

This book is intended to serve as a text for an introductory course in geochemistry for undergraduate/graduate students with at least an elementary-level background in earth sciences, chemistry, and mathematics. The text, containing 83 tables and 181 figures, covers a wide variety of topics – ranging from atomic structure to chemical and isotopic equilibria to modern biogeochemical cycles – which are divided into four interrelated parts: Crystal Chemistry; Chemical Reactions (and biochemical reactions involving bacteria); Isotope Geochemistry (radiogenic and stable isotopes); and The Earth Supersystem, which includes discussions pertinent to the evolution of the solid Earth, the atmosphere, and the hydrosphere.


In keeping with the modern trend in the field of geochemistry, the book emphasizes computational techniques by developing appropriate mathematical relations, solving a variety of problems to illustrate application of the mathematical relations, and leaving a set of questions at the end of each chapter to be solved by students. However, so as not to interrupt the flow of the text, involved chemical concepts and mathematical derivations are separated in the form of boxes. Supplementary materials are packaged into ten appendixes that include a standard-state (298.15 K, 1 bar) thermodynamic data table and a listing of answers to selected chapter-end questions.

KULA C. MISRA is a Professor of Geology (Emeritus) at the University of Tennessee where he has taught geochemistry, economic geology, and environmental geology for more than 30 years. He received a M.Tech degree in Applied Geology from the Indian Institute of Technology (Kharagpur) and, after working for about ten years as a field geologist, a Ph.D. degree in Geology from the University of Western Ontario (Canada). His research papers have been published in several professional journals, and he is the author of the textbook *Understanding Mineral Deposits* published in the year 2000. He is a member of several professional organizations and has served as a consultant to corporations and government agencies on subjects related to mineral deposits and environmental geochemistry.

Cover image: Lava flowing into the ocean; Puu Oo vent, Mount Kilauea, Hawaii Volcano National Park, 1991. Mark Newman/Science Photo Library.
Cover design by Design Deluxe

Companion Website

This book has a companion website www.wiley.com/go/misra/geochemistry with Figures and Tables from the book for downloading.

 Also available
as an e-book

 **WILEY-BLACKWELL**
www.wiley.com/wiley-blackwell

ISBN 978-1-4443-5095-1

9 781444 350951

Contents

Preface, xiii

1 Introduction, 1

- 1.1 Units of measurement, 1
 - 1.1.1 *The SI system of units*, 1
 - 1.1.2 *Concentration units for solutions*, 3
- 1.2 The Geologic Time Scale, 3
- 1.3 Recapitulation, 5
- 1.4 Questions, 5

PART I CRYSTAL CHEMISTRY, 7

2 Atomic Structure, 9

- 2.1 Historical development, 9
 - 2.1.1 *Discovery of the electron*, 9
 - 2.1.2 *The Rutherford-Bohr atom*, 10
 - 2.1.3 *Wave mechanics*, 12
- 2.2 The working model, 13
 - 2.2.1 *Quantum numbers*, 14
 - 2.2.2 *Energy levels of the atomic orbitals*, 16
- 2.3 The ground state electron configuration of elements, 17
 - 2.3.1 *Filling atomic orbitals with electrons: the Aufbau principle*, 17
 - 2.3.2 *The Periodic Table*, 18
 - 2.3.3 *Transition elements*, 18
- 2.4 Chemical behavior of elements, 18
 - 2.4.1 *Ionization potential and electron affinity*, 18
 - 2.4.2 *Classification of elements*, 20
- 2.5 Summary, 21
- 2.6 Recapitulation, 21
- 2.7 Questions, 22

3 Chemical Bonding, 23

- 3.1 Ionic bonding, 24
 - 3.1.1 *Ionic radii*, 24
 - 3.1.2 *Coordination number and radius ratio*, 25
 - 3.1.3 *Lattice energy of ideal ionic crystals*, 28
- 3.2 Crystal structures of silicate minerals, 31

- 3.3 Ionic substitution in crystals, 31
 - 3.3.1 *Goldschmidt's rules*, 31
 - 3.3.2 *Ringwood's rule*, 32
- 3.4 Crystal-field theory, 33
 - 3.4.1 *Crystal-field stabilization energy*, 33
 - 3.4.2 *Nickel enrichment in early-formed magmatic olivine*, 35
 - 3.4.3 *Colors of transition-metal complexes*, 35
- 3.5 Isomorphism, polymorphism, and solid solutions, 36
 - 3.5.1 *Isomorphism*, 36
 - 3.5.2 *Polymorphism*, 36
 - 3.5.3 *Solid solutions*, 36
- 3.6 Covalent bonding, 37
 - 3.6.1 *Valence bond theory versus molecular orbital theory*, 37
 - 3.6.2 *Covalent radii*, 38
 - 3.6.3 *Hybridization of atomic orbitals*, 38
 - 3.6.4 *Sigma (σ), pi (π), and delta (δ) molecular orbitals*, 39
 - 3.6.5 *The degree of ionic character of a chemical bond: Electronegativity*, 40
- 3.7 Metallic bonds, 43
- 3.8 Van der Waals bonds, 44
- 3.9 Hydrogen bond, 44
- 3.10 Comparison of bond types, 45
- 3.11 Goldschmidt's classification of elements, 45
- 3.12 Summary, 47
- 3.13 Recapitulation, 48
- 3.14 Questions, 48

PART II CHEMICAL REACTIONS, 49

4 Basic Thermodynamic Concepts, 51

- 4.1 Chemical equilibrium, 51
 - 4.1.1 *Law of Mass Action – equilibrium constant (K_{eq})*, 51
 - 4.1.2 *Le Chatelier's principle*, 54
- 4.2 Thermodynamic systems, 54
 - 4.2.1 *Attributes of a thermodynamic system*, 54
 - 4.2.2 *State functions*, 56

- 4.2.3 *The Gibbs phase rule*, 56
- 4.2.4 *Equations of state*, 57
- 4.2.5 *Kinds of thermodynamic systems and processes*, 58
- 4.3 *Laws of thermodynamics*, 58
 - 4.3.1 *The first law: conservation of energy*, 58
 - 4.3.2 *The second law: the concept and definition of entropy (S)*, 59
 - 4.3.3 *The fundamental equation: the first and second laws combined*, 60
 - 4.3.4 *The third law: the entropy scale*, 60
- 4.4 *Auxiliary thermodynamic functions*, 61
 - 4.4.1 *Enthalpy (H)*, 61
 - 4.4.2 *Heat capacity (C_p , C_v)*, 61
 - 4.4.3 *Gibbs free energy (G)*, 63
 - 4.4.4 *Computation of the molar free energy of a substance at T and P (\bar{G}_T^P)*, 64
- 4.5 *Free energy change of a reaction at T and P ($\Delta G_{r,T}^P$)*, 67
 - 4.5.1 *Computation of $\Delta G_{r,T}^P$* , 67
 - 4.5.2 *Evaluation of the volume integral*, 68
 - 4.5.3 *General equation for $\Delta G_{r,T}^P$* , 68
- 4.6 *Conditions for thermodynamic equilibrium and spontaneity in a closed system*, 68
- 4.7 *Metastability*, 71
- 4.8 *Computation of simple P–T phase diagrams*, 71
 - 4.8.1 *Procedure*, 71
 - 4.8.2 *The Clapeyron equation*, 72
- 4.9 *Thermodynamic data tables*, 74
- 4.10 *Summary*, 75
- 4.11 *Recapitulation*, 76
- 4.12 *Questions*, 76
- 5 Thermodynamics of Solutions, 79**
 - 5.1 *Chemical potential*, 80
 - 5.1.1 *Partial molar properties*, 80
 - 5.1.2 *Definition of chemical potential (μ)*, 81
 - 5.1.3 *Expression for free energy in terms of chemical potentials*, 81
 - 5.1.4 *Criteria for equilibrium and spontaneous change among phases of variable composition*, 82
 - 5.1.5 *Criteria for equilibrium and spontaneous change for a reaction*, 83
 - 5.1.6 *The Gibbs–Duhem equation*, 83
 - 5.2 *Variation of chemical potential (μ_i^α) with temperature, pressure, and composition*, 84
 - 5.2.1 *Temperature dependence of chemical potential*, 84
 - 5.2.2 *Pressure dependence of chemical potential*, 84
 - 5.2.3 *Dependence of chemical potential on composition: the concept of activity*, 84
 - 5.3 *Relationship between Gibbs free energy change and equilibrium constant for a reaction*, 86
 - 5.4 *Gases*, 87
 - 5.4.1 *Pure ideal gases and ideal gas mixtures*, 87
 - 5.4.2 *Pure nonideal gases: fugacity and fugacity coefficient*, 88
 - 5.4.3 *Nonideal gas mixtures*, 89
 - 5.5 *Ideal solutions involving condensed phases*, 92
 - 5.5.1 *Mixing properties of ideal solutions*, 92
 - 5.5.2 *Raoult's Law*, 93
 - 5.5.3 *Henry's Law*, 95
 - 5.5.4 *The Lewis Fugacity Rule*, 96
 - 5.5.5 *Activities of constituents in ideal solutions*, 96
 - 5.6 *Nonideal solutions involving condensed phases*, 97
 - 5.7 *Excess functions*, 98
 - 5.8 *Ideal crystalline solutions*, 98
 - 5.8.1 *Application of the mixing-on-sites model to some silicate minerals*, 98
 - 5.8.2 *Application of the local charge balance model to some silicate minerals*, 100
 - 5.9 *Nonideal crystalline solutions*, 101
 - 5.9.1 *General expressions*, 101
 - 5.9.2 *Regular solution*, 102
 - 5.10 *Summary*, 103
 - 5.11 *Recapitulation*, 104
 - 5.12 *Questions*, 104
- 6 Geothermometry and Geobarometry, 107**
 - 6.1 *Tools for geothermobarometry*, 107
 - 6.2 *Selection of reactions for thermobarometry*, 110
 - 6.3 *Dependence of equilibrium constant on temperature and pressure*, 111
 - 6.4 *Univariant reactions and displaced equilibria*, 114
 - 6.4.1 *Al_2SiO_5 polymorphs*, 114
 - 6.4.2 *Garnet–rutile– Al_2SiO_5 polymorph–ilmenite–quartz (GRAIL) barometry*, 115
 - 6.4.3 *Garnet–plagioclase–pyroxene–quartz (GAPES and GADS) barometry*, 116
 - 6.5 *Exchange reactions*, 118
 - 6.5.1 *Garnet–clinopyroxene thermometry*, 119
 - 6.5.2 *Garnet–biotite (GABI) thermometry*, 120
 - 6.5.3 *Magnetite–ilmenite thermometry and oxygen barometry*, 122
 - 6.6 *Solvus equilibria*, 126
 - 6.7 *Uncertainties in thermobarometric estimates*, 127
 - 6.8 *Fluid inclusion thermobarometry*, 128
 - 6.9 *Summary*, 130
 - 6.10 *Recapitulation*, 131
 - 6.11 *Questions*, 131
- 7 Reactions Involving Aqueous Solutions, 134**
 - 7.1 *Water as a solvent*, 134
 - 7.2 *Activity–concentration relationships in aqueous electrolyte solutions*, 135

- 7.2.1 Activity coefficient of a solute, 135
 - 7.2.2 Standard state of an aqueous solute, 135
 - 7.2.3 Estimation of activity coefficients of solutes, 136
 - 7.3 Dissociation of acids and bases, 139
 - 7.4 Solubility of salts, 140
 - 7.4.1 The concept of solubility, 140
 - 7.4.2 Solubility product, 141
 - 7.4.3 Saturation index, 144
 - 7.4.4 Ion pairs, 145
 - 7.4.5 Aqueous complexes of ore metals, 146
 - 7.5 Dissociation of H_2CO_3 acid – the carbonic acid system, 146
 - 7.5.1 Open system, 147
 - 7.5.2 Closed system, 147
 - 7.6 Acidity and alkalinity of a solution, 149
 - 7.7 pH buffers, 150
 - 7.8 Dissolution and precipitation of calcium carbonate, 151
 - 7.8.1 Solubility of calcite in pure water, 151
 - 7.8.2 Carbonate equilibria in the $\text{CaCO}_3\text{--CO}_2\text{--H}_2\text{O}$ system, 151
 - 7.8.3 Factors affecting calcite solubility, 153
 - 7.8.4 Abiological precipitation of calcium carbonate in the oceans, 154
 - 7.8.5 Biological precipitation of calcium carbonate in the oceans, 156
 - 7.8.6 Carbonate compensation depth, 157
 - 7.9 Chemical weathering of silicate minerals, 158
 - 7.9.1 Mechanisms of chemical weathering, 158
 - 7.9.2 Solubility of Silica, 159
 - 7.9.3 Equilibria in the system $\text{K}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$, 161
 - 7.10 Summary, 164
 - 7.11 Recapitulation, 165
 - 7.12 Questions, 165
-
- 8 **Oxidation–Reduction Reactions, 167**
 - 8.1 Definitions, 167
 - 8.2 Voltaic cells, 168
 - 8.2.1 Zinc–hydrogen cell, 168
 - 8.2.2 Standard hydrogen electrode and standard electrode potential, 170
 - 8.2.3 Zinc–copper cell, 170
 - 8.2.4 Electromotive series, 171
 - 8.2.5 Hydrogen–oxygen fuel cell, 172
 - 8.3 Relationship between free energy change (ΔG_r) and electrode potential (E) – the Nernst equation, 173
 - 8.4 Oxidation potential (E_h), 174
 - 8.5 The variable p_e , 175
 - 8.6 E_h –pH stability diagrams, 176
 - 8.6.1 Stability limits of surface water, 176
 - 8.6.2 Procedure for construction of E_h –pH diagrams, 179
 - 8.6.3 Geochemical classification of sedimentary redox environments, 182
 - 8.7 Role of microorganisms in oxidation–reduction reactions, 182
 - 8.7.1 Geochemically important microorganisms, 182
 - 8.7.2 Examples of oxidation–reduction reactions mediated by microorganism, 184
 - 8.8 Oxidation of sulfide minerals, 186
 - 8.8.1 Mediation by microorganisms, 186
 - 8.8.2 Oxidation of pyrite, 186
 - 8.8.3 Acid mine drainage, 187
 - 8.8.4 Bioleaching, 188
 - 8.8.5 Biooxidation, 190
 - 8.8.6 Biofiltration, 190
 - 8.9 Oxygen fugacity, 191
 - 8.9.1 Oxygen buffers, 191
 - 8.9.2 Oxygen fugacity–sulfur fugacity diagrams, 192
 - 8.10 Summary, 193
 - 8.11 Recapitulation, 194
 - 8.12 Questions, 194
 - 9 **Kinetics of Chemical Reactions, 197**
 - 9.1 Rates of chemical reactions (R): basic principles, 197
 - 9.1.1 Elementary and overall reactions, 197
 - 9.1.2 Rate–law expression, 198
 - 9.1.3 Integrated rate equations for elementary reactions, 199
 - 9.1.4 Principle of detailed balancing, 201
 - 9.1.5 Sequential elementary reactions, 202
 - 9.1.6 Parallel elementary reactions, 203
 - 9.2 Temperature dependence of rate constants, 204
 - 9.2.1 The Arrhenius equation – activation energy, 204
 - 9.2.2 Transition states, 206
 - 9.3 Relationship between rate and free energy change of an elementary reaction (ΔG_r), 208
 - 9.4 Catalysts, 209
 - 9.4.1 Homogeneous catalysis, 209
 - 9.4.2 Heterogeneous catalysis, 209
 - 9.5 Mass transfer in aqueous solutions, 210
 - 9.5.1 Advection–diffusion equation, 210
 - 9.5.2 The temperature dependence of diffusion coefficient, 212
 - 9.6 Kinetics of geochemical processes – some examples, 212
 - 9.6.1 Diffusion-controlled and surface-controlled reaction mechanisms, 212
 - 9.6.2 Dissolution and precipitation of calcite in aqueous solutions, 213
 - 9.6.3 Dissolution of silicate minerals, 216
 - 9.7 Summary, 218
 - 9.8 Recapitulation, 219
 - 9.9 Questions, 220

PART III ISOTOPE GEOCHEMISTRY, 223

10 Radiogenic Isotopes, 225

- 10.1 Radioactive decay, 225
 - 10.1.1 *Abundance and stability of nuclides*, 225
 - 10.1.2 *Mechanisms of radioactive decay*, 226
- 10.2 Principles of radiometric geochronology, 227
 - 10.2.1 *Decay of a parent radionuclide to a stable daughter*, 227
 - 10.2.2 *Basic equation for radiometric age determination*, 228
 - 10.2.3 *Decay series*, 230
- 10.3 Selected methods of geochronology, 230
 - 10.3.1 *Rubidium–strontium system*, 230
 - 10.3.2 *Samarium–neodymium system*, 232
 - 10.3.3 *Uranium–thorium–lead system*, 233
 - 10.3.4 *Rhenium–osmium system*, 240
 - 10.3.5 *Potassium (^{40}K)–argon (^{40}Ar) method*, 241
 - 10.3.6 *Argon (^{40}Ar)–argon (^{39}Ar) method*, 243
 - 10.3.7 *Carbon-14 method*, 244
- 10.4 Isotope ratios as petrogenetic indicators, 245
 - 10.4.1 *Strontium isotope ratios*, 246
 - 10.4.2 *Neodymium isotope ratios*, 246
 - 10.4.3 *Combination of strontium and neodymium isotope ratios*, 247
 - 10.4.4 *Osmium isotope ratios*, 248
- 10.5 Summary, 249
- 10.6 Recapitulation, 250
- 10.7 Questions, 250

11 Stable Isotopes, 253

- 11.1 Isotopic fractionation, 254
 - 11.1.1 *Causes of isotopic fractionation*, 254
 - 11.1.2 *Mechanisms of isotopic fractionation*, 255
 - 11.1.3 *Fractionation factor*, 255
 - 11.1.4 *The delta (δ) notation*, 256
 - 11.1.5 *Calculation of the fractionation factor from δ values*, 256
- 11.2 Types of isotopic fractionation, 258
 - 11.2.1 *Equilibrium isotope effects*, 258
 - 11.2.2 *Kinetic isotope effects*, 259
- 11.3 Stable isotope geothermometry, 259
 - 11.3.1 *Oxygen isotope geothermometry*, 260
 - 11.3.2 *Sulfur isotope geothermometry*, 262
- 11.4 Evaporation and condensation processes, 262
 - 11.4.1 *Evaporation of ocean water*, 262
 - 11.4.2 *Condensation of water vapor*, 263
 - 11.4.3 *Meteoric water line*, 265
- 11.5 Source(s) of water in hydrothermal fluids, 265
- 11.6 Estimation of water: rock ratios from oxygen isotope ratios, 267

- 11.7 Sulfur isotopes in sedimentary systems, 268
 - 11.7.1 *Bacterial sulfate reduction (BSR)*, 269
 - 11.7.2 *Thermochemical sulfate reduction (TSR)*, 270
 - 11.7.3 *Sulfur isotopic composition of seawater sulfate through geologic time*, 270
 - 11.7.4 *Open versus closed sedimentary systems with respect to sulfate and sulfide*, 271
 - 11.7.5 *Sulfur isotope ratios of sulfides in marine sediments*, 272
- 11.8 Mass-independent fractionation (MIF) of sulfur isotopes, 273
- 11.9 Iron isotopes: geochemical applications, 275
 - 11.9.1 *Fractionation of iron isotopes*, 275
 - 11.9.2 *Abiotic versus biotic precipitation of Fe minerals in banded iron formations*, 276
- 11.10 Summary, 277
- 11.11 Recapitulation, 278
- 11.12 Questions, 278

PART IV THE EARTH SUPERSYSTEM, 281

12 The Core–Mantle–Crust System, 283

- 12.1 Cosmic perspective, 283
 - 12.1.1 *The Big Bang: the beginning of the universe*, 283
 - 12.1.2 *Nucleosynthesis: creation of the elements*, 285
 - 12.1.3 *The Solar System*, 290
 - 12.1.4 *Meteorites*, 292
 - 12.1.5 *Solar System abundances of the elements*, 294
 - 12.1.6 *Origin of the Solar System: the planetesimal model*, 295
- 12.2 Evolution of the Earth, 296
 - 12.2.1 *The internal structure of the Earth*, 296
 - 12.2.2 *Bulk Earth composition*, 299
 - 12.2.3 *The primary geochemical differentiation of the proto-Earth: formation of the Earth's core and mantle*, 301
 - 12.2.4 *Formation and growth of the Earth's crust*, 306
- 12.3 Generation and crystallization of magmas, 310
 - 12.3.1 *Geochemical characteristics of primary magmas*, 310
 - 12.3.2 *Behavior of trace elements during partial melting of source rocks*, 311
 - 12.3.3 *Behavior of trace elements during magmatic crystallization*, 316
 - 12.3.4 *Chemical variation diagrams*, 318
 - 12.3.5 *Rare earth elements*, 318
- 12.4 Geochemical discrimination of paleotectonic settings of mafic volcanic suites, 319
 - 12.4.1 *Tectonomagmatic discrimination diagrams*, 319
 - 12.4.2 *Spider diagrams*, 321

12.5	Summary, 323	13.6	Geosphere–hydrosphere–atmosphere–biosphere interaction: global biogeochemical cycles, 362
12.6	Recapitulation, 324	13.6.1	<i>The carbon cycle</i> , 363
12.7	Questions, 324	13.6.2	<i>The oxygen cycle</i> , 365
13	The Crust–Hydrosphere–Atmosphere System, 326	13.6.3	<i>The nitrogen cycle</i> , 366
13.1	The present atmosphere, 326	13.6.4	<i>The sulfur cycle</i> , 367
13.1.1	<i>Temperature and pressure distribution in the atmosphere</i> , 326	13.6.5	<i>The phosphorus cycle</i> , 368
13.1.2	<i>Photochemical reactions in the atmosphere</i> , 329	13.7	Summary, 368
13.1.3	<i>The Ozone layer in the stratosphere</i> , 329	13.8	Recapitulation, 369
13.1.4	<i>Composition of the atmosphere</i> , 331	13.9	Questions, 370
13.2	Evolution of the Earth's atmosphere over geologic time, 333	APPENDIX 1	<i>Units of measurement and physical constants</i> , 372
13.2.1	<i>Origin of the atmosphere</i> , 333	APPENDIX 2	<i>Electronic configurations of elements in ground state</i> , 374
13.2.2	<i>A warm Archean Earth: the roles of carbon dioxide and methane</i> , 335	APPENDIX 3	<i>First ionization potential, electron affinity, electronegativity (Pauling scale), and coordination numbers of selected elements</i> , 377
13.2.3	<i>Oxygenation of the atmosphere</i> , 336	APPENDIX 4	<i>Thermodynamic symbols</i> , 379
13.2.4	<i>The Great Oxidation Event (GOE)</i> , 337	APPENDIX 5	<i>Standard state (298.15 K, 10⁵ Pa) thermodynamic data for selected elements, ionic species, and compounds</i> , 382
13.2.5	<i>A model for the evolution of the atmosphere</i> , 342	APPENDIX 6	<i>Fugacities of H₂O and CO₂ in the range 0.5–10.0 kbar and 200–1000°C</i> , 396
13.2.6	<i>The Phanerozoic atmosphere</i> , 343	APPENDIX 7	<i>Equations for activity coefficients in multicomponent regular solid solutions</i> , 398
13.3	Air pollution: processes and consequences, 344	APPENDIX 8	<i>Some commonly used computer codes for modeling of geochemical processes in aqueous solutions</i> , 400
13.3.1	<i>Depletion of stratospheric ozone – the “ozone hole”</i> , 344	APPENDIX 9	<i>Solar system abundances of the elements in units of number of atoms per 10⁶ silicon atoms</i> , 402
13.3.2	<i>Smogs</i> , 347	APPENDIX 10	<i>Answers to selected chapter-end questions</i> , 403
13.3.3	<i>Acid deposition</i> , 350	References	406
13.3.4	<i>Greenhouse gases and global warming</i> , 351	Index	431
13.4	The hydrosphere, 354		
13.4.1	<i>Composition of modern seawater</i> , 354		
13.4.2	<i>Mass balance of dissolved constituents in seawater</i> , 356		
13.5	Evolution of the oceans over geologic time, 357		
13.5.1	<i>Origin of the oceans</i> , 357		
13.5.2	<i>Oxidation state of the oceans</i> , 360		
13.5.3	<i>Composition of the oceans</i> , 361		