

Contents

Preface — V

1 Introduction — 1

2 Structure and properties of water — 7

- 2.1 Structure of water — 7
- 2.2 Properties of water — 10
 - 2.2.1 Density — 10
 - 2.2.2 Phase diagram – melting point and boiling point — 13
 - 2.2.3 Energetic quantities — 15
 - 2.2.4 Viscosity — 17
 - 2.2.5 Surface tension — 18
- 2.3 Water as a solvent — 23
- 2.4 Problems — 26

3 Concentrations and activities — 27

- 3.1 Introduction — 27
- 3.2 Concentrations — 27
- 3.3 Conversion of concentration units — 31
 - 3.3.1 Introduction and basic equations — 31
 - 3.3.2 Conversion of mass concentration — 31
 - 3.3.3 Conversion of molar concentration — 32
 - 3.3.4 Conversion of molality — 33
 - 3.3.5 Conversion of mole fraction — 33
 - 3.3.6 Conversion of mass fraction — 34
- 3.4 Element-related concentrations — 35
- 3.5 Gas phase concentrations — 36
- 3.6 Electroneutrality condition and ion balance — 37
- 3.7 Hardness as a specific concentration measure — 38
- 3.8 Activities and activity coefficients — 42
- 3.9 Problems — 46

4 Colligative properties — 47

- 4.1 Introduction — 47
- 4.2 Vapor pressure lowering — 47
- 4.3 Boiling point elevation and freezing point depression — 49
- 4.4 Osmotic pressure — 51
- 4.5 Colligative properties of real solutions — 53
- 4.6 Problems — 53

5	The chemical equilibrium: Some general aspects — 55
5.1	Introduction — 55
5.2	Law of mass action and equilibrium constants — 55
5.3	Conventions on the use of concentration measures in the law of mass action — 57
5.4	Relationships between Gibbs energy of reaction, equilibrium constants, and reaction quotients — 58
5.5	Estimation of equilibrium constants — 59
5.6	Equilibrium constants of reverse and overall reactions — 60
5.7	Problems — 61
6	Gas–water partitioning — 63
6.1	Introduction — 63
6.2	Henry's law — 63
6.3	Alternative formulations of Henry's law — 65
6.4	Estimation of Henry's law constants for volatile substances — 67
6.5	Open and closed systems — 67
6.6	Solubilities of atmospheric gases in water — 68
6.7	Calculation of equilibrium concentrations in closed systems — 70
6.8	Problems — 72
7	Acid/base equilibria — 73
7.1	Introduction — 73
7.2	Brønsted's acid/base theory — 73
7.3	Water as an acid/base system — 76
7.4	Protolysis of acids and bases — 77
7.5	pH of aqueous solutions of acids, bases, and salts — 81
7.5.1	pH of acid solutions — 81
7.5.2	pH of base solutions — 84
7.5.3	pH of salt solutions — 84
7.5.4	Buffer systems — 89
7.6	Degree of protolysis and acid/base speciation — 91
7.6.1	Monoprotic acids — 91
7.6.2	Polyprotic acids — 93
7.7	Carbonic acid — 95
7.7.1	Relevance — 95
7.7.2	Speciation of carbonic acid — 96
7.7.3	Determination of the carbonic acid species by acid/base titrations — 96
7.7.4	General definitions of the alkalinities and acidities on the basis of proton balances — 104
7.7.5	The conservative character of alkalinity — 105

7.7.6	Determination of dissolved inorganic carbon (DIC) —	106
7.7.7	pH of pristine rain water —	107
7.8	Problems —	108
8	Precipitation/dissolution equilibria —	110
8.1	Introduction —	110
8.2	The solubility product —	110
8.3	Solubility product and solubility —	111
8.3.1	Relationship between solubility product and solubility —	111
8.3.2	Influence of the ionic strength on the solubility —	113
8.3.3	Influence of side reactions on the solubility —	114
8.4	Assessment of the saturation state of a solution —	116
8.5	Problems —	117
9	Calco-carbonic equilibrium —	119
9.1	Introduction —	119
9.2	Basic equations —	120
9.3	Graphical representation of the calco-carbonic equilibrium: Tillmans curve —	122
9.4	Assessment of the calcite saturation state —	126
9.5	Outlook: Assessment of the calcite saturation state under consideration of complex formation —	130
9.6	Special case: Fixed CO_2 partial pressure —	131
9.7	Problems —	132
10	Redox equilibria —	134
10.1	Introduction —	134
10.2	Estimation of oxidation numbers (oxidation states) —	134
10.3	Redox equilibria: Definitions and basic concepts —	137
10.4	Half-reactions —	138
10.4.1	Law of mass action and redox intensity —	138
10.4.2	Redox intensity versus redox potential —	143
10.4.3	Special case: Redox reactions with dissolved gases —	145
10.4.4	Crossover points between predominance areas of reduced and oxidized species —	146
10.4.5	Speciation as a function of p_e —	148
10.4.6	Water as a redox system —	149
10.5	Construction of p_e -pH diagrams —	152
10.5.1	Introduction —	152
10.5.2	Boundary lines for pure acid/base systems —	153
10.5.3	Boundary lines for complex acid/base systems —	153

10.5.4	Boundary lines for pure redox systems with oxidant and reductant in dissolved form —	154
10.5.5	Boundary lines for pH-dependent redox systems with oxidant and reductant in dissolved form —	155
10.5.6	Boundary lines for pH-dependent redox systems where only one partner occurs in dissolved form —	155
10.5.7	Example: The pe–pH diagram of iron —	156
10.5.8	Example: The pe–pH diagram of sulfur —	162
10.6	Complete redox reactions —	164
10.6.1	Basic relationships —	164
10.6.2	Redox reactions within the global carbon cycle —	170
10.6.3	Further oxidation reactions mediated by microorganisms —	172
10.7	Problems —	173
11	Complex formation —	175
11.1	Introduction —	175
11.2	Ligands in aquatic systems —	177
11.3	Equilibrium relationships and constants —	179
11.4	Strength of complexation: Monodentate versus polydentate ligands —	180
11.5	Complex formation and solubility —	182
11.6	Hydrolysis of hydrated metal ions —	183
11.7	Speciation of metal ions —	185
11.7.1	Introduction —	185
11.7.2	Speciation of dissolved metal ions at constant total metal concentration —	185
11.7.3	Speciation in presence of a solid that determines the liquid-phase concentrations —	190
11.8	Problems —	193
12	Sorption —	196
12.1	Introduction —	196
12.2	Geosorbents —	197
12.3	Sorption isotherms —	198
12.3.1	General considerations —	198
12.3.2	Isotherm equations —	199
12.3.3	Speciation —	203
12.4	Sorption onto charged surfaces —	204
12.4.1	Introduction —	204
12.4.2	Mathematical description of the surface protonation/deprotonation —	205
12.4.3	Modeling of ion sorption —	211

- 12.5 Sorption of organic species onto organic material — 214
- 12.6 Problems — 218

13 Solutions to the problems — 219

A Appendix — 263

- A.1 Some important constants — 263
- A.2 Some important logarithm rules — 263
- A.3 List of important equations — 264

Nomenclature — 277

Bibliography — 283

Index — 284