

# Contents

<b>Preface</b>	<b>vii</b>	
<b>1 Thermochemical Principles</b>	<b>1</b>	
1.1 Some Basic Definitions and Concepts	1	2.4 Effect of Temperature on Reaction Rates 60
1.2 Enthalpy and Entropy	4	2.5 Mineral Precipitation/Dissolution Reaction Kinetics 64
1.3 Gibbs Free Energy, Chemical Potential, and the Equilibrium Constant	7	2.6 Absolute Rate (Transition State) Theory and the Activated Complex 65
1.4 Equilibrium Calculations	10	2.7 Some Kinetic Examples of Geochemical Interest 68
1.4.1 Pure Solids and Liquids and Their Mixtures	10	2.7.1 The $\text{FeSO}_4$ Complex 68
1.4.2 Gases	15	2.7.2 Radioactive Decay: The Example of $^{14}\text{C}$ 68
1.4.3 Solutes	17	2.7.3 Oxidation of Organic Matter and Sulfate Reduction 70
1.4.4 Solvent Water	18	2.7.4 Gypsum Dissolution 71
1.5 Summation of Reaction-Thermodynamic Properties	18	2.7.5 Oxidation of Ferrous Iron 71
1.6 The Effect of Changes in Temperature and Pressure on the Equilibrium Constant	19	2.7.6 Pyrite and Marcasite Oxidation by Ferric Iron 73
1.6.1 Introduction	19	2.7.7 Calcite Dissolution and Precipitation 73
1.6.2 Effect of Temperature	20	2.7.8 Silica Polymorphs, Dissolution, and Precipitation 74
1.6.3 Effect of Pressure	28	2.7.9 Silicates Including Feldspars, Dissolution, and Precipitation 75
Study Questions	32	2.8 Summary Observations 78
Problems	33	Study Questions 79
Chapter 1 Appendix	38	Problems 79
<b>2 Chemical Kinetics</b>	<b>50</b>	<b>3 Aqueous Complexes</b> 82
2.1 Chemical Equilibrium and Chemical Kinetic Concepts	50	3.1 Introduction and Overview 82
2.2 Elementary and Overall Reactions	56	3.1.1 Outer- and Inner-Sphere Complexes 84
2.3 Rate Laws	57	3.1.2 General Observations on Complexation 88
		3.2 Metal Cation-Ligand Relations in Complexes 88

3.3	Complexation Mass-Balance and Equilibria Equations	90	5.3.2	Carbonic Acid/pH Relations in Natural Waters	155
3.4	Hydrolysis of Cations in Water and Ionic Potential	95	5.4	Humic and Fulvic Acids	161
3.5	Electronegativity and the Stabilities of Inner-Sphere Complexes	99	5.5	Summary of Controls on the pH of Natural Waters	162
3.6	Schwarzenbach's Classes A, B, and C, and Pearson's Hard and Soft Acids and Bases	103	5.6	Acidity	165
3.7	Model-Prediction of the Stabilities of Complexes	109	5.7	Alkalinity	166
3.8	The Thermodynamics of Complexation	111	5.8	Acid-Base Properties of Minerals and Rocks	167
3.9	Distribution of Complex Species as a Function of pH	112	5.9	Acidity and Alkalinity Determination	168
3.10	Toxicity and the Role of Soft-Acid Metal Cations	114	5.9.1	The Titration Mass Balance	168
3.11	Summary	118	5.9.2	Acidity Titration	168
	Study Questions	119	5.9.3	Alkalinity Titration	173
	Problems	120	5.9.4	Calculation of Titration Curves for Acid and Base Determination	174
<b>4</b>	<b>Activity Coefficients of Dissolved Species</b>	<b>123</b>	<b>5.10</b>	<b>Buffer Capacity of Aqueous Species and Mineral Systems</b>	<b>180</b>
4.1	Activities of Dissolved Species, Ionic Strength	123	5.10.1	Buffer Capacity of Water	181
4.2	Activity Coefficients of Ions	124	5.10.2	Weak Monoprotic Acids	182
4.2.1	Mean Ion-Activity Coefficients	124	5.10.3	Polyprotic Acids	183
4.2.2	Dilute Solutions and the Debye-Hückel Equation	127	5.10.4	Carbonic Acid	183
4.2.3	Intermediate Ionic Strengths: The Davies and Truesdell-Jones Equations, Specific Ion-Interaction Theory	129	5.10.5	Calcite-Carbonic Acid	185
4.2.4	Stoichiometric and Effective Ionic Strength	135	5.10.6	Clays	187
4.2.5	High Ionic Strengths and the Pitzer Model	138	Study Questions	189	
4.3	Overview of Activity Coefficient Models for Ions	142	Problems	190	
4.4	Activity Coefficients of Molecular Species	144	<b>6</b>	<b>Carbonate Chemistry</b>	<b>193</b>
	Study Questions	145	6.1	Occurrence and Stability of the Calcium-Magnesium Carbonates	193
	Problems	146	6.2	Calcite Solubility as a Function of CO <sub>2</sub> Pressure	197
<b>5</b>	<b>Acids and Bases</b>	<b>149</b>	6.3	Calcite Solubility as a Function of pH and CO <sub>2</sub> Pressure	199
5.1	The Significance and Measurement of pH	149	6.4	Influences on the Solubility and Saturation State of Carbonate Minerals	202
5.2	Acids and Bases: Overview	152	6.4.1	Dissolution and Exsolution of CO <sub>2</sub>	202
5.3	Carbon Dioxide and Carbonic Acid Species in Natural Waters	153	6.4.2	Photosynthesis, Aerobic Decay, and Respiration	204
	5.3.1 Theoretical Relationships	153	6.4.3	Evaporation	204

6.11	The Carbonate Mineral Saturation State of Some Representative Groundwaters and Seawater	225	9	<b>The Geochemistry of Clay Minerals</b>	<b>312</b>
	Study Questions	228	9.1	Introduction	312
	Problems	229	9.2	Crystal Chemistry of Important Clay Minerals	312
			9.2.1	The Kaolinite Group and Other Two-Layer Phyllosilicates	313
			9.2.2	Three-Layer Phyllosilicates	316
<b>7</b>	<b>Chemical Weathering</b>	<b>231</b>	9.3	The Occurrence of Common Clay Minerals	319
7.1	General Observations	231	9.4	Applicability of Equilibrium Concepts	322
7.2	Weathering Rates of Some Rock-Forming Minerals	233	9.5	Clay Mineral Equilibria and Phase Diagrams	324
7.3	A Weathering Example	234	9.6	The Thermodynamic Stability of Complex Clay Minerals	337
7.4	Soil Classification and Processes	236		Study Questions	339
7.5	Aqueous Silica Species and the Solubilities of Quartz, Amorphous Silica, and Other Silica Polymorphs	241		Problems	340
7.6	Silica in Natural Waters	245			
7.7	Solubility of the Aluminum Oxyhydroxides, Kaolinite, and the Ferric Oxyhydroxides as a Function of pH	248	<b>10</b>	<b>Adsorption-Desorption Reactions</b>	<b>343</b>
7.8	Chemical Weathering Models	256	10.1	Properties of Sorbent Minerals	343
	Study Questions	263	10.1.1	Particle Size and Surface Area	343
	Problems	265	10.1.2	Surface Charge and Surface-Site Density	344
<b>8</b>	<b>General Controls on Natural Water Chemistry</b>	<b>266</b>	10.1.3	Cation Exchange Capacity of Some Natural Materials	351
8.1	The Hydrologic Cycle, Residence Time, and Water-Rock Ratio	266	10.2	Sorption Isotherms and the Distribution Coefficient	353
8.2	Water in the Hydrosphere	267	10.2.1	The Freundlich Adsorption Isotherm and the Distribution Coefficient $K_d$	353
8.3	Controls on the Composition of Subsurface Waters	270	10.2.2	The Langmuir Adsorption Isotherm	360
8.4	Precipitation Chemistry and Acid Rain	274	10.2.3	General Discussion of the Adsorption Isotherm Models	361
8.4.1	The pH of Rain Due to Atmospheric Carbon Dioxide	274	10.2.4	The Adsorption Isotherm Models as Defined in MINTEQA2	364
8.4.2	The General Composition of Precipitation	275	10.3	Ion-Exchange Type Models and Concepts	365
8.4.3	Acid Rain	278	10.3.1	Simple Ion Exchange	365
8.4.4	Trace Elements in Rain	289	10.3.2	The Power Exchange Function	366
8.5	Soil-Moisture Chemistry	290	10.4	Electrostatic Adsorption Models	369
8.6	General Chemistry of Surface- and Groundwaters	293	10.4.1	Introduction	369
8.7	Controls on the Chemical Composition of Rivers	296	10.4.2	General Assumptions and Attributes of Three Models	372
8.8	Comparison of Mean River Water and Seawater	296	10.4.3	Diffuse-Layer and Constant Capacitance Models	376
8.9	Water Quality versus Quantity	298	10.4.4	Triple-Layer Model	381
8.9.1	Mixing of Waters	298	10.4.5	Comparison of the Models	385
8.9.2	Stream Flow versus Quality	300	10.4.6	Estimation of Intrinsic Adsorption Constants	387
8.10	The Importance of Defining Background Water Quality	304	10.4.7	Application of the Electrostatic Adsorption Models to Natural Systems	391
	Study Questions	307	10.5	Adsorption Models and Contaminant Transport Modeling	393
	Problems	309			

Study Questions	395	13.1.2 Modes of Radioactive Decay	487
Problems	396	13.1.3 Units of Radioactivity and Decay Laws	487
<b>11 Oxidation-Reduction Concepts</b>	<b>403</b>	13.1.4 Natural Thorium, Uranium, and Plutonium	488
11.1 Redox Theory and Measurement	403	13.1.5 Radioactive Decay Series	489
11.1.1 General Redox Reaction	403	13.1.6 Radioactive Equilibrium and Steady State	491
11.1.2 The Standard Hydrogen Electrode	407	13.1.7 Alpha Recoil and Radon Emanation	492
11.1.3 The Eh-pH Stability Field of Water	408	13.1.8 Measuring Radioactivity and the Mass of Radionuclides	494
11.1.4 Measured versus Theoretical Redox Potentials	409	<b>13.2 Aqueous Geochemistry of Uranium</b>	495
<b>11.2 The Redox Behavior of Natural Systems</b>	<b>416</b>	13.2.1 Introduction	495
11.2.1 Redox Reaction Sequences and Redox Ladders	416	13.2.2 Selected Thermodynamic Data	496
11.2.2 General Controls on the Redox State of Natural Waters	420	13.2.3 Aqueous Speciation and Solution-Mineral Equilibria	496
11.2.3 Berner's Redox Classification and Oxidative and Reductive Capacity	421	13.2.4 Adsorption-Desorption Reactions and Models	508
11.2.4 The Redox Interface	424	<b>13.3 Uranium Ore Deposits</b>	512
Study Questions	427	13.3.1 Origin of Low-Temperature Uranium Deposits	512
Problems	429	13.3.2 Uranium Ore Deposits as Analogs for a Nuclear Waste Repository	512
<b>12 Iron and Sulfur Geochemistry</b>	<b>431</b>	<b>13.4 Nuclear Power and High-Level Nuclear Wastes</b>	515
12.1 Iron Geochemistry	431	13.4.1 Composition of Nuclear Fuel and High-Level Nuclear Wastes	515
12.1.1 Introduction	431	13.4.2 The Long-Term Health Risk of High-Level Nuclear Wastes in a Geologic Repository	517
12.1.2 Stability Constants of Aqueous Complexes	431	<b>13.5 Geochemistry of Important Radionuclides in a Geological Repository</b>	519
12.1.3 Ferric Oxyhydroxides	435	13.5.1 Thermodynamic Stability and Geochemistry of I, Tc, Am, Np, and Pu Aqueous Species and Solids	519
12.1.4 Eh-pH Diagram for the Fe-O <sub>2</sub> -CO <sub>2</sub> -S-H <sub>2</sub> O System	441	13.5.2 Solubility Controls on Releases	531
12.2 Sulfur Geochemistry	445	13.5.3 Adsorption Controls on Releases	536
12.2.1 Thermodynamic Data for Substances in the System S-O <sub>2</sub> -H <sub>2</sub> O	445	Study Questions	543
12.2.2 Acid-Base Reactions	445	Problems	544
12.2.3 Redox Reactions	449	Chapter 13 Appendix	547
12.3 Iron-Sulfur Redox Chemistry	453	<b>Geochemical Computer Models</b>	558
12.3.1 Occurrence and Solubility of Fe(II)-Sulfide Minerals	453	Some Example Geochemical Computer Models	558
12.3.2 Eh-pH Relationships in the System Fe-O <sub>2</sub> -CO <sub>2</sub> -S-H <sub>2</sub> O	455	Obtaining Geochemical Software	560
12.3.3 Acid Mine Waters	457	<b>References</b>	562
Study Questions	475	<b>Index</b>	590
Problems	475		
Chapter 12 Appendix	479		
<b>13 Actinides and Their Daughter and Fission Products</b>	<b>486</b>		
13.1 Radioactivity	487		
13.1.1 Stable and Unstable Nuclei	487		