Contents

Preface 5

List of Symbols 12

Chapter 1 Introduction 17

1.1 General Scheme of Analytical Determinations 18
1.1.1 Sampling and Sample Preparation 18
1.1.2 Transformation of the Constituent to be Determined into Measurable Form 19
1.1.3 Measurements in Analytical Applications 20
1.1.4 Calculation and Interpretation of Analytical Results 21

References 22

Chapter 2 Thermodynamics and Kinetics of Chemical Reactions 23

2.1 Thermodynamics of Chemical Reactions 24
2.1.1 Thermodynamics of Chemical Equilibrium 24
2.1.2 Activity 26
2.1.3 Thermodynamic Equilibrium Constant 26
2.1.4 Activity and Concentration Scales 27
2.1.5 Standard State 28
2.1.6 Relationship between Molal and Molar Scales of Concentration and Activity Coefficients 28
2.1.7 Mean Activity and Mean Activity Coefficients 30
2.1.8 The Dependence of Activity Coefficients of Electrolytes upon Salt Concentration 30
2.1.9 Activity Coefficients of Non-Electrolytes 35
2.1.10 Thermodynamic and Concentration Equilibrium Constants 36
2.1.11 Ion Association and Activity of Ions 39

2.2 Kinetics of Chemical Reactions 41
2.2.1 Reaction Mechanism 41
2.2.2 Reaction Rate 42
2.2.3 Order and Molecularity of a Reaction 43
2.2.4 Simple or Isolated Elementary Reactions 45
2.2.5 Reversible Reactions 45
2.2.6 Consecutive Reactions 47
2.2.7 Induced Reactions 49
2.2.8 Catalytic Reactions 50
2.2.9 Factors Affecting the Reaction Rate 53
2.2.10 Kinetics of Oxidation-Reduction Processes in Solutions 58

2.3 Thermodynamic and Kinetic Criteria for Analytical Applications of Chemical Reactions 61

2.4 Problems 62

References 63

Chapter 3 Graphical Representation of Ionic Equilibria in Solutions . . 65

3.1 Distribution Diagrams 66
3.1.1 Distribution Diagram of the Equilibrium System with Species A, AB and AB_2 69
3.1.2 Distribution Diagrams of Systems Containing Polynuclear Complexes 73
3.1.3 Distribution Diagram for the Presence of Solid Phase 74
3.1.4 Significance of Distribution Diagrams 76

3.2 Logarithmic Concentration Diagrams 76
3.2.1 Logarithmic Concentration Diagram for the System A, AB, AB_2 77
3.2.2 Logarithmic Solubility Diagram 82
3.2.3 Significance of Logarithmic Diagrams 83

3.3 Diagrams for Systems of Two Variables 84
3.3.1 Predominance-Area Diagrams 84

References 86

Chapter 4 Protolytic Equilibria 88

4.1 Concepts of Acids and Bases 88
4.1.1 Constants of Protolytic Equilibria 91

4.2 Solvent Effects on Protolytic Equilibria 93
4.2.1 Classification of Solvents 93
4.2.2 The Ionic Product of the Solvent 94
4.2.3 Medium Effects of Ionizing Solvents 95

4.3 Dissociation Constants of Acids and Bases in Non-Aqueous Medium 103
4.3.1 Scheme of Solvation and Dissociation Equilibria 103
4.3.2 Medium Effect on the Dissociation Constant of an Acid in Ionizing Solvents 107
4.3.3 Protolytic Equilibria in Solvents of Low Dielectric Constant 116
4.3.4 Differentiating Effect of Solvents 117

4.4 Scales of Acidity and pH 123
4.4.1 Definitions of pH Scales for Aqueous Medium 123
4.4.2 Activity Scales for Non-Aqueous Solvents 129
4.4.3 Hammett Acidity Function 131
4.4.4 Conventional Operational pH Scale for Amphiprotic and Mixed Solvents 133

4.5 Problems 136

References 136

Chapter 5 Protolytic Systems in Aqueous Medium 138

5.1 Calculation of pH and of the Composition of a Protolytic System 138

5.2 Calculating pH in Simple Acid-Base Systems 140
5.2.1 Solution of a Strong Acid or Base 140
5.2.2 Solutions of Monoprotic Weak Acids and Bases or Mixtures of Conjugate Acids and Bases 140

5.3 Calculation of Acid-Base Equilibria of Polyprotic Acids or Bases 144
5.3.1 Calculation of the pH of a Solution of a Weak Polyprotic Acid 146
5.3.2 Solutions of Ampholytes Formed from a Polyprotic Weak Acid 147

5.4 Logarithmic Concentration Diagrams 149
5.4.1 Diagram of a Simple Protolytic System 149
5.4.2 Logarithmic Concentration Diagram of a Polyprotic Acid 151

Chapter 3 Graphical Representation of Ionic Equilibria in Solutions . . 65

3.1 Distribution Diagrams 66
3.1.1 Distribution Diagram of the Equilibrium System with Species A, AB and AB_2 69
3.1.2 Distribution Diagrams of Systems Containing Polynuclear Complexes 73
3.1.3 Distribution Diagram for the Presence of Solid Phase 74
3.1.4 Significance of Distribution Diagrams 76

3.2 Logarithmic Concentration Diagrams 76
3.2.1 Logarithmic Concentration Diagram for the System A, AB, AB_2 77
3.2.2 Logarithmic Solubility Diagram 82
3.2.3 Significance of Logarithmic Diagrams 83

3.3 Diagrams for Systems of Two Variables 84
3.3.1 Predominance-Area Diagrams 84

References 86

Chapter 4 Protolytic Equilibria 88

4.1 Concepts of Acids and Bases 88
4.1.1 Constants of Protolytic Equilibria 91

4.2 Solvent Effects on Protolytic Equilibria 93
4.2.1 Classification of Solvents 93
4.2.2 The Ionic Product of the Solvent 94
4.2.3 Medium Effects of Ionizing Solvents 95

4.3 Dissociation Constants of Acids and Bases in Non-Aqueous Medium 103
4.3.1 Scheme of Solvation and Dissociation Equilibria 103
4.3.2 Medium Effect on the Dissociation Constant of an Acid in Ionizing Solvents 107
4.3.3 Protolytic Equilibria in Solvents of Low Dielectric Constant 116
4.3.4 Differentiating Effect of Solvents 117

4.4 Scales of Acidity and pH 123
4.4.1 Definitions of pH Scales for Aqueous Medium 123
4.4.2 Activity Scales for Non-Aqueous Solvents 129
4.4.3 Hammett Acidity Function 131
4.4.4 Conventional Operational pH Scale for Amphiprotic and Mixed Solvents 133

4.5 Problems 136

References 136

Chapter 5 Protolytic Systems in Aqueous Medium 138

5.1 Calculation of pH and of the Composition of a Protolytic System 138

5.2 Calculating pH in Simple Acid-Base Systems 140
5.2.1 Solution of a Strong Acid or Base 140
5.2.2 Solutions of Monoprotic Weak Acids and Bases or Mixtures of Conjugate Acids and Bases 140

5.3 Calculation of Acid-Base Equilibria of Polyprotic Acids or Bases 144
5.3.1 Calculation of the pH of a Solution of a Weak Polyprotic Acid 146
5.3.2 Solutions of Ampholytes Formed from a Polyprotic Weak Acid 147

5.4 Logarithmic Concentration Diagrams 149
5.4.1 Diagram of a Simple Protolytic System 149
5.4.2 Logarithmic Concentration Diagram of a Polyprotic Acid 151

Chapter 3 GRAPHICAL REPRESENTATION OF IONIC EQUILIBRIA IN SOLUTIONS . . 65

3.1 Distribution Diagrams 66
3.1.1 Distribution Diagram of the Equilibrium System with Species A, AB and AB_2 69
3.1.2 Distribution Diagrams of Systems Containing Polynuclear Complexes 73
3.1.3 Distribution Diagram for the Presence of Solid Phase 74
3.1.4 Significance of Distribution Diagrams 76

3.2 Logarithmic Concentration Diagrams 76
3.2.1 Logarithmic Concentration Diagram for the System A, AB, AB_2 77
3.2.2 Logarithmic Solubility Diagram 82
3.2.3 Significance of Logarithmic Diagrams 83

3.3 Diagrams for Systems of Two Variables 84
3.3.1 Predominance-Area Diagrams 84

References 86

Chapter 4 PROTOLYTIC EQUILIBRIA 88

4.1 Concepts of Acids and Bases 88
4.1.1 Constants of Protolytic Equilibria 91

4.2 Solvent Effects on Protolytic Equilibria 93
4.2.1 Classification of Solvents 93
4.2.2 The Ionic Product of the Solvent 94
4.2.3 Medium Effects of Ionizing Solvents 95

4.3 Dissociation Constants of Acids and Bases in Non-Aqueous Medium 103
4.3.1 Scheme of Solvation and Dissociation Equilibria 103
4.3.2 Medium Effect on the Dissociation Constant of an Acid in Ionizing Solvents 107
4.3.3 Protolytic Equilibria in Solvents of Low Dielectric Constant 116
4.3.4 Differentiating Effect of Solvents 117

4.4 Scales of Acidity and pH 123
4.4.1 Definitions of pH Scales for Aqueous Medium 123
4.4.2 Activity Scales for Non-Aqueous Solvents 129
4.4.3 HAMMETT Acidity Function 131
4.4.4 Conventional Operational pH Scale for Amphiprotic and Mixed Solvents 133

4.5 Problems 136

References 136

Chapter 5 PROTOLYTIC SYSTEMS IN AQUEOUS MEDIUM 138

5.1 Calculation of pH and of the Composition of a Protolytic System 138

5.2 Calculating pH in Simple Acid-Base Systems 140
5.2.1 Solution of a Strong Acid or Base 140
5.2.2 Solutions of Monoprotic Weak Acids and Bases or Mixtures of Conjugate Acids and Bases 140

5.3 Calculation of Acid-Base Equilibria of Polyprotic Acids or Bases 144
5.3.1 Calculation of the pH of a Solution of a Weak Polyprotic Acid 146
5.3.2 Solutions of Ampholytes Formed from a Polyprotic Weak Acid 147

5.4 Logarithmic Concentration Diagrams 149
5.4.1 Diagram of a Simple Protolytic System 149
5.4.2 Logarithmic Concentration Diagram of a Polyprotic Acid 151

Chapter 3 Graphical Representation of Ionic Equilibria in Solutions . . 65

3.1 Distribution Diagrams 66
3.1.1 Distribution Diagram of the Equilibrium System with Species A, AB and AB_2 69
3.1.2 Distribution Diagrams of Systems Containing Polynuclear Complexes 73
3.1.3 Distribution Diagram for the Presence of Solid Phase 74
3.1.4 Significance of Distribution Diagrams 76

3.2 Logarithmic Concentration Diagrams 76
3.2.1 Logarithmic Concentration Diagram for the System A, AB, AB_2 77
3.2.2 Logarithmic Solubility Diagram 82
3.2.3 Significance of Logarithmic Diagrams 83

3.3 Diagrams for Systems of Two Variables 84
3.3.1 Predominance-Area Diagrams 84

References 86

Chapter 4 Protolytic Equilibria 88

4.1 Concepts of Acids and Bases 88
4.1.1 Constants of Protolytic Equilibria 91

4.2 Solvent Effects on Protolytic Equilibria 93
4.2.1 Classification of Solvents 93
4.2.2 The Ionic Product of the Solvent 94
4.2.3 Medium Effects of Ionizing Solvents 95

4.3 Dissociation Constants of Acids and Bases in Non-Aqueous Medium 103
4.3.1 Scheme of Solvation and Dissociation Equilibria 103
4.3.2 Medium Effect on the Dissociation Constant of an Acid in Ionizing Solvents 107
4.3.3 Protolytic Equilibria in Solvents of Low Dielectric Constant 116
4.3.4 Differentiating Effect of Solvents 117

4.4 Scales of Acidity and pH 123
4.4.1 Definitions of pH Scales for Aqueous Medium 123
4.4.2 Activity Scales for Non-Aqueous Solvents 129
4.4.3 Hammett Acidity Function 131
4.4.4 Conventional Operational pH Scale for Amphiprotic and Mixed Solvents 133

4.5 Problems 136

References 136

Chapter 5 Protolytic Systems in Aqueous Medium 138

5.1 Calculation of pH and of the Composition of a Protolytic System 138

5.2 Calculating pH in Simple Acid-Base Systems 140
5.2.1 Solution of a Strong Acid or Base 140
5.2.2 Solutions of Monoprotic Weak Acids and Bases or Mixtures of Conjugate Acids and Bases 140

5.3 Calculation of Acid-Base Equilibria of Polyprotic Acids or Bases 144
5.3.1 Calculation of the pH of a Solution of a Weak Polyprotic Acid 146
5.3.2 Solutions of Ampholytes Formed from a Polyprotic Weak Acid 147

5.4 Logarithmic Concentration Diagrams 149
5.4.1 Diagram of a Simple Protolytic System 149
5.4.2 Logarithmic Concentration Diagram of a Polyprotic Acid 151

5.5 Buffer Solutions 154
5.5.1 Buffer Capacity 155
5.5.2 Dilution Effects 157
5.5.3 Salt Effects 158
5.5.4 Influence of Temperature 158
5.5.5 General Considerations in Practical Applications of Buffer Solutions 159

5.6 Problems 161

References 163

Chapter 6 METAL COMPLEX EQUILIBRIA 165

6.1 Complex Compounds 165

6.2 Complex Equilibria in Solution 166
6.2.1 Competition of Aquo-Complexes 166
6.2.2 Reaction Rates of Complex Formation 167

6.3 Significance of Thermodynamic Functions for Complex Formation 169
6.3.1 The Ratio of Consecutive Stability Constants 169
6.3.2 The Chelate Effect 171

6.4 Factors Determining the Stability and Other Analytical Properties of Complex Compounds 173
6.4.1 Effects of the Central Ion 174
6.4.2 Influence of the Properties of the Ligand 179
6.4.3 Analytical Functional Groups 184

6.5 Consecutive Complex Formation Equilibria 185
6.5.1 BJERRUM Formation Function 185
6.5.2 Calculation of Relative and Equilibrium Concentrations in a System of Stepwise Complexation 187
6.5.3 Polynuclear Complexes 191

6.6 Influence of Side-Reactions 193

6.7 Masking 205
6.7.1 Masking in Complexation Reactions 205
6.7.2 Demasking 207

6.8 Problems 208

References 209

Chapter 7 EQUILIBRIA OF PRECIPITATION REACTIONS 211

7.1 Influence of Various Factors on the Solubility of Substances 211
7.1.1 Ideal and Real Solutions 212
7.1.2 Solubility of Electrolytes 212
7.1.3 Particle Size Effect on Solubility 214
7.1.4 Formation of Precipitates and Their Properties 215

7.2 Solubility Product 225
7.2.1 Calculation of the Solubility of Sparingly Soluble Substances 226
7.2.2 Influence of Protolytic or Complexation Reactions on Solubility 229
7.2.3 Effects of Complexation Reactions 233

7.3 Selective Dissolution 239

7.4 Graphical Representation of Precipitation Equilibria 240
7.4.1 Logarithmic Concentration Diagram of a Precipitation Reaction without Side-Reaction Effects 240
7.4.2 Logarithmic Concentration Diagram for Precipitation Influenced by Formation of Complexes 241

7.4.3 Predominance-Area Diagram for the Precipitation Equilibrium as a Function of pH . . . 245

7.5 Problems . . . 249

References . . . 251

Chapter 8 Oxidation-Reduction Equilibria . . . 253

8.1 Oxidation-Reduction Processes in Aqueous Solutions and Galvanic Cells . . . 253
8.1.1 Equilibrium Constant . . . 255
8.1.2 Potentials of Electrodes . . . 256
8.1.3 The Potential of a Redox Pair . . . 256
8.1.4 Calculation of the Equilibrium Constant from Standard Potentials . . . 257

8.2 Formal Redox Potentials . . . 258
8.2.1 Salt Effect . . . 258
8.2.2 The Influence of Hydrogen Ions . . . 259
8.2.3 Effect of Complex Formation . . . 259
8.2.4 Effect of the Precipitation of Sparingly Soluble Substances . . . 262

8.3 Logarithmic Diagrams of Oxidation Reduction Equilibria . . . 263
8.3.1 Logarithmic Activity (or Concentration) Ratio Diagram . . . 264
8.3.2 Logarithmic Concentration Diagram of Redox Equilibria . . . 265

8.4 Predominance-Area Redox Diagrams . . . 267

8.5 Problems . . . 268

References . . . 269

Chapter 9 Titration Curves and End-Point Detection . . . 271

9.1 Reaction Equilibrium and the Course of the Titration . . . 271

9.2 Acid-Base Titrations . . . 273
9.2.1 Protolytic Titration Curves . . . 273
9.2.2 Sharpness Index . . . 277
9.2.3 Theoretical Accuracy of Acid-Base Titrations . . . 279
9.2.4 Acid-Base Indicators . . . 279

9.3 Chelatometric Titrations . . . 288
9.3.1 The Titration Curve $pH = f(a)$ . . . 288
9.3.2 The Effect of pH . . . 290
9.3.3 Indicators for Chelatometric Titrations . . . 293
9.3.4 Titration in the Presence of a Competing Metal Ion . . . 304
9.3.5 The Criteria for the Accuracy of Chelatometric Titrations . . . 304

9.4 Precipitation Titrations . . . 308
9.4.1 Titration Curves of Precipitation Titrations . . . 309
9.4.2 Indicators for Precipitation Titrations . . . 311

9.5 Oxidation-Reduction Titrations . . . 315
9.5.1 Redox Titration Curves . . . 315
9.5.2 Completeness of a Redox Titration . . . 318
9.5.3 Redox Indicators . . . 319

9.6 Titrations in Non-Aqueous Solvents . . . 323

9.7 Problems . . . 326

References . . . 327

Chapter 10 EXTRACTION EQUILIBRIA 329

10.1 An Outline of Extraction Methods 329
10.2 Partition Constant, Extraction Coefficient and Recovery Factor 330
10.3 Liquid-Liquid Partition from a Stepwise System of Metal Complexes 332
10.4 The Effect of Competing Equilibria upon Extraction 336
10.5 Completeness of Liquid-Liquid Extraction 344
10.6 Problems 346
References 347

Chapter 11 KINETIC METHODS OF CHEMICAL ANALYSIS 349

11.1 Measurement of Reaction Rates; Methods and Conditions 349
11.1.1 Precision and Accuracy of Kinetic Methods of Analysis 351
11.2 Treatment of Experimental Kinetic Data 352
11.2.1 Tangent Method 352
11.2.2 Fixed Time Procedure 354
11.2.3 Variable Time Procedure 355
11.2.4 Method of Standard Additions 355
11.2.5 Kinetic Methods for Analysis of a Mixture of Substances 356
11.2.6 Sensitivity Limits in Kinetic Methods Based on Catalysed Reactions 359
11.2.7 Examples of Kinetic Methods of Analysis 360
11.3 Problems 364
References 366
INDEX 368