

## TABLE OF CONTENTS

## PART I: THE GEOCHEMICAL TOOLBOX

<b>Chapter 1: Introduction.....</b>	<b>1</b>
Geochemistry .....	1
This Book .....	2
The Philosophy of Science .....	4
Building Scientific Understanding .....	4
The Scientist as Skeptic .....	5
Elements, Atoms, and Chemical Bonds .....	6
The Periodic Table.....	6
Electrons and Orbita.....	7
Some Chemical Properties of the Elements.....	9
Chemical Bonding.....	11
A Brief Look at the Earth.....	14
Structure of the Earth .....	14
Plate Tectonics and the Hydrologic Cycle .....	15
Earth Materials.....	17
References and Suggestions for Further Reading.....	19
<b>Chapter 2: Energy, Entropy and Fundamental Thermodynamic Concepts .....</b>	<b>20</b>
The Thermodynamic Perspective.....	20
Thermodynamic Systems and Equilibrium .....	20
Fundamental Thermodynamic Variables .....	22
Equations of State .....	24
Ideal Gas Law.....	24
Equations of State for Real Gases.....	25
Equation of State for Other Substances .....	26
Temperature, Absolute Zero, and The Zeroth Law Of Thermodynamics .....	26
Energy and The First Law of Thermodynamics.....	27
Energy .....	27
Work.....	28
Path independence, Exact differentials, State functions, and the First Law.....	29
The Second Law and Entropy .....	30
Statement.....	30
Statistical Mechanics: A Microscopic Perspective of Entropy .....	31
Integrating Factors and Exact Differentials .....	37
Enthalpy.....	39
Heat Capacity .....	40
Constant Volume Heat Capacity .....	40
Constant Pressure Heat Capacity .....	40
Energy Associated with Volume Occupied and the Relationship between $C_v$ and $C_p$ .....	41
Heat Capacity of Solids: A Problem in Quantum Physics .....	42
Relationship of Entropy to Other State Variables .....	47
Additive Nature of Silicate Heat Capacities.....	48
The Third Law and Absolute Entropy .....	48
Statement of the Third Law.....	48
Absolute Entropy .....	48
Calculating Enthalpy and Entropy Changes .....	49
Enthalpy Changes Due to Changes in Temperature and Pressure .....	49
Changes in Enthalpy Due to Reactions and Changes of State .....	50
Entropies of Reaction.....	51
Free Energy .....	52
Helmholtz Free Energy .....	53
Gibbs Free Energy .....	54
Criteria for Equilibrium and Spontaneity .....	54
Temperature and Pressure Dependence of the Gibbs Free Energy .....	55
The Maxwell Relations .....	58

References and Suggestions for Further Reading.....	58
Problems .....	59
<b>Chapter 3: Solutions and Thermodynamics of Multicomponent Systems.....</b>	<b>61</b>
Introduction .....	61
Phase Equilibria .....	61
Some Definitions .....	61
The Gibbs Phase Rule .....	64
The Clapeyron Equation.....	65
Solutions .....	65
Raoult's Law .....	67
Henry's Law .....	68
The Chemical Potential.....	68
Partial Molar Quantities.....	68
Definition of Chemical Potential and Relationship to Gibbs Free Energy.....	69
Properties of the Chemical Potential.....	69
The Gibbs-Duhem Relation.....	70
Derivation of the Phase Rule .....	71
Ideal Solutions .....	71
Chemical Potential in Ideal Solutions .....	71
Volume, Enthalpy, Entropy, and Free Energy Changes in Ideal Solutions.....	72
Real solutions.....	74
Chemical Potential in Real Solutions .....	74
Fugacities .....	75
Activities and Activity Coefficients.....	76
Excess Functions.....	78
Electrolyte Solutions.....	80
The Nature of Water and Water-Electrolyte Interaction .....	80
Some Definitions and Conventions.....	81
Activities in Electrolytes .....	84
Solid Solutions and Their Activities .....	87
Mixing on Site Model .....	88
Local Charge Balance Model .....	89
Equilibrium Constants.....	90
Derivation and Definition .....	91
The Law of Mass Action .....	91
K <sub>D</sub> Values, Apparent Equilibrium Constants and the Solubility Product .....	93
Henry's Law and Gas Solubilities .....	94
Temperature Dependence of Equilibrium Constant .....	94
Pressure Dependence of Equilibrium Constant .....	96
Practical Approach to Electrolyte Equilibrium .....	96
Choosing Components and Species .....	96
Mass Balance .....	96
Electrical Neutrality .....	98
Equilibrium Constant Expressions .....	98
Oxidation and Reduction .....	99
Redox in Aqueous Solutions.....	100
Redox in Magmatic Systems .....	107
References and Suggestions for Further Reading.....	109
Problems .....	109
<b>Chapter 4: Applications of Thermodynamics to the Earth.....</b>	<b>113</b>
Introduction .....	113
Activities in Non-Ideal Solid Solutions .....	113
Mathematical Models of Real Solutions .....	113
Exsolution Phenomena .....	116
Thermodynamics and Phase Diagrams .....	119
The Thermodynamics of Melting .....	120
Thermodynamics of Phase Diagrams for Binary Systems .....	121

Geothermometry and Geobarometry .....	125
Theoretical considerations.....	125
Practical Thermobarometers.....	126
Thermodynamic Models of Magmas .....	134
Structure of Silicate Melts.....	135
Magma Solution Models.....	137
Reprise: Thermodynamics of Electrolyte Solutions .....	141
Mean Ionic Quantities .....	141
Activities in High Ionic Strength Solutions .....	144
References and Suggestions For Further Reading .....	149
Problems .....	152
<b>Chapter 5: Kinetics: The Pace of Things .....</b>	<b>155</b>
Introduction .....	155
Reaction Kinetics.....	156
Elementary and Overall Reactions .....	156
Reaction Mechanisms.....	156
Reaction Rates .....	157
Rates of Complex Reactions.....	162
Steady-State and Equilibrium.....	165
Relationships between Kinetics and Thermodynamics .....	167
Principle of Detailed Balancing .....	167
Enthalpy and Activation Energy .....	168
Aspects of Transition State Theory.....	168
Diffusion .....	173
Diffusion Flux and Fick's Laws .....	173
The Diffusion Coefficient and Diffusion in Multicomponent Systems .....	176
Diffusion in Solids and the Temperature Dependence of the Diffusion Coefficient.....	181
Diffusion in Liquids.....	183
Surfaces, Interfaces, and Interface Processes .....	184
The Surface Free Energy .....	184
The Kelvin Effect .....	185
Nucleation and Crystal Growth.....	186
Adsorption.....	190
Catalysis .....	192
Kinetics of Dissolution and Leaching .....	195
Simple Oxides .....	195
Silicates .....	196
Diagenesis.....	200
Compositional Gradients in Accumulating Sediment .....	200
Reduction of Sulfate in Accumulating Sediment .....	203
References and Suggestions for Further Reading .....	204
Problems .....	206
<b>Chapter 6: Aquatic Chemistry.....</b>	<b>210</b>
Introduction .....	210
Acid-Base Reactions .....	210
Proton Accounting, Charge Balance, and Conservation Equations.....	211
The Carbonate System.....	214
Conservative and Non-Conservative Ions.....	217
Total Alkalinity and Carbonate Alkalinity .....	218
Buffer Intensity .....	221
Complexation .....	223
Stability Constants .....	223
Water-Related Complexes.....	225
Other Complexes.....	226
Complexation in Fresh Waters .....	228
Dissolution and Precipitation Reactions.....	230
Dissolution of Carbonates by Ground and Surface Waters .....	230

Solubility of Mg .....	231
Solubility of SiO <sub>2</sub> .....	235
Solubility of Al(OH) <sub>3</sub> and Other Hydroxides .....	236
Dissolution of Silicates and Related Minerals.....	238
Clays and Their Properties .....	240
Clay Mineralogy .....	240
Ion-Exchange Properties of Clays.....	243
Mineral Surfaces and Their Interaction With Solutions .....	244
Adsorption.....	244
Development of Surface Charge and the Electric Double Layer .....	247
References and Suggestions for Further Reading.....	255
Problems .....	255
<b>Chapter 7: Trace Elements in Igneous Processes .....</b>	<b>258</b>
Introduction .....	258
What is a Trace Element? .....	259
Behavior of the Elements .....	260
Goldschmidt's Classification.....	260
The Geochemical Periodic Table.....	261
Distribution of Trace Elements Between Co-existing Phases.....	271
The Partition Coefficient.....	271
Factors Governing the Value of Partition Coefficients .....	273
Temperature and Pressure Dependence of the Partition Coefficient .....	273
Ionic Size and Charge .....	273
Compositional Dependency.....	277
Mineral-Liquid Partition Coefficients for Mafic and Ultramafic Systems.....	281
Crystal-Field Effects .....	284
Crystal Field Influences on Transition Metal Partitioning .....	288
Trace Element Distribution During Partial Melting.....	290
Equilibrium or Batch Melting .....	290
Fractional Melting .....	291
Zone Refining.....	291
Multiphase Solids.....	291
Continuous Melting.....	293
Constraints on Melting Models.....	294
Trace Element Distribution during Crystallization.....	301
Equilibrium Crystallization .....	301
Fractional Crystallization .....	301
<i>In Situ</i> Crystallization .....	302
Crystallization in Open System Magma Chambers.....	304
Summary of Trace Element Variations during Melting and Crystallization.....	306
References and Suggestions for Further Reading.....	307
Problems .....	310
<b>Chapter 8: Radiogenic Isotope Geochemistry .....</b>	<b>312</b>
Introduction .....	318
Physics of the Nucleus and the Structure of Nuclei.....	319
Nuclear Structure and Energetics.....	319
The Decay of Excited and Unstable Nuclei .....	323
Basics of Radiogenic Isotope Geochemistry.....	327
Geochronology .....	328
Decay Systems and Their Applications .....	329
Rb-Sr.....	329
Sm-Nd.....	332
Lu-Hf.....	337
Re-Os.....	338
La-Ce .....	341
U-Th-Pb .....	341

U and Th Decay Series Isotopes.....	345
Isotopes of He and Other Rare Gases .....	351
Cosmogenic and Fossil Isotopes.....	355
<sup>14</sup> C .....	356
<sup>36</sup> Cl in hydrology .....	356
<sup>10</sup> Be in Subduction Zone Studies.....	357
Cosmic-Ray Exposure Ages of Meteorites.....	357
Fossil Nuclides .....	358
References and Suggestions for Further Reading.....	358
Problems .....	360
<b>Chapter 9: Stable Isotope Geochemistry.....</b>	<b>363</b>
Introduction .....	363
Scope of Stable Isotope Geochemistry .....	363
Notation.....	364
Theoretical Considerations.....	365
Equilibrium Isotope Fractionations .....	365
Kinetic Isotope Fractionations .....	371
Isotope Geothermometry .....	373
Isotope Fractionation in the Hydrologic System .....	376
Isotope Fractionation in Biological Systems .....	378
Carbon Isotope Fractionation During Photosynthesis.....	379
Nitrogen Isotope Fractionation in Biological Processes.....	381
Oxygen and Hydrogen Isotope Fractionation by Plants .....	381
Biological Fractionation of Sulfur Isotopes.....	382
Isotopes and Diet: You Are What You Eat.....	383
Paleoclimatology.....	386
The Marine Quaternary $\delta^{18}\text{O}$ Record and Milankovitch Cycles .....	387
The Record in Glacial Ice .....	390
Soils and Paleosols .....	392
Hydrothermal Systems and Ore Deposits.....	393
Water-Rock Ratios.....	394
Sulfur Isotopes and Ore Deposits .....	395
Stable Isotopes in the Mantle and Magmatic Systems.....	398
Stable Isotopic Composition of the Mantle.....	398
Stable Isotopes in Crystallizing Magmas .....	403
Combined Fractional Crystallization and Assimilation .....	405
Isotopes of Boron and Lithium .....	406
References and Suggestions for Further Reading.....	410
Problems .....	413