Contents

1 Foundations, Definitions and Concepts **1**

- 1.1 Ions, Electrolytes and the Quantisation of Electrical Charge 1
- 1.2 Transition from Electronic to Ionic Conductivity in an Electrochemical Cell 3
- 1.3 Electrolysis Cells and Galvanic Cells: The Decomposition Potential and the Concept of EMF 4
- 1.4 Faraday's Laws 7
- 1.5 Systems of Units 9

2 Electrical Conductivity and Interionic Interactions 12

- 2.1 Fundamentals 12
- 2.1.1 The Concept of Electrolytic Conductivity 12
- 2.1.2 The Measurement of Electrolyte Conductance 13
- 2.1.3 The Conductivity 17
- 2.1.4 Numerical Values of Conductivity 18
- 2.2 Empirical Laws of Electrolyte Conductivity 20
- 2.2.1 The Concentration Dependence of the Conductivity 20
- 2.2.2 Molar and Equivalent Conductivities 21
- 2.2.3 Kohlrausch's Law and the Determination of the Limiting Conductivities of Strong Electrolytes 21
- 2.2.4 The Law of Independent Migration of Ions and the Determination of the Molar Conductivity of Weak Electrolytes 23
- 2.3 Ionic Mobility and Hittorf Transport 26
- 2.3.1 Transport Numbers and the Determination of Limiting Ionic Conductivities 26
- 2.3.2 Experimental Determination of Transport Numbers 28
- 2.3.3 Magnitudes of Transport Numbers and Limiting Ionic Conductivities 29
- 2.3.4 Hydration of Ions 30
- 2.3.5 The Enhanced Conductivity of the Proton, the Structure of the H_3O^+ Ion and the Hydration Number of the Proton 32
- 2.3.6 The Determination of Ionic Mobilities and Ionic Radii: Walden's Rule 35
- 2.4 The Theory of Electrolyte Conductivity: The Debye-Hückel-Onsager Theory of Dilute Electrolytes 36
- 2.4.1 Introduction to the Model: Ionic Cloud, Relaxation and Electrophoretic Effects 36
- 2.4.2 The Calculation of the Potential due to the Central Ion and its Ionic Cloud: Ionic Strength and Radius of the Ionic Cloud 37

- 2.4.3 The Debye-Onsager Equation for the Conductivity of Dilute Electrolyte Solutions 42
- 2.4.4 The Influence of Alternating Electric Fields and Strong Electric Fields on the Electrolyte Conductivity 43
- 2.5 The Concept of Activity from the Electrochemical Viewpoint 44
- 2.5.1 The Activity Coefficient 44
- 2.5.2 Calculation of the Concentration Dependence of the Activity Coefficient 45
- 2.5.3 Activity Coefficients in Concentrated Electrolytes and Activity Coefficients of Neutral Molecules 48
- 2.6 The Properties of Weak Electrolytes 51
- 2.6.1 The Ostwald Dilution Law 51
- 2.6.2 The Dissociation Field Effect 53
- 2.7 The Concept of pH and the Idea of Buffer Solutions 54
- 2.8 Non-aqueous Solutions 57
- 2.8.1 Ion Solvation in Non-aqueous Solvents 57
- 2.8.2 Electrolytic Conductivity in Non-aqueous Solutions 58
- 2.8.3 The pH-Scale in Protonic Non-aqueous Solvents 59
- 2.9 Simple Applications of Conductivity Measurements 60
- 2.9.1 The Determination of the Ionic Product of Water 60
- 2.9.2 The Determination of the Solubility Product of a Slightly Soluble Salt 62
- 2.9.3 The Determination of the Heat of Solution of a Slightly Soluble Salt 62
- 2.9.4 The Determination of the Thermodynamic Dissociation Constant of a Weak Electrolyte 63
- 2.9.5 The Principle of Conductivity Titrations 63

3 Electrode Potentials and Double-layer Structure at Phase Boundaries 66

- 3.1 Electrode Potentials and their Dependence on Concentration, Gas-pressure and Temperature 66
- 3.1.1 The EMF of Galvanic Cells and the Maximum Useful Energy from Chemical Reactions 66
- 3.1.2 The Origin of Electrode Potentials, Galvani Potential Differences and the Electrochemical Potential 67
- 3.1.3 Calculation of the Electrode Potential and the Equilibrium Galvani Potential Difference Between a Metal and a Solution of its Ions – The Nernst Equation 70
- 3.1.4 The Nernst Equation for Redox Electrodes 71
- 3.1.5 The Nernst Equation for Gas Electrodes 72
- 3.1.6 The Measurement of Electrode Potentials and Cell Voltages 73
- 3.1.7 Calculation of Cell \psc EMF's from Thermodynamic Data 77
- 3.1.8 The Temperature Dependence of the Cell Voltage 79
- 3.1.9 The Pressure Dependence of the Cell Voltage Residual Current for the Electrolysis of Aqueous Solutions 80
- 3.1.10 Reference Electrodes and the Electrochemical Series 82

- 3.1.11 Reference Electrodes of the Second Kind 86
- 3.1.12 The Electrochemical Series in Non-aqueous Solvents 91
- 3.1.13 Reference Electrodes in Non-aqueous Systems and Usable Potential Ranges 92
- 3.2 Liquid-junction Potentials 93
- 3.2.1 The Origin of Liquid-junction Potentials 93
- 3.2.2 The Calculation of Diffusion Potentials 95
- 3.2.3 Concentration Cells with and without Transference 96
- 3.2.4 Henderson's Equation 97
- 3.2.5 The Elimination of Diffusion Potentials 99
- 3.3 Membrane Potentials 101
- 3.4 The Electrolyte Double-layer and Electrokinetic Effects 103
- 3.4.1 Helmholtz and Diffuse Double Layer: the Zeta Potential 104
- 3.4.2 Adsorption of Ions, Dipoles and Neutral Molecules -the Potential of Zero Charge 108
- 3.4.3 The Double-layer Capacity 110
- 3.4.4 Some Data for Electrolytic Double Layers 111
- 3.4.5 Electrocapillarity 113
- 3.4.5.1 Other Methods for the Determination of the Potential of Zero Charge (pzc) 115
- 3.4.6 Electrokinetic Effects Electrophoresis, Electra-osmosis, Dorn-effect and Streaming Potential 117
- 3.5 Potential and Phase Boundary Behaviour at Semiconductor Electrodes 119
- 3.5.1 Metallic Conductors, Semiconductors and Insulators 119
- 3.5.2 Electrochemical Equilibria on Semiconductor Electrodes 123
- 3.6 Simple Applications of Potential Difference Measurements 125
- 3.6.1 The experimental determination of Standard Potentials and Mean Activity Coefficients 125
- 3.6.2 Solubility Products of Slightly Soluble Salts 128
- 3.6.3 The Determination of the Ionic Product of Water 128
- 3.6.4 Dissociation Constants of Weak Acids 128
- 3.6.5 The Determination of the Thermodynamic State Functions $(\Delta_r G^0, \Delta_r H^0)$ and $\Delta_r S^0$ and the Corresponding Equilibrium Constants for Chemical Reactions 130
- 3.6.6 pH Measurement with the Hydrogen Electrode 131
- 3.6.7 pH Measurement with the Glass Electrode 135
- 3.6.8 The Principle of Potentiometric Titrations 140

4 Electrical Potentials and Electrical Current 143

- 4.1 Cell Voltage and Electrode Potential During Current Flow: an Overview 143
- 4.1.1 The Concept of Overpotential 145

- 4.1.2 The Measurement of Overpotential: the Current-potential Curve for a Single Electrode 146
- 4.2 The Electron-transfer Region of the Current-potential Curve 148
- 4.2.1 Understanding the Origin of the Current-potential Curve in the Electron-Transfer-Limited Region with the help of the Arrhenius Equation. 148
- 4.2.2 The Meaning of the Exchange Current Density j_0 and the Asymmetry Parameter β 152
- 4.2.3 The Concentration Dependence of the Exchange Current Density 155
- 4.2.4 Electrode Reactions with Consecutive Transfer of Several Electrons 156
- 4.2.5 Electron Transfer with Coupled Chemical Equilibria: the Electrochemical Reaction Order 159
- 4.2.6 Further Theoretical Considerations of Electron Transfer 161
- 4.2.6.1 Calculation of the Critical Ligand-ion Separation x_S 161
- 4.2.6.2 Reorganisation Energy and the Electrochemical Rate Constant 163
- 4.2.6.3 Exchange Current Density and Current-voltage Curves 165
- 4.2.7 Determination of Activation Parameters and the Temperature Dependence of Electrochemical Reactions 166
- 4.3 The Concentration Overpotential The Effect of Transport of Material on the Current-voltage Curve 167
- 4.3.1 The Relationship Between the Concentration Overpotential and the Butler-Volmer Equation 168
- 4.3.2 Diffusion Overpotential and the Diffusion layer 169
- 4.3.3 Current-time Behaviour at Constant Potential and Constant Surface Concentration c^s 171
- 4.3.4 Potential-time Behaviour at Constant Current: Galvanostatic Electrolysis 172
- 4.3.5 Transport by Convection 173
- 4.3.6 Mass Transport Through Migration the Nernst-Planck Equation 178
- 4.3.7 Spherical Diffusion 179
- 4.3.8 Micro-electrodes 180
- 4.3.8.1 Time Dependence of the Current at a Microelectrode 181
- 4.3.8.2 Further Advantages of Microelectrodes 182
- 4.4 The Effect of Simultaneous Chemical Processes on the Current Voltage Curve 182
- 4.4.1 Reaction Overpotential, Reaction-limited Current and Reaction Layer Thickness 184
- 4.5 Adsorption Processes 186
- 4.5.1 Forms of Adsorption Isotherms 187
- 4.5.2 Adsorption Enthalpies and Pauling's Equation 190
- 4.5.3 Current-potential Behaviour and Adsorption-limited Current 190
- 4.5.4 Dependence of Exchange Current Density on Adsorption Enthalpy 191
- 4.6 Electrocrystallisation Metal Deposition and Dissolution 192
- 4.6.1 Simple Model of Metal Deposition 193
- 4.6.1.1 Electrodeposition with Surface Diffusion 193

- 4.6.1.2 Direct Discharge onto Line Defects 195
- 4.6.1.3 Two-dimensional Nucleation 195
- 4.6.2 Crystal Growth in the Presence of Screw Dislocations 195
- 4.6.3 Under-potential Deposition 196
- 4.6.4 The Kinetics of Metal Dissolution and Metal Passivation 198
- 4.6.5 Electrochemical Materials Science and Electrochemical Surface Technology 199
- 4.6.5.1 Preparation of Metal Powders 199
- 4.6.5.2 Electrochemical Machining and Polishing 200
- 4.6.5.3 Galvanoplastics 201
- 4.7 Mixed Electrodes and Corrosion 202
- 4.7.1 Mechanism of Acid Corrosion 202
- 4.7.2 Oxygen Corrosion 203
- 4.7.3 Potential-pH Diagrams or Pourbaix Diagrams 204
- 4.7.4 Corrosion Protection 205
- 4.7.4.1 Cathodic Corrosion Protection 206
- 4.7.4.2 Inhibition of Corrosion Through Film Formation 206
- 4.7.4.3 Electrophoretic Coating of Metals 207
- 4.8 Current Flows on Semiconductor Electrodes 207
- 4.8.1 Photoeffects in Semiconductors 209
- 4.8.2 Photoelectrochemistry 211
- 4.8.3 Photogalvanic Cells 212
- 4.8.4 Detoxification Using Photoelectrochemical Technology 213

5 Methods for the Study of the Electrode/Electrolyte Interface 216

- 5.1 The Measurement of Stationary Current-potential Curves 216
- 5.1.1 The Potentiostat 216
- 5.1.2 Measurements with Controlled Mass Transport 217
- 5.1.3 Stationary Measurement of Very Rapid Reactions with Turbulent Flow 219
- 5.2 Quasi-stationary Methods 221
- 5.2.1 Cyclic Voltammetry: Studies of Electrode Films and Electrode Processes – "Electrochemical Spectroscopy" 222
- 5.2.1.1 The Cyclic Voltammogram 222
- 5.2.1.2 Cyclic Voltammetry in the Presence of an Electrochemically Active Substance in the Electrolyte 225
- 5.2.1.3 The Theory of Cyclic Voltammetry I Single Potential Sweep in Unstirred Solutions 227
- 5.2.1.4 The Theory of Cyclic Voltammetry II: Multiple Potential Sweeps 229+
- 5.2.1.5 Multiple Potential Sweeps Experimental Considerations 232
- 5.2.1.6 Correction for *iR* Drop 234
- 5.2.2 AC Measurements 236
- 5.2.2.1 Influence of Transport Processes on the *ac* Impedance of an Electrochemical Cell 237

- 5.2.2.2 Equivalent Circuit for an Electrode Diffusion-limited Reaction 239
- 5.2.2.3 AC Impedance of an Electrode Where the Electron Transfer Process is Rate Limiting 240
- 5.2.2.4 Logarithmic or Bode Plot Representations 242
- 5.2.2.5 Electrode Reactions Under Mixed Control 242
- 5.3 Electrochemical Methods for the Study of Electrode Films 244
- 5.3.1 Measurement of Charge Passed 244
- 5.3.2 Capacitance Measurements 247
- 5.4 Spectroelectrochemical and Other Non-classical Methods 247
- 5.4.1 Introduction 247
- 5.4.2 Infra-red Spectroelectrochemistry 249
- 5.4.2.1 Basics 249
- 5.4.2.2 Spectroelectrochemical Cells 251
- 5.4.2.3 Examples of Different Methodologies in IR and Some Results 251
- 5.4.3 Electron Spin Resonance 255
- 5.4.3.1 Basics 255
- 5.4.3.2 Electrochemical Electron Spin Resonance 256
- 5.4.4 Electrochemical Mass Spectroscopy 259
- 5.4.4.1 Basis of Mass Spectroscopy 259
- 5.4.4.2 The Coupling of the Electrochemical Experiment to the Mass Spectrometer 260
- 5.4.5 Additional Methods of Importance 263
- 5.4.5.1 Radiotracer Methods 263
- 5.4.5.2 Microbalance Methods 265
- 5.4.5.3 Scanning Tunnelling Microscopy (STM) 265
- 5.4.5.4 Optical Methods 268

6 Reaction Mechanisms 275

- 6.1 Silver Deposition from Cyanide Solution 275
- 6.2 The Hydrogen Electrode 277
- 6.2.1 Influence of Adsorbed Intermediates on *i-V* Curves 278
- 6.2.2 Influence of the pH-value of the Solution and the Catalyst Surface 280
- 6.3 The Oxygen Electrode 281
- 6.3.1 Investigation of the Oxygen Reduction Reaction with Rotating Ring-disk Electrode 282
- 6.4 Reaction Mechanisms in Electra-organic Chemistry 283
- 6.4.1 General Issues 283
- 6.4.2 Classification of Electrode Processes 284
- 6.4.3 Oxidation Processes: Potentials, Intermediates and End Products 285
- 6.4.4 Reduction Processes: Potentials, Intermediates and Products 287
- 6.4.5 Electrochemical Polymerisation 288

7 Solid and Molten-salt Ionic Conductors as Electrolytes 291

- 7.1 Ionically Conducting Solids 291
- 7.1.1 Origins of Ionic Conductivity in Solids 291
- 7.1.2 Current/Voltage Measurements on Solid Electrodes 294
- 7.2 Solid Polymer Electrolytes (SPE's) 295
- 7.2.1 Current/Voltage Measurements with SPE's 297
- 7.3 Ionically-conducting Melts 298
- 7.3.1 Conductivity 298
- 7.3.2 Current-voltage Studies 299

8 Industrial Electrochemical Processes 301

- 8.1 Introduction and Fundamentals 301
- 8.1.1 Special Features of Electrochemical Processes 301
- 8.1.2 Classical Cell Designs and the Space-time Yield 302
- 8.1.3 Morphology of Electrocatalysts 305
- 8.1.4 The Activation Overpotential 306
- 8.2 The Electrochemical Preparation of Chlorine and NaOH 307
- 8.2.1 Electrode Reactions During the Electrolysis of Aqueous NaCl 308
- 8.2.2 The Diaphragm Cell 308
- 8.2.3 The Amalgam Cell 309
- 8.2.4 The Membrane Process 312
- 8.2.5 Additional Comments 313
- 8.3 The Electrochemical Extraction and Purification of Metals 315
- 8.3.1 Extraction from Aqueous Solution 315
- 8.3.2 Metal Purification in Aqueous Solution 316
- 8.3.3 Molten Salt Electrolysis 317
- 8.4 Special Preparation Methods for Inorganic Chemicals 318
- 8.4.1 Hypochlorite, Chlorate and Perchlorate 319
- 8.4.2 Hydrogen Peroxide and Peroxodisulphate 320
- 8.4.3 Classical Water Electrolysis 320
- 8.4.4 Modern Water Electrolysis and Hydrogen Technology 321
- 8.5 Electra-organic Synthesis 323
- 8.5.1 An Overview of Processes and Specific Features 323
- 8.5.2 Adiponitrile The Monsanto Process 323
- 8.6 Modern Cell Designs 325
- 8.7 Future Possibilities for Electrocatalysis 327
- 8.7.1 Electrochemical Modification of Catalytic Activity in Heterogeneous Chemical Reactions – the NEMCA Effect 328
- 8.8 Component Separation Methods 330
- 8.8.1 Treatment of Waste Water 330
- 8.8.2 Electra-dialysis 331
- 8.8.3 Electrophoresis 332
- 8.8.4 Electrochemical Separation Procedures in the Nuclear Industry 333

9 Galvanic Cells 338

- 9.1 Basics 338
- 9.2 Properties, Components and Characteristics of Batteries 340
- 9.2.1 Function and Construction of Lead-acid Batteries 340
- 9.2.2 Function and Construction of Leclanché Cells 341
- 9.2.3 Electrolyte and Self-discharge 342
- 9.2.4 Open-circuit Voltage, Specific Capacity and Energy Density 343
- 9.2.5 Current-voltage Characteristics, Power Density and Power-density/Energy-density Diagrams 344
- 9.2.6 Battery Discharge Characteristics 345
- 9.2.7 Charge Characteristics, Current and Energy Yield and Cycle Number 346
- 9.2.8 Cost of Electrical Energy and of Installed Battery Power 348
- 9.3 Secondary Systems 348
- 9.3.1 Conventional Secondary Batteries 348
- 9.3.1.1 The Nickel-Cadmium and Nickel-Iron Batteries 348
- 9.3.1.2 The Silver-Zinc Battery 350
- 9.3.2 New Developments 351
- 9.3.2.1 Developments in Conventional Systems 351
- 9.3.2.2 Experimental Secondary Batteries with Zinc Anodes 352
- 9.3.2.3 Sodium-sulfur and Sodium-nickel-chloride (ZEBRA) Batteries 353
- 9.3.2.4 Lithium Secondary Batteries 355
- 9.3.3 Summary of Data for Secondary Battery Systems 358
- 9.4 Primary Systems other than Leclanché Batteries 362
- 9.4.1 Alkaline-Manganese Cells 362
- 9.4.2 The Zinc-Mercury Oxide Battery 362
- 9.4.3 Lithium Primary Batteries 363
- 9.4.4 Electrode and Battery Characteristics for Primary Systems 3649.5 Fuel Cells 365
- 9.5.1 Fuel Cells with Gaseous Fuels 366
- 9.5.1.1 Gas Diffusion Electrodes 366
- 9.5.1.2 The Apollo Cell 368
- 9.5.2 More Recent Developments 369
- 9.5.2.1 Summary of Fuel-cell Characteristics 373
- 9.5.3 Fuel Cells with Liquid Fuels 376
- 9.5.4 The Problems of Electrical Vehicles 377
- 9.5.4.1 Requirements of Power and Energy Density in Electric-vehicle Batteries 378
- 9.5.4.2 Realisable Vehicle Types with Secondary Batteries as Energy Sources 378
- 9.5.4.3 Fuel Cells as Power Sources 379
- 9.5.4.4 Economics of Electric Vehicles 380
- 9.6 Primary and Secondary Air Batteries 383

- 9.6.1 Metal-air Primary Batteries 383
- 9.6.2 Metal-air Secondary Systems 384
- 9.7 Efficiency of Batteries and Fuel Cells 384

10 Analytical Applications 388

- 10.1 Titration Processes Using Electrochemical Indicators 388
- 10.2 Electra-analytical Methods 391
- 10.2.1 Polarography and Voltammetry 391
- 10.2.1.1 The Principles of dd Polarography 391
- 10.2.1.2 Modern Instrumental Improvements in Sensitivity and Resolution in Polarography 394
- 10.2.1.3 Polarographic Methods Using a Stationary Mercury Electrode 397
- 10.2.1.4 Final Remarks on Polarography 399
- 10.2.2 Further Methods Coulometry, Electrogravimetry and Chronopotentiometry 399
- 10.3 Electrochemical Sensors 401
- 10.3.1 Conductivity and pH Measurement 402
- 10.3.2 Redox Electrodes 402
- 10.3.3 Ion-sensitive Electrodes 403
- 10.3.3.1 Glass-membrane Electrodes 404
- 10.3.3.2 Solid and Liquid Membrane Electrodes 404
- 10.3.3.3 ISFETs 406
- 10.3.4 Sensors for the Analysis of Gases 407
- 10.3.4.1 Conductimetric Sensors 407
- 10.3.4.2 Potentiometric Gas Sensors 407
- 10.3.4.3 Amperometric Gas Sensors 408

Index 415