

1 INTRODUCTION AND FUNDAMENTALS

1

- 1.1 Introduction / 1
- 1.2 Nomenclature and Classes of Electrochemical Methodology / 3
- 1.3 Sign and Graphical Conventions / 6
- 1.4 Utilization of Electrochemistry for Chemical Characterization / 6
- 1.5 The Fundamentals / 9
 - The Hydrated Electron / 10
 - Electron Transfer in Electrochemistry / 11
- 1.6 Nucleophile–Electrophile Electron Transfer / 16
- 1.7 The Dynamics of Electron Transfer (Kinetics and Thermodynamics) / 17
 - References / 21

2 POTENTIOMETRY MEASUREMENTS

24

- 2.1 Introduction / 24
- 2.2 Principles and Fundamental Relations / 25
- 2.3 Electrode Systems / 30
- 2.4 Applications of Potentiometry / 38
 - References / 51

- 3.1 Introduction / 53
 - Control of Potential and Measurement of Current / 53
- 3.2 Principles and Fundamental Relations / 55
 - Diffusion to a Planar Electrode / 55
- 3.3 Polarography / 57
 - Current-Sampled Polarography / 63
 - AC Polarography / 65
 - Square-Wave Polarography / 66
 - Pulse Polarography / 66
 - Stripping Analysis / 66
- 3.4 Linear Sweep and Cyclic Voltammetry / 68
 - Adsorption / 77
- 3.5 Microelectrode Voltammetry / 78
- 3.6 Ring-Disk Voltammetry / 79
- 3.7 Chronoamperometry and Chronocoulometry / 84
- 3.8 Controlled-Potential Bulk Electrolysis / 86
- 3.9 Methodology / 87
- 3.10 Application of Controlled-Potential Methods / 98
 - References / 135

4 ELECTROCHEMICAL TITRATIONS AND CONTROLLED-CURRENT METHODS**139**

- 4.1 Introduction / 139
- 4.2 Endpoint Detection Methods / 139
 - Potentiometric Methods / 139
 - Amperometric Methods / 144
 - Conductometric Methods / 148
- 4.3 Autotitrators / 149
- 4.4 pH-Stats / 151
- 4.5 Coulometric Titrations / 152
- 4.6 Controlled-Current Methods / 159
 - References / 168

5 INDICATOR ELECTRODES**170**

- 5.1 Measurement of Electrode Potentials / 170
 - Junction Potentials / 172
 - Cells with Liquid Junctions and Elimination of Junction Potentials / 175

Some Practical Considerations in the Use of Salt
Bridges / 182

5.2 Reference Electrodes / 184

Properties of the Ideal Reference Electrode / 184

Reference Electrodes for Use in Aqueous Solutions / 185

Reference Electrodes for Use in Polar Aprotic
Solvents / 199

Reference Electrodes for Use in Nonpolar Solvents / 204

Reference Electrodes for Use in Fused-Salt Systems / 204

5.3 Voltammetric Indicator Electrodes / 206

Electrode Materials and Their Electrochemical
Behavior / 206

Measurement of Electrode Area / 216

Electrode Pretreatment / 219

Construction and Mass-Transport Properties of
Voltammetric Electrodes / 220

5.4 Optically Transparent Electrodes / 234

5.5 Mercury Indicator Electrodes / 235

5.6 Solid Indicator Electrodes / 238

pH-Sensitive Solid Indicator Electrodes / 239

5.7 Selective-Ion Electrodes / 239

References / 243

6 ELECTROCHEMICAL CELLS AND INSTRUMENTATION 249

6.1 Electrochemical Cells: Introduction / 249

General Requirements / 249

Materials for the Construction of Cells and
Electrodes / 257

Changes in Solution Composition Caused by Structural
Materials / 261

The Maintenance of an Inert Atmosphere / 264

6.2 Description of General-Purpose Cells / 271

Cells for Voltammetry and Polarography / 271

Cells for Coulometric and Preparative
Electrochemistry / 274

Control of Temperature and Pressure / 279

Cells for Conductimetry / 281

Microcells / 282

Flow and Circulation Cells / 283

Cells for Spectroelectrochemistry / 284

6.3 Instrumentation: Measurements / 286

Voltage / 286

Current / 288

Bridge Measurements of Resistance, Capacitance, and Inductance / 288

6.4 Sources / 294

References / 295

7 SOLVENTS AND ELECTROLYTES

299

7.1 Introduction / 299

The Physicochemical Properties of Solvents and Their Relevance to Electrochemistry / 299

Classification of Solvents / 311

7.2 Role of the Solvent-Supporting Electrolyte System in Electrochemistry / 313

7.3 Role of the Supporting Electrolyte / 316

Control of Cell Resistance / 316

Control of Solution Acidity / 319

Complex Formation / 322

Ion-Pairing and Double-Layer Effects / 322

Micellar Aggregates / 324

7.4 Electrochemical Properties of Water and Selected Organic Solvents / 324

Water / 324

Nonaqueous Solvents / 327

7.5 Preparation and Purification of Supporting Electrolytes / 335

7.6 Sources / 337

References / 337

8 HYDRONIUM IONS (H_3O^+), BRØNSTED ACIDS (HA), AND MOLECULAR HYDROGEN (H_2)

342

8.1 Introduction / 342

8.2 Hydronium Ion (H_3O^+) Reduction / 343

8.3 Brønsted Acid (HA) Reduction and Evaluation of $\text{p}K_{\text{a}(\text{sol})}$ / 346

8.4 Oxidation of Dissolved Dihydrogen (H_2) / 350

References / 357

**9 DIOXYGEN SPECIES (O_2 , $HOO\cdot$, O_2^- , $HOOH$, HOO^-),
OZONE (O_3), AND ATOMIC OXYGEN**

358

- 9.1 Introduction; Redox Thermodynamics / 358
 - Molecular Oxygen / 358
 - Superoxide Ion / 361
 - Atomic Oxygen / 362
- 9.2 Electrochemistry of Dioxygen / 364
 - Electron-Transfer Reduction of O_2 / 367
 - Aprotic Media / 370
 - Protic and Electrophilic Substrates / 373
 - Electrode Material Effects / 379
 - Transition-Metal Complexes (ML_x); O_2 Reduction Catalysts / 380
 - Chemical Reduction / 392
 - Reduction of O_2 by Atom Transfer / 393
 - Concerted One-Electron Reductions / 394
 - Applications / 397
- 9.3 Reduction of $HOOH$ / 398
- 9.4 Oxidation of $HOOH$ and HOO^- / 399
- 9.5 Summary / 399
 - References / 400

10 METALS AND METAL COMPLEXES

403

- 10.1 Oxidation of Metals / 403
 - Metal-X Bond Energies / 404
- 10.2 Oxidation-Reduction of Transition-Metal Complexes / 407
 - Metal-Ligand Bond Energies / 407
 - References / 419

11 NONMETALS (SULFUR, NITROGEN, AND CARBON COMPOUNDS)

420

- 11.1 Introduction / 420
- 11.2 Sulfur / 421
 - Elemental Sulfur (S_8) / 421
 - Sulfur Dioxide (SO_2) / 422
 - Propane-1,3-dithiol [$HS(CH_2)_3SH$] / 425

- 11.3 Nitrogen / 427
 - Nitric Oxide ($\cdot\text{NO}$) / 427
 - Nitrous Acid ($\text{HON}=\text{O}$) / 428
 - Nitrous Oxide (N_2O) / 429
 - Hydroxylamine (H_2NOH) / 429
 - Hydrazines and Amines / 430
 - Phenazine (Phen) / 434
- 11.4 Carbon / 436
 - Carbon Dioxide (CO_2) / 436
 - Carbon Monoxide (CO) / 438
 - Cyanide Ion (NC^-) / 438
 - References / 440

12 ORGANIC COMPOUNDS

442

- 12.1 Introduction / 442
- 12.2 Reduction of Electrophilic Substrates (Lewis Acids) / 444
 - Alkyl- and Aryl-Halides / 444
 - Quinones, Semiquinones, and Catechols / 446
 - Dehydroascorbic Acid and Ascorbic Acid / 451
 - Carbonyl Groups, Olefins, and Aromatic Hydrocarbons / 455
 - Brønsted Acids / 457
 - Viologens / 457
- 12.3 Oxidation of Nucleophilic Substrates and Lewis Bases / 457
 - Catechols and Hydroquinones / 458
 - Phenols / 460
 - Benzyl Alcohols / 461
 - Aromatic Hydrocarbons / 461
 - Dithiols / 463
 - References / 464

13 ORGANOMETALLIC COMPOUNDS AND METALLOPORPHYRINS

466

- 13.1 Introduction / 466
- 13.2 Organometallic Molecules / 467
 - Ferrocene / 467
 - Iron-Pentacarbonyl / 469
 - Gold-Catalyzed Oxidation of Carbon Monoxide / 469

13.3 Metalloporphyrins / 470

**Nucleophilic Character of Iron- and Cobalt-Porphyrin
Anions; Evaluation of Their Metal-Carbon Bond
Energies / 482**

References / 492