1.2 Energetics of 1*e* Electron-Transfer Reactions *654*
15.1.3 Adsorption Energies *657*
15.2 Electrocatalytic Reaction Mechanisms *657*
15.2.1 Hydrogen Evolution Reaction *657*
15.2.2 Tafel Plot Analysis of HER Kinetics *660*
15.3 Additional Examples of Inner-Sphere Reactions *667*
15.3.1 Oxygen Reduction Reaction *667*
15.3.2 Chlorine Evolution *670*
15.3.3 Methanol Oxidation *670*
15.3.4 CO_2 Reduction *673*
15.3.5 Oxidation of NH_3 to N_2 *674*
15.3.6 Organic Halide Reduction *676*
15.3.7 Hydrogen Peroxide Oxidation and Reduction *677*
15.4 Computational Analyses of Inner-Sphere Electron-Transfer Reactions *678*
15.4.1 Density Functional Theory Analysis of Electrocatalytic Reactions *679*
15.4.2 Hydrogen Evolution Reaction *679*
15.4.3 Oxygen Reduction Reaction *681*
15.5 Electrocatalytic Correlations *684*
15.6 Electrochemical Phase Transformations *688*
15.6.1 Nucleation and Growth of a New Phase *688*
15.6.2 Classical Nucleation Theory *689*
15.6.3 Electrodeposition *699*
15.6.4 Gas Evolution *707*
15.7 References *713*
15.8 Problems *718*

16 Electrochemical Instrumentation *721*
16.1 Operational Amplifiers *721*
16.1.1 Ideal Properties *721*
16.1.2 Nonidealities *723*
16.2 Current Feedback *725*
16.2.1 Current Follower *725*

16.2.2 Scaler/Inverter *726*
16.2.3 Adders *726*
16.2.4 Integrators *727*
16.3 Voltage Feedback *728*
16.3.1 Voltage Follower *728*
16.3.2 Control Functions *729*
16.4 Potentiostats *730*
16.4.1 Basic Considerations *730*
16.4.2 The Adder Potentiostat *731*
16.4.3 Refinements to the Adder Potentiostat *732*
16.4.4 Bipotentiostats *733*
16.4.5 Four-Electrode Potentiostats *734*
16.5 Galvanostats *734*
16.6 Integrated Electrochemical Instrumentation *736*
16.7 Difficulties with Potential Control *737*
16.7.1 Types of Control Problems *737*
16.7.2 Cell Properties and Electrode Placement *740*
16.7.3 Electronic Compensation of Resistance *740*
16.8 Measurement of Low Currents *744*
16.8.1 Fundamental Limits *744*
16.8.2 Practical Considerations *746*
16.8.3 Current Amplifier *746*
16.8.4 Simplified Instruments and Cells *746*
16.9 Instruments for Short Time Scales *748*
16.10 Lab Note: Practical Use of Electrochemical Instruments *749*
16.10.1 Caution Regarding Electrochemical Workstations *749*
16.10.2 Troubleshooting Electrochemical Systems *749*
16.11 References *751*
16.12 Problems *752*

17 Electroactive Layers and Modified Electrodes *755*
17.1 Monolayers and Submonolayers on Electrodes *756*
17.2 Cyclic Voltammetry of Adsorbed Layers *757*
17.2.1 Fundamentals *757*
17.2.2 Reversible Adsorbate Couples *758*
17.2.3 Irreversible Adsorbate Couples *763*
17.2.4 Nernstian Processes Involving Adsorbates and Solutes *766*
17.2.5 More Complex Systems *770*
17.2.6 Electric-Field-Driven Acid–Base Chemistry in Adsorbate Layers *771*
17.3 Other Useful Methods for Adsorbed Monolayers *775*
17.3.1 Chronocoulometry *775*
17.3.2 Coulometry in Thin-Layer Cells *777*
17.3.3 Impedance Measurements *778*
17.3.4 Chronopotentiometry *779*
17.4 Thick Modification Layers on Electrodes *780*
17.5 Dynamics in Modification Layers *782*
17.5.1 Steady State at a Rotating Disk *783*
17.5.2 Principal Dynamic Processes in Modifying Films *784*
17.5.3 Interplay of Dynamical Elements *789*

17.6 Blocking Layers *791*
17.6.1 Permeation Through Pores and Pinholes *792*
17.6.2 Tunneling Through Blocking Films *796*
17.7 Other Methods for Characterizing Layers on Electrodes *798*
17.8 Electrochemical Methods Based on Electroactive Layers or Electrode Modification *798*
17.8.1 Electrocatalysis *799*
17.8.2 Bioelectrocatalysis Based on Enzyme-Modified Electrodes *799*
17.8.3 Electrochemical Sensors *803*
17.8.4 Faradaic Electrochemical Measurements *in vivo* *809*
17.9 References *812*
17.10 Problems *817*

18 Scanning Electrochemical Microscopy *819*
18.1 Principles *819*
18.2 Approach Curves *821*
18.3 Imaging Surface Topography and Reactivity *825*
18.3.1 Imaging Based on Conductivity of the Substrate *825*
18.3.2 Imaging Based on Heterogeneous Electron-Transfer Reactivity *826*
18.3.3 Simultaneous Imaging of Topography and Reactivity *827*
18.4 Measurements of Kinetics *828*
18.4.1 Heterogeneous Electron-Transfer Reactions *828*
18.4.2 Homogeneous Reactions *831*
18.5 Surface Interrogation *835*
18.6 Potentiometric Tips *839*
18.7 Other Applications *839*
18.7.1 Detection of Species Released from Surfaces, Films, or Pores *839*
18.7.2 Biological Systems *840*
18.7.3 Probing the Interior of a Layer on a Substrate *841*
18.8 Scanning Electrochemical Cell Microscopy *841*
18.9 References *846*
18.10 Problems *849*

19 Single-Particle Electrochemistry *851*
19.1 General Considerations in Single-Particle Electrochemistry *851*
19.2 Particle Collision Experiments *852*
19.3 Particle Collision Rate at a Disk-Shaped UME *854*
19.3.1 Collision Frequency *854*
19.3.2 Variance in the Number of Particle Collisions *855*
19.3.3 Time of First Arrival *856*
19.4 Nanoparticle Collision Behavior *857*
19.4.1 Blocking Collisions *857*
19.4.2 Electrocatalytic Amplification Collisions *861*
19.4.3 Electrolysis Collisions *864*
19.5 Electrochemistry at Single Atoms and Atomic Clusters *870*
19.6 Single-Molecule Electrochemistry *875*
19.7 References *879*
19.8 Problems *881*

20 Photoelectrochemistry and Electrogenerated Chemiluminescence *885*
20.1 Solid Materials *885*
20.1.1 The Band Model *885*
20.1.2 Categories of Pure Crystalline Solids *886*
20.1.3 Doped Semiconductors *889*
20.1.4 Fermi Energy *890*
20.1.5 Highly Conducting Oxides *891*
20.2 Semiconductor Electrodes *892*
20.2.1 Interface at a Semiconducting Electrode in the Dark *892*
20.2.2 Current–Potential Curves at Semiconductor Electrodes *896*
20.2.3 Conducting Polymer Electrodes *899*
20.3 Photoelectrochemistry at Semiconductors *901*
20.3.1 Photoeffects at Semiconductor Electrodes *901*
20.3.2 Photoelectrochemical Systems *903*
20.3.3 Dye Sensitization *905*
20.3.4 Surface Photocatalytic Processes at Semiconductor Particles *906*
20.4 Radiolytic Products in Solution *908*
20.4.1 Photoemission of Electrons from an Electrode *908*
20.4.2 Detection and Use of Radiolytic Products in Solution *909*
20.4.3 Photogalvanic Cells *909*
20.5 Electrogenerated Chemiluminescence *910*
20.5.1 Chemical Fundamentals *910*
20.5.2 Fundamental Studies of Radical-Ion Annihilation *912*
20.5.3 Single-Potential Generation Based on a Coreactant *916*
20.5.4 ECL Based on Quantum Dots *917*
20.5.5 Analytical Applications of ECL *918*
20.5.6 ECL Beyond the Solution Phase *922*
20.6 References *922*
20.7 Problems *927*

21 *In situ* Characterization of Electrochemical Systems *931*
21.1 Microscopy *931*
21.1.1 Scanning Tunneling Microscopy *932*
21.1.2 Atomic Force Microscopy *934*
21.1.3 Optical Microscopy *937*
21.1.4 Transmission Electron Microscopy *938*
21.2 Quartz Crystal Microbalance *940*
21.2.1 Basic Method *940*
21.2.2 QCM with Dissipation Monitoring *942*
21.3 UV–Visible Spectrometry *942*
21.3.1 Absorption Spectroscopy with Thin-Layer Cells *942*
21.3.2 Ellipsometry *945*
21.3.3 Surface Plasmon Resonance *946*
21.4 Vibrational Spectroscopy *947*
21.4.1 Infrared Spectroscopy *947*
21.4.2 Raman Spectroscopy *950*
21.5 X-Ray Methods *953*
21.6 Mass Spectrometry *954*
21.7 Magnetic Resonance Spectroscopy *955*

21.7.1 ESR *955*
21.7.2 NMR *956*
21.8 *Ex-situ* Techniques *957*
21.8.1 Electron Microscopy *957*
21.8.2 Electron and Ion Spectrometry *958*
21.9 References *960*

Appendix A Mathematical Methods *967*
A.1 Solving Differential Equations by the Laplace Transform Technique *967*
A.1.1 Partial Differential Equations *967*
A.1.2 Introduction to the Laplace Transformation *968*
A.1.3 Fundamental Properties of the Transform *969*
A.1.4 Solving Ordinary Differential Equations by Laplace Transformation *970*
A.1.5 Simultaneous Linear Ordinary Differential Equations *972*
A.1.6 Mass-Transfer Problems Based on Partial Differential Equations *973*
A.1.7 The Zero-Shift Theorem *975*
A.2 Taylor Expansions *976*
A.2.1 Expansion of a Function of Several Variables *976*
A.2.2 Expansion of a Function of a Single Variable *977*
A.2.3 Maclaurin Series *977*
A.3 The Error Function and the Gaussian Distribution *977*
A.4 Leibnitz Rule *979*
A.5 Complex Notation *979*
A.6 Fourier Series and Fourier Transformation *981*
A.7 References *982*
A.8 Problems *983*

Appendix B Basic Concepts of Simulation *985*
B.1 Setting Up the Model *985*
B.1.1 A Discrete System *985*
B.1.2 Diffusion *986*
B.1.3 Dimensionless Parameters *987*
B.1.4 Time *990*
B.1.5 Distance *990*
B.1.6 Current *991*
B.1.7 Thickness of the Diffusion Layer *992*
B.1.8 Diffusion Coefficients *993*
B.2 An Example *993*
B.2.1 Organization of the Spreadsheet *993*
B.2.2 Concentration Arrays *996*
B.2.3 Results and Error Detection *996*
B.2.4 Performance *997*
B.3 Incorporating Homogeneous Kinetics *999*
B.3.1 Unimolecular Reactions *999*
B.3.2 Bimolecular Reactions *1000*
B.4 Boundary Conditions for Various Techniques *1001*
B.4.1 Potential Steps in Nernstian Systems *1001*
B.4.2 Heterogeneous Kinetics *1002*

B.4.3 Potential Sweeps *1003*
B.4.4 Controlled Current *1003*
B.5 More Complex Systems *1004*
B.6 References *1005*
B.7 Problems *1005*

Appendix C Reference Tables *1007*
References *1013*

Index *1015*