

Contents

Preface *xi*

About the Companion Website *xiv*

1	Introduction to the Chemistry of Natural Waters	1
1.1	Water: Its Properties and Global Cycle	1
1.1.1	Physical and Chemical Properties of Water	1
1.1.1.1	The Global Water Cycle	5
1.2	Chemical Processes in Natural Waters	6
1.2.1	Water and CO ₂ : Acid–Base Reactions	6
1.2.2	The Global Carbon Cycle	7
1.2.3	Weathering Processes: Water, CO ₂ , and Minerals	8
1.2.4	Interactions Between Organisms and Water: Photosynthesis and Respiration	10
1.2.5	The Global Nitrogen Cycle	11
1.2.6	The Global Phosphorus Cycle	12
1.3	Conservation, Thermodynamics, and Kinetics	13
	References	16
2	Conservation Principles and Equilibrium Calculations	17
2.1	Mole Balance Equations	18
2.1.1	Preliminary Notion	18
2.1.2	Definition of Components	19
2.2	Properties of Components	21
2.2.1	Independence of Components	21
2.2.2	Alternative Choices of Components	22
2.2.3	Number of Components	24
2.2.4	Rules for Choosing Components	24
2.2.5	The Electroneutrality Condition	24
2.3	Solving Chemical Equilibrium Problems	25
2.3.1	Equilibrium Composition of Example 2.1	25
2.3.2	A Better Choice of Components for Example 2.1	27
2.3.3	The log C–pH Diagram for Inorganic Carbon	28
2.3.4	The Graphical Solution to Example 2.1	31
2.3.5	Inorganic Carbon Equilibrium with Gas and Solid Phases	32
2.4	Some Practical Considerations	34
2.5	Notation, Symbols, and Units	35

2.5.1	Equal Signs	35
2.5.2	Types of Concentration	35
2.5.3	Concentration Units	36
2.6	Components: A Matter of Terminology and History	38
	Problems	40
	References	42

3 Thermodynamics and Kinetics in Natural Waters 43

3.1	The Free Energy of Chemical Systems	45
3.1.1	Standard Molar Free Energy μ_i^0	46
3.1.2	Concentration Term ($RT \ln X_i$)	47
3.2	Energetics of Chemical Reactions	48
3.3	Reaction Rates and Mechanisms	50
3.3.1	Encounter Theory	50
3.3.2	Unidirectional Reactions	51
3.3.3	Reversible Reactions	52
3.3.4	Multistep Reactions	54
3.3.5	Activated Complex Theory	54
3.3.6	Enzyme Kinetics	55
3.4	Effects of Ionic Strength on Equilibrium	56
3.4.1	Dilute Solutions: The Debye–Hückel Theory	58
3.4.2	Empirical Formulae for Activity Coefficients at High Ionic Strength	59
3.4.3	Activity Coefficients of Neutral Molecules	61
3.4.4	Nonideal Effects in Mass Law Equations	61
3.5	Effect of Ionic Strength on Kinetics	62
3.6	Effect of Pressure on Equilibrium	63
3.7	Effect of Pressure on Kinetics	65
3.8	Effect of Temperature on Equilibrium	66
3.9	Effect of Temperature on Kinetics	68
3.10	Concentration Gradients in Equilibrium Systems	69
3.10.1	Extended Expression of Molar Free Energy	70
3.10.2	Distribution of Species in a Tall Water Column	70
3.10.3	Chemical Equilibrium in a Tall Water Column	71
	Problems	73
	References	77

4 Acids and Bases: Alkalinity and pH in Natural Waters 79

4.1	Natural Weak Acids and Bases	80
4.2	Alkalinity and Related Concepts	82
4.2.1	Pure Solutions of CO_2 : The Equivalence Point	82
4.2.2	Alkalinity: Preliminary Notion	85
4.2.3	Alkalinity: Mathematical Definition	86
4.2.4	Alkalinity: Experimental Definition	87
4.2.5	Other Related Definitions and Quantities	90
4.3	Acid–Base Calculations for Natural Waters	91
4.3.1	pH of a Freshwater Given C_T and Alkalinity	92
4.3.2	pH of a Phosphate-Containing Freshwater	94

4.3.3	Use of Ionization Fraction Parameters	95
4.4	Equilibrium with the Gas Phase	97
4.4.1	Equilibrium with Atmospheric CO ₂	97
4.4.2	Ocean Acidification	101
4.4.3	Other Volatile Species	105
4.4.3.1	Hydrogen Sulfide	105
4.4.3.2	Ammonia	106
4.4.3.3	Sulfur Dioxide (SO ₂)	106
4.4.4	Acid Rain	108
4.4.4.1	The Acidity of Rainwater	108
4.4.4.2	Interactions of Acid Rain with Surface Waters and Soils	110
4.5	Mixing of Two Waters	110
4.6	Effects of Biological Processes on pH and Alkalinity	113
4.6.1	Photosynthesis and Respiration	113
4.6.2	Other Microbial Processes	115
4.7	Humic Acids in Natural Waters	118
4.7.1	Acid–Base Chemistry of Humic Acids	119
4.7.2	Coulombic Interactions	121
4.7.3	Intrinsic Variability in the Acidity of Humates and a Practical Approach	122
4.8	Exchange Between Natural Waters and the Atmosphere	123
4.8.1	Formation of Aerosols at the Ocean Surface (Provided by Luc Deike)	123
4.8.2	Gas Exchange at the Air–Water Interface	124
4.8.3	Ebullition of Supersaturated Gases	127
	Problems	131
	References	135
5	Solid Dissolution and Precipitation: Acquisition and Control of Alkalinity	138
5.1	The Chemical Nature of Rocks	140
5.2	The Solubility of the Major Elements in the Upper Continental Crust: Si, Al, and Fe (+O)	147
5.2.1	The Solubility of Silica	147
5.2.2	The Solubility of Aluminum Hydroxide	148
5.2.3	The Solubility of Ferric Hydroxide	149
5.3	Alkalinity in Freshwaters: The Solubility of Ca, Mg, Na, and K	150
5.3.1	CO ₂ in Groundwater	153
5.3.2	Equilibrium with P _{CO₂} and CaCO ₃ (s) in Soils	153
5.3.3	Seasonal Dissolution and Precipitation of CaCO ₃ (s) at the Surface of Lakes	155
5.3.4	Equilibrium with P _{CO₂} and Aluminosilicates in Soils	156
5.3.5	Solubility of Minerals as a Function of P _{CO₂}	159
5.3.6	Negative Alkalinity from Sulfidic Waters	160
5.4	The Control of Alkalinity in the Oceans	161
5.4.1	Seawater Alkalinity over Geological Times	161
5.4.2	Alkalinity Variations in the Water Column	163
5.4.3	Ocean Acidification and CaCO ₃ Precipitation	166
5.5	Solubility of Trace Metals	166
5.6	The Phase Rule	176

5.7	Kinetics of Precipitation and Dissolution	178
5.7.1	The Solid–Solution Interface at the Molecular Level	178
5.7.2	Effects of Particle Size	180
5.7.3	Surface- and Transport-Controlled Dissolution	181
5.7.4	Kinetics of Transport-Controlled Dissolution	181
5.7.5	Kinetics of Surface-Controlled Dissolution	182
5.7.6	Precipitation Kinetics	186
5.7.6.1	Kinetics of Crystal Growth	186
5.7.7	Rates of Chemical Weathering	188
	Problems	189
	References	192
6	Complexation	195
6.1	Aqueous Complexes	196
6.1.1	Thermodynamics of Complex Formation	199
6.1.2	Electronic Configurations of Metals and Interactions in Metal Complexes	200
6.1.3	Quantification of Metal Speciation	204
6.2	Interactions Among Major Ions in Natural Waters	204
6.2.1	Interactions Among Major Ions in Seawater	204
6.2.2	Interactions Among Major Ions in Brines	207
6.3	Inorganic Complexation of Trace Metals	207
6.3.1	Inorganic Complexation of Copper and Zinc in a Freshwater	208
6.3.2	Inorganic Complexation of Copper and Zinc in Seawater	209
6.3.3	Inorganic Complexes of Trace Metals in Oxidic Waters	210
6.3.4	Inorganic Complexes of Trace Metals in Sulfidic Waters	212
6.3.5	Case Study: Dissolution of Cadmium in the Gironde Estuary (Based on Kraepiel et al. [15])	214
6.4	Organic Complexation	217
6.4.1	Trace Metal Complexation by Strong Anthropogenic Chelating Agents	221
6.4.1.1	Complexation of Copper and Zinc by EDTA in a Freshwater	221
6.4.1.2	Complexation of Copper and Zinc by EDTA in Seawater	223
6.4.2	Trace Metal Complexation by Strong Biogenic Chelating Agents	225
6.4.2.1	Iron Complexation by Siderophores	226
6.4.2.2	Metal-Detoxifying Molecules	229
6.4.3	Trace Metal Complexation by Humic Compounds	231
6.4.4	Organometallic Compounds	233
6.5	Complexation Kinetics	236
6.5.1	Kinetics of Complex Formation and Dissociation	239
6.5.2	Kinetics of Metal- and Ligand-Exchange Reactions	242
6.5.3	Kinetics of Double-Exchange Reactions	243
6.5.4	Case Study: Kinetics of Exchange of Zn with Fe Complexed to EDTA in a River (Based on Xue et al. [108])	244
6.6	Trace Metal Bioavailability to Microorganisms: The Case of Zn	247
6.6.1	Zn Requirements in Phytoplankton	248
6.6.2	Zn Complexation and Bioavailability	249

6.6.3	Electrochemical Measurements of Bioavailable Zn	250
6.6.4	Zinc Bioavailability and Acidification of Seawater	251
	Problems	253
	References	255
7	Oxidation–Reduction	262
7.1	Definitions, Notations, and Conventions	264
7.1.1	The Electron as a Component	264
7.1.2	Half-Redox Reactions	264
7.1.3	Electron Activities and Redox Potentials	267
7.2	Comparison Among Redox Couples	274
7.2.1	Redox Reactions as Irreversible Reactions	274
7.2.2	pe's of Dominant Redox Couples	275
7.2.2.1	The pe of Oxidic Waters: The Oxygen/Water Couple	277
7.2.2.2	The pe of Sulfidic Waters: The Sulfate/Sulfide Couple	277
7.2.2.3	The pe of the Organic Matter/CO ₂ Couple	277
7.2.2.4	The pe of the CH ₄ /CO ₂ Couple	278
7.2.2.5	The pe's of the N ₂ /NH ₄ ⁺ and the NO ₃ [−] /N ₂ Couples	278
7.3	Energetics of Microbial Processes	280
7.3.1	Energetics of Microbial Reactions	281
7.3.2	Temporal Sequences and Spatial Distributions of Redox Reactions	286
7.3.3	Case Study: The Chemistry of Lake Rot During Stratification	287
7.3.3.1	Dissolved Oxygen and Carbon in Lake Rot	288
7.3.3.2	Nitrogen Species in Lake Rot	289
7.3.3.3	Sulfur Species in Lake Rot	291
7.3.3.4	Iron and Manganese in Lake Rot	291
7.3.4	Redox in Sediments of Lake Greifen	291
7.3.5	Other Redox Couples in the Environment	293
7.4	Redox Equilibrium Calculations	293
7.4.1	Anoxic Conditions at the Bottom of a Lake	293
7.4.2	Redox in Hydrothermal Oceanic Vents	296
7.4.2.1	The Chemistry of the Vent in the Sulfidic Region	296
7.4.2.2	The Transition Between the Sulfidic and the Oxidic Domains	299
7.4.2.3	The Chemistry of the Vent in the Oxidic Region	299
7.5	pe–pH Diagrams	300
7.5.1	The Water, O ₂ , H ₂ System	301
7.5.2	The Sulfate–Sulfide System	303
7.5.3	Metals in Carbonate and Sulfur-Bearing Waters	306
7.6	Reactive Redox Species in Natural Waters	309
7.6.1	Input, Absorption, and Attenuation of Light in Natural Waters	309
7.6.2	General Principles of Photochemistry	311
7.6.3	Photochemical Oxidation of Dissolved Organic Matter	312
7.6.4	Biological Production of O ₂ [−] and H ₂ O ₂	313
7.6.5	Direct Photoredox Reactions of Trace Metals	315
7.6.5.1	Photoreduction of Dissolved Fe(III)	316

7.6.5.2	Photoreduction of Mn(IV)	317
7.6.5.3	Photochemical Reduction of Dissolved Cu(II)	319
7.7	Redox Kinetics	319
7.7.1	Rate Laws for Redox Reactions	320
7.7.2	Redox Reaction Mechanisms	321
7.7.2.1	Outer-Sphere Electron Transfer	323
7.7.2.2	Inner-Sphere Electron Transfer	324
7.7.3	Microbial Redox Reactions	325
7.8	The Bioavailability of Iron in Natural Waters	326
7.8.1	The Bioavailability of Unchelated Fe(III) to Eukaryotic Phytoplankton	326
7.8.2	Uptake of Fe(III) via a Reductive Mechanism	327
7.8.3	Uptake of Fe(III) via a Phytotransferrin	327
7.8.4	Endocytosis Uptake of Fe(III)-Siderophore Complexes	328
7.8.5	Uptake of Fe from Fe-(hydr)oxides by <i>Trichodesmium</i>	329
	Problems	330
	References	331

8	Reactions on Solid Surfaces	336
8.1	Aquatic Particles	337
8.2	Coordinative Properties of Surfaces	340
8.2.1	General Considerations	340
8.2.1.1	Acid–Base and Coordinative Properties of Oxide Surfaces	341
8.2.1.2	Long-Range Coulombic Interactions at Surfaces	341
8.2.1.3	Other Interactions at Surfaces	343
8.2.2	Adsorption Isotherms	343
8.2.3	The Surface Complexation Model for Adsorption	344
8.3	Chemical Reactions at (Conceptually) Isolated Surface Sites	345
8.4	Electrostatic Interactions on Surfaces	351
8.4.1	Including the Coulombic Term in Surface Complexation Calculations	354
8.5	Acid–Base Reactions on Hydrated Ferric Oxide (HFO)	357
8.6	Adsorption of Metals and Ligands on Hydrated Ferric Oxide (HFO)	364
8.7	Other Reactions Involving Solid Phases	367
8.7.1	Adsorption on Other Solid Phases	367
8.7.2	Adsorption on Particulate Organic Matter	368
8.7.3	Partitioning of Solutes into Bulk Particulate Phases	368
8.7.3.1	Ion Exchange	368
8.7.3.2	Solid Solution	369
8.7.3.3	Organic Film Solvation	369
8.8	Kinetic Considerations	369
8.8.1	Adsorption Kinetics	370
8.8.2	Effects of Adsorption on the Kinetics of Surface Reactions	370
	Problems	371
	References	372