
CONTENTS

CHAPTER ONE - INTRODUCTION	1
1.1. Properties of Water	1
1.2. Composition of Several Types of Water	3
1.3. Methods of Expressing Concentration	14
1.4. Additional Reading	23
CHAPTER TWO - CHEMICAL KINETICS	24
2.1. Introduction	24
2.2. Collisions of Reacting Species	25
2.3. Orientation of Reactants	26
2.4. The Rate Law	27
2.5. Reaction Mechanism	36
2.6. Effect of Temperature on Reaction Rate	40
2.7. Catalysis	44
2.8. Empirical Rate Laws	48
2.9. Problems	55
2.10. Additional Reading	57
CHAPTER THREE - CHEMICAL EQUILIBRIUM	58
3.1. Introduction	58
3.2. The Dynamic Nature of Chemical Equilibrium	58
3.3. The Thermodynamic Basis of Chemical Equilibrium	60
3.4. Enthalpy and the Temperature Dependence of the Equilibrium Constant	71
3.5. Nonideal Behavior of Ions and Molecules in Solution	74
3.6. Problems	82
3.7. Additional Reading	85

CHAPTER FOUR - ACID-BASE CHEMISTRY	86
4.1. Introduction	86
4.2. Definition of Terms	86
4.3. Rate of Reaction	93
4.4. Equilibrium Calculations—A General Approach	95
4.4.1. Mass Balances	95
4.4.2. Equilibrium Relationships	96
4.4.3. The Proton Condition	97
4.4.4. The Charge Balance or Electroneutrality Equation	98
4.5. Strong Acid-Strong Base Calculations	102
4.6. Weak Acid-Weak Base Calculations	108
4.7. Graphical Procedure for Equilibrium Calculations—pC-pH Diagrams	114
4.8. Determination of Temperature and Ionic Strength Effects on Equilibria Using pC-pH Diagrams	122
4.9. Multiprotic Acid-Conjugate Base Equilibrium Calculations	125
4.10. Ionization Fractions and Distribution Diagrams	134
4.11. Mixtures of Acids and Bases—pH Calculation	136
4.11.1. Strong Acid-Strong Base Mixtures	136
4.11.2. Weak Acid-Strong Base and Strong Acid-Weak Base Mixtures	139
4.12. pH Buffers and Buffer Intensity	146
4.12.1. Buffer pH	147
4.12.2. Buffer Intensity	149
4.13. The Carbonate System	156
4.13.1. The Carbonate Species and Their Acid-Base Equilibria	156
4.13.2. Calculation of Carbonate Species Concentrations in Open and Closed Systems	162
4.13.3. Alkalinity and Acidity	173
4.13.4. Alkalinity and Acidity Endpoints	180
4.13.5. Analytical Definition of Alkalinity and Acidity	183

CHAPTER FOUR - ACID-BASE CHEMISTRY	86
4.1. Introduction	86
4.2. Definition of Terms	86
4.3. Rate of Reaction	93
4.4. Equilibrium Calculations—A General Approach	95
4.4.1. Mass Balances	95
4.4.2. Equilibrium Relationships	96
4.4.3. The Proton Condition	97
4.4.4. The Charge Balance or Electroneutrality Equation	98
4.5. Strong Acid-Strong Base Calculations	102
4.6. Weak Acid-Weak Base Calculations	108
4.7. Graphical Procedure for Equilibrium Calculations—pC-pH Diagrams	114
4.8. Determination of Temperature and Ionic Strength Effects on Equilibria Using pC-pH Diagrams	122
4.9. Multiprotic Acid-Conjugate Base Equilibrium Calculations	125
4.10. Ionization Fractions and Distribution Diagrams	134
4.11. Mixtures of Acids and Bases—pH Calculation	136
4.11.1. Strong Acid-Strong Base Mixtures	136
4.11.2. Weak Acid-Strong Base and Strong Acid-Weak Base Mixtures	139
4.12. pH Buffers and Buffer Intensity	146
4.12.1. Buffer pH	147
4.12.2. Buffer Intensity	149
4.13. The Carbonate System	156
4.13.1. The Carbonate Species and Their Acid-Base Equilibria	156
4.13.2. Calculation of Carbonate Species Concentrations in Open and Closed Systems	162
4.13.3. Alkalinity and Acidity	173
4.13.4. Alkalinity and Acidity Endpoints	180
4.13.5. Analytical Definition of Alkalinity and Acidity	183

4.14.	Problems	192
4.15.	Additional Reading	195
CHAPTER FIVE - COORDINATION CHEMISTRY		197
5.1.	Introduction	197
5.2.	Nomenclature and Definition of Terms	197
5.3.	Reaction Rate	200
5.4.	Complex Stability and Equilibrium Calculations	201
5.5.	Metal Ion Hydrolysis— H_2O and OH^- as Ligands	209
5.6.	Complexes with Other Inorganic Ligands	217
5.7.	Complexes with Organic Ligands	223
5.7.1.	The Nature of Copper in Water and Wastewater	225
5.7.2.	Complexation by NTA	226
5.7.3.	Metal Ion Association with Humic Substances	231
5.8.	Problems	241
5.9.	Additional Reading	242
CHAPTER SIX - PRECIPITATION AND DISSOLUTION		243
6.1.	Introduction	243
6.2.	Precipitation and Dissolution Kinetics	244
6.2.1.	Nucleation	244
6.2.2.	Crystal Growth	245
6.2.3.	Agglomeration and Ripening	246
6.2.4.	Dissolution	247
6.3.	Equilibrium Calculations	247
6.3.1.	The Solubility Product	248
6.3.2.	Effect of Temperature on Solubility	251
6.3.3.	The Common Ion Effect	252
6.3.4.	Conditional Solubility Product	253
6.3.5.	Log Concentration Diagrams	254
6.4.	Solubility of Salts of Weak Acids and Bases	258

6.5.	Effect of Complexation on Solubility	262
6.6.	Competitive Effects of Several Ligands	270
6.6.1.	Precipitation of $\text{Fe}(\text{OH})_{2(s)}$ and $\text{FeCO}_{3(s)}$ —pC-pH and Predominance Area Diagrams	271
6.2.2.	Aluminum Phosphate Precipitation	279
6.7.	Calcium Carbonate Solubility and Water Stability	282
6.7.1.	Calcium Carbonate Solubility in Open and Closed Systems	282
6.7.2.	The Effect of Complex Formation on the Solubility of $\text{CaCO}_{3(s)}$	295
6.8.	Phosphate Chemistry	298
6.8.1.	Reactions of Phosphates	298
6.8.2.	Magnesium Ammonium Phosphate Precipitation	306
6.8.3.	Iron Phosphate Precipitation from Wastewater	310
6.9.	Problems	313
6.10.	Additional Reading	315
CHAPTER SEVEN - OXIDATION - REDUCTION REACTIONS		316
7.1.	Introduction	316
7.2.	Redox Stoichiometry	316
7.3.	Redox Equilibria	322
7.3.1.	Direction of Reaction	322
7.3.2.	Free Energy and Potential of Half-Reactions	324
7.3.3.	Combination of Half-Reactions	330
7.3.4.	The Nernst Equation	331
7.3.5.	Formal Potentials	336
7.3.6.	The Electron Balance and Equilibrium Calculations	336
7.4.	Electron Activity and p_e	338
7.5.	Graphical Representation of Redox Equilibria	343
7.5.1.	The p_e -pC Diagrams	344
7.5.2.	The p_e -pH Predominance Area Diagrams	348

7.5.3.	Other Predominance Area Diagrams	354
7.5.4.	The $p\epsilon$ -pH Diagrams Incorporating Solids	358
7.6.	Corrosion	363
7.6.1.	The Corrosion Cell	363
7.6.2.	The Galvanic (or Electromotive) Series	366
7.6.3.	Corrosion Reactions	368
7.6.4.	Concentration Cells	371
7.6.5.	Corrosion Control	374
7.7.	Iron Chemistry	378
7.7.1.	Iron in Groundwaters	378
7.7.2.	Acid Mine Drainage	382
7.8.	Chlorine Chemistry	386
7.8.1.	Forms of Aqueous Chlorine	387
7.8.2.	Chlorine Equilibria	388
7.8.3.	Chlorine Reactions with Inorganic Species	390
7.8.4.	Chlorine Reactions with Organic Substances	399
7.9.	Biologically Important Redox Reactions	404
7.9.1.	The Nitrogen Cycle	405
7.9.2.	Electron Acceptors in Microbial Systems	407
7.9.3.	Microbial Yields	412
7.10.	Electrochemical Measurements	414
7.10.1.	Potentiometric Measurements	414
7.10.2.	Amperometric (Polarographic) Measurements	422
7.11.	Problems	426
7.12.	Additional Reading	430
	Appendix 1. Ionization Fractions	431
	Appendix 2. Answers to Problems	435
	Appendix 3. Useful Data	442
	Index	453