

Table of Contents

1 Theoretical Background.....	1
1.1 Equilibrium reactions.....	1
1.1.1 Introduction.....	1
1.1.2 Thermodynamic fundamentals.....	5
1.1.2.1 Mass-action law	5
1.1.2.2 Gibbs free energy	7
1.1.2.3 Gibbs phase rule	8
1.1.2.4 Activity.....	8
1.1.2.5 Ionic strength.....	10
1.1.2.6 Calculation of activity coefficient	10
1.1.2.6.1. Theory of ion-association	10
1.1.2.6.2. Theory of ion-interaction.....	13
1.1.2.7 Comparison ion-association versus ion-interaction theory.....	14
1.1.3 Interactions at the liquid-gaseous phase boundary.....	17
1.1.3.1 Henry Law.....	17
1.1.4 Interactions at the liquid-solid phase boundary.....	19
1.1.4.1 Dissolution and precipitation.....	19
1.1.4.1.1. Solubility-product.....	19
1.1.4.1.2. Saturation index.....	22
1.1.4.1.3. Limiting mineral phases	22
1.1.4.2 Sorption.....	25
1.1.4.2.1. Hydrophobic/hydrophilic substances	25
1.1.4.2.2. Ion exchange.....	25
1.1.4.2.3. Mathematical description of the sorption	30
1.1.5 Interactions in the liquid phase	35
1.1.5.1 Complexation.....	35
1.1.5.2 Redox processes.....	37
1.1.5.2.1. Measurement of the redox potential	37
1.1.5.2.2. Calculation of the redox potential	38
1.1.5.2.3. Presentation in predominance diagrams	43
1.1.5.2.4. Redox buffer.....	47
1.1.5.2.5. Significance of redox reactions	47
1.2 Kinetics.....	50
1.2.1 Kinetics of various chemical processes.....	50
1.2.1.1 Half-life	50
1.2.1.2 Kinetics of mineral dissolution.....	51
1.2.2 Calculation of the reaction rate	52
1.2.2.1 Subsequent reactions	53

1.2.2.2 Parallel reactions	54
1.2.3 Controlling factors on the reaction rate	54
1.2.4 Empirical approaches for kinetically controlled reactions	55
1.3 Reactive mass transport	58
1.3.1 Introduction	58
1.3.2 Flow models	58
1.3.3 Transport models	59
1.3.3.1 Definition	59
1.3.3.2 Idealized transport conditions	61
1.3.3.3 Real transport conditions	61
1.3.3.3.1. Exchange within double-porosity aquifers	62
1.3.3.4 Numerical methods of transport modeling	63
1.3.3.4.1. Finite-difference/finite-element method	65
1.3.3.4.2. Coupled methods	66
2 Hydrogeochemical Modeling Programs	69
2.1 General	69
2.1.1 Geochemical algorithms	69
2.1.2 Programs based on minimizing free energy	71
2.1.3 Programs based on equilibrium constants	72
2.1.3.1 PHREEQC	72
2.1.3.2 EQ 3/6	74
2.1.4 Thermodynamic databases	76
2.1.4.1 General	76
2.1.4.2 Structure of thermodynamic databases	78
2.1.5 Problems and sources of error in geochemical modeling	81
2.2 Use of PHREEQC	85
2.2.1 The structure of PHREEQC and its graphical user interfaces	85
2.2.1.1 Input	88
2.2.1.2 Database	95
2.2.1.3 Output	96
2.2.1.4 Grid	97
2.2.1.5 Chart	97
2.2.2 Introductory Examples for PHREEQC Modeling	97
2.2.2.1 Equilibrium reactions	97
2.2.2.1.1. Example 1a standard output – seawater analysis	98
2.2.2.1.2. Example 1b equilibrium – solution of gypsum	100
2.2.2.1.3. Example 1c equilibrium – solution of calcite with CO ₂	101
2.2.2.1.4. Example 1d: Modeling uncertainties – LJUNGSKILE	103
2.2.2.2 Introductory example for sorption	107
2.2.2.3 Introductory examples for kinetics	114
2.2.2.3.1. Defining reaction rates	115
2.2.2.3.2. BASIC within PHREEQC	117
2.2.2.4 Introductory example for isotope fractionation	122
2.2.2.5 Introductory examples for reactive mass transport	126

2.2.2.5.1. Simple 1D transport: column experiment.....	126
2.2.2.5.2. 1D transport, dilution, and surface complexation in an abandoned uranium mine	130
2.2.2.5.3. 3D transport with PHAST	134
3 Exercises	141
3.1 Equilibrium reactions.....	143
3.1.1 Groundwater – Lithosphere	143
3.1.1.1 Standard output well analysis.....	143
3.1.1.2 Equilibrium reaction – solubility of gypsum.....	144
3.1.1.3 Disequilibrium reaction – solubility of gypsum	144
3.1.1.4 Temperature dependency of gypsum solubility in well water ..	144
3.1.1.5 Temperature dependency of gypsum solubility in pure water..	144
3.1.1.6 Temperature- and $P(\text{CO}_2)$ -dependent calcite solubility.....	144
3.1.1.7 Calcite precipitation and dolomite dissolution	145
3.1.1.8 Calcite solubility in an open and a closed system	145
3.1.1.9 Pyrite weathering	145
3.1.2 Atmosphere – Groundwater – Lithosphere	146
3.1.2.1 Precipitation under the influence of soil CO_2	146
3.1.2.2 Buffering systems in the soil	147
3.1.2.3 Mineral precipitates at hot sulfur springs	147
3.1.2.4 Formation of stalactites in karst caves.....	148
3.1.2.5 Evaporation	149
3.1.3 Groundwater	150
3.1.3.1 The pE-pH diagram for the system iron.....	150
3.1.3.2 The Fe pE-pH diagram considering carbon and sulfur.....	152
3.1.3.3 The pH dependency of uranium species.....	152
3.1.4 Origin of groundwater.....	153
3.1.4.1 Pumping of fossil groundwater in arid regions	155
3.1.4.2 Salt water/fresh water interface.....	156
3.1.5 Anthropogenic use of groundwater.....	157
3.1.5.1 Sampling: Ca titration with EDTA.....	157
3.1.5.2 Carbonic acid aggressiveness.....	157
3.1.5.3 Water treatment by aeration – well water.....	158
3.1.5.4 Water treatment by aeration – sulfur spring	158
3.1.5.5 Mixing of waters	159
3.1.6 Rehabilitation of groundwater.....	159
3.1.6.1 Reduction of nitrate with methanol	159
3.1.6.2 Fe(0) barriers.....	160
3.1.6.3 Increase in pH through a calcite barrier	160
3.2 Reaction kinetics.....	160
3.2.1 Pyrite weathering	160
3.2.2 Quartz-feldspar-dissolution.....	161
3.2.3 Degradation of organic matter within the aquifer on reduction of redox-sensitive elements (Fe, As, U, Cu, Mn, S).....	162

3.2.4 Degradation of tritium in the unsaturated zone	163
3.3 Reactive transport	166
3.3.1 Lysimeter	166
3.3.2 Karst spring discharge	167
3.3.3 Karstification (corrosion along a karst fracture)	168
3.3.4 The pH increase of an acid mine water	169
3.3.5 In-situ leaching	170
3.3.6 3D Transport – Uranium and arsenic contamination plume	171
4 Solutions.....	173
4.1 Equilibrium reactions.....	173
4.1.1 Groundwater – Lithosphere	173
4.1.1.1 Standard output well analysis.....	173
4.1.1.2 Equilibrium reaction – solubility of gypsum.....	175
4.1.1.3 Disequilibrium reaction – solubility of gypsum	175
4.1.1.4 Temperature dependency of gypsum solubility in well water....	176
4.1.1.5 Temperature dependency of gypsum solubility in pure water...177	
4.1.1.6 Temperature- and $P(\text{CO}_2)$ -dependent calcite solubility	177
4.1.1.7 Calcite precipitation and dolomite dissolution	178
4.1.1.8 Comparison of the calcite solubility in an open and a closed system	179
4.1.1.9 Pyrite weathering	179
4.1.2 Atmosphere – Groundwater – Lithosphere	181
4.1.2.1 Precipitation under the influence of soil CO_2	181
4.1.2.2 Buffering systems in the soil	181
4.1.2.3 Mineral precipitations at hot sulfur springs.....	182
4.1.2.4 Formation of stalactites in karst caves.....	183
4.1.2.5 Evaporation	183
4.1.3 Groundwater	184
4.1.3.1 The pE-pH diagram for the system iron	184
4.1.3.2 The Fe pE-pH diagram considering carbon and sulfur.....	186
4.1.3.3 The pH dependency of uranium species.....	187
4.1.4 Origin of groundwater.....	188
4.1.4.1 Pumping of fossil groundwater in arid regions	188
4.1.4.2 Salt water/fresh water interface	189
4.1.5 Anthropogenic use of groundwater.....	190
4.1.5.1 Sampling: Ca titration with EDTA.....	190
4.1.5.2 Carbonic acid aggressiveness.....	191
4.1.5.3 Water treatment by aeration – well water.....	191
4.1.5.4 Water treatment by aeration – sulfur spring	191
4.1.5.5 Mixing of waters	193
4.1.6 Rehabilitation of groundwater.....	194
4.1.6.1 Reduction of nitrate with methanol	194
4.1.6.2 Fe(0) barriers.....	195
4.1.6.3 Increase in pH through a calcite barrier	196

4.2 Reaction kinetics.....	197
4.2.1 Pyrite weathering	197
4.2.2 Quartz-feldspar-dissolution.....	199
4.2.3 Degradation of organic matter within the aquifer on reduction of redox-sensitive elements (Fe, As, U, Cu, Mn, S).....	201
4.2.4 Degradation of tritium in the unsaturated zone	203
4.3 Reactive transport	205
4.3.1 Lysimeter	205
4.3.2 Karst spring discharge.....	205
4.3.3 Karstification (corrosion along a karst fracture)	207
4.3.4 The pH increase of an acid mine water	208
4.3.5 In-situ leaching.....	210
4.3.6 3D Transport – Uranium and arsenic contamination plume	212
 References.....	 215
 Index.....	 221