

ELEMENTS OF ENVIRONMENTAL ENGINEERING

Thermodynamics and Kinetics

Third Edition

KALLIAT T. VALSARAJ

Contents

Preface.....	xi
Author	xv
1 Introduction	1
1.1 Energy, Population, and Pollution	1
1.2 Environmental Standards and Criteria	2
1.3 The Discipline of Environmental Engineering.....	2
1.4 Chemical Thermodynamics and Kinetics in Environmental Engineering.....	4
1.4.1 Applications of Thermodynamics and Kinetics	4
1.4.1.1 Equilibrium Partitioning.....	4
1.4.1.2 Fate and Transport Modeling.....	5
1.4.1.3 Design of Separation Processes	8
1.5 Units and Dimensions.....	11
1.6 Structure of the Book	12
References.....	12
2 Basic Chemical Thermodynamics	13
2.1 Equilibrium.....	13
2.2 Fundamental Laws of Thermodynamics	14
2.2.1 Zeroth Law of Thermodynamics.....	15
2.2.2 First Law of Thermodynamics	16
2.2.3 Second Law of Thermodynamics	17
2.2.4 Third Law of Thermodynamics.....	18
2.2.5 Enthalpy and Heat Capacity	22
2.2.6 Thermodynamic Standard States: Enthalpies of Reaction, Formation, and Combustion	23
2.2.7 Combination of First and Second Laws	25
2.3 Chemical Equilibrium and Gibbs Free Energy	26
2.3.1 Free Energy Variation with Temperature and Pressure	26
2.4 Concept of Maximum Work	28
2.5 Gibbs Free Energy and Chemical Potential.....	29
2.5.1 Gibbs–Duhem Relationship for a Single Phase	30
2.5.2 Standard States for Chemical Potential.....	31
2.6 Thermodynamics of Surfaces and Colloidal Systems	32
2.6.1 Surface Tension.....	32
2.6.2 Curved Interfaces and the Young–Laplace Equation	33
2.6.3 Surface Thickness and Gibbs Dividing Surface.....	35

2.6.4	Surface Thermodynamics and Gibbs Equation	36
2.6.5	Gibbs Adsorption Equation	37
	Problems	37
	References	41
3	Multicomponent Equilibrium Thermodynamics	43
3.1	Ideal and Nonideal Fluids	43
3.1.1	Concentration Units in Environmental Engineering	44
3.1.2	Dilute Solution Definition	45
3.2	Fugacity	45
3.2.1	Fugacity of Gases	46
3.2.2	Fugacity of Condensed Phases (Liquids and Solids)	46
3.2.3	Activities of Solutes and Activity Coefficients	47
3.2.4	Ionic Strength and Activity Coefficients	49
3.2.5	Fugacity and Environmental Models	51
3.3	Ideal Solutions and Dilute Solutions	55
3.3.1	Vapor–Liquid Equilibrium: Henry’s and Raoult’s Laws	55
3.3.1.1	Henry’s Law	55
3.3.1.2	Raoult’s Law	56
3.3.2	Vapor Pressure of Organic Compounds, Clausius–Clapeyron Equation	58
3.3.3	Vapor Pressure over Curved Surfaces	63
3.3.4	Liquid–Liquid Equilibrium	66
3.3.4.1	Octanol–Water Partition Constant	66
3.3.4.2	Linear Free Energy Relationships	69
3.4	Nonideal Solutions	69
3.4.1	Activity Coefficient for Nonideal Systems	69
3.4.1.1	Excess Functions and Activity Coefficients	70
3.4.2	Activity Coefficient and Solubility	70
3.4.3	Correlations with Hydrophobicity	72
3.4.3.1	Special Structural Features of Water	73
3.4.3.2	Hydrophobic Hydration of Nonpolar Solutes	75
3.4.3.3	Hydrophobic Interactions between Solutes	78
3.4.3.4	Hydrophilic Interactions for Solutes in Water	79
3.4.3.5	Molecular Theories of Solubility: An Overview	80
3.4.4	Structure–Activity Relationships and Activity Coefficients in Water	82
3.4.5	Theoretical and Semi-Empirical Approaches to Aqueous Solubility Prediction	83
3.4.5.1	First-Generation Group Contribution Methods	83
3.4.5.2	Excess Gibbs Free Energy Models	86
3.4.5.3	Second-Generation Group Contribution Methods: The UNIFAC Method	86
3.4.6	Solubility of Inorganic Compounds in Water	88
3.5	Adsorption on Surfaces and Interfaces	88

3.5.1	Gibbs Equation for Nonionic and Ionic Systems	89
3.5.2	Equilibrium Adsorption Isotherms at Interfaces	90
3.5.3	Adsorption at Charged Surfaces	101
	Problems	103
	References	116
4	Applications of Equilibrium Thermodynamics	119
4.1	Air–Water Phase Equilibrium	119
4.1.1	Estimation of Henry’s Constant from Group Contributions	123
4.1.2	Experimental Determination of Henry’s Law Constants	125
4.1.3	Effects of Environmental Variables on K_{aw}	126
4.2	Air–Water Equilibrium in Atmospheric Chemistry	136
4.2.1	Wet Deposition of Vapor Species	137
4.2.2	Wet Deposition of Aerosol-Bound Fraction	138
4.2.3	Dry Deposition of Aerosol-Bound Pollutants	143
4.2.4	Dry Deposition Flux of Gases from the Atmosphere	144
4.2.5	Thermodynamics of Aqueous Droplets in the Atmosphere	147
4.2.6	Air/Water Equilibrium in Waste Treatment Systems	150
4.3	Soil–Water and Sediment–Water Equilibrium	152
4.3.1	Partitioning into Soils and Sediments from Water	153
4.3.2	Adsorption of Metal Ions on Soils and Sediments	155
4.3.3	Adsorption of Organic Molecules on Soils and Sediments	159
4.4	Biota/Water Partition Constant (Bioconcentration Factor)	164
4.5	Air-to-Aerosol Partition Constant	167
4.6	Air-to-Vegetation Partition Constant	171
4.7	Adsorption on Activated Carbon for Wastewater Treatment	172
	Problems	175
	References	183
5	Concepts from Chemical Reaction Kinetics	189
5.1	Progress toward Equilibrium in a Chemical Reaction	190
5.2	Reaction Rate, Order, and Rate Constant	193
5.3	Kinetic Rate Laws	194
5.3.1	Isolation Method	195
5.3.2	Initial Rate Method	195
5.3.3	Integrated Rate Laws	195
5.3.3.1	Reversible Reactions	198
5.3.3.2	Series Reactions and Steady-State Approximation	201
5.3.4	Parallel Reactions	207
5.4	Activation Energy	208
5.4.1	Activated Complex Theory	210
5.4.2	Effect of Solvent on Reaction Rates	213
5.4.3	Linear Free Energy Relationships	215

5.5	Reaction Mechanisms	216
5.5.1	Chain Reactions	216
5.6	Reactions in Solutions	219
5.6.1	Effects of Ionic Strength on Rate Constants	219
5.7	Environmental Catalysis	221
5.7.1	Mechanisms and Rate Expressions for Catalyzed Reactions	222
5.7.2	Homogeneous Catalysis	224
5.7.3	Heterogeneous Catalysis	228
5.7.4	General Mechanisms of Surface Catalysis	228
5.7.5	Autocatalysis in Environmental Reactions	234
5.8	Redox Reactions in Environmental Systems	237
5.8.1	Rates of Redox Reactions	240
5.9	Environmental Photochemical Reactions	244
5.10	Enzyme Catalysis	247
5.10.1	Michaelis-Menten Kinetics and Monod Kinetics	247
	Problems	254
	References	264
6	Applications of Chemical Kinetics in Environmental Systems	267
6.1	Types of Reactors	267
6.1.1	Ideal Reactors	267
6.1.1.1	Batch Reactor	269
6.1.1.2	Continuous-Flow Stirred Tank Reactor	269
6.1.1.3	Plug-Flow Reactor (PFR) or Tubular Reactor	270
6.1.1.4	Design Equations for CSTR and PFR	271
6.1.1.5	Relationship between Steady State and Equilibrium for a CSTR	276
6.1.2	Nonideal Reactors	277
6.1.2.1	Dispersion Model	277
6.1.2.2	Tanks-in-Series Model	278
6.1.3	Dispersion and Reaction	280
6.1.4	Reaction in a Heterogeneous Medium	281
6.1.4.1	Kinetics and Transport at Fluid-Fluid Interfaces	284
6.1.5	Diffusion and Reaction in a Porous Medium	286
6.2	The Water Environment	290
6.2.1	Fate and Transport	290
6.2.1.1	Chemicals in Lakes and Oceans	290
6.2.1.2	Chemicals in Surface Waters	293
6.2.1.3	Biochemical Oxygen Demand in Natural Streams	295
6.2.2	Water Pollution Control	299
6.2.2.1	Air Stripping in Aeration Basins	299
6.2.2.2	Oxidation Reactor	303

6.2.2.3	Photochemical Reactions and Wastewater Treatment.....	309
6.2.2.4	Photochemical Reactions in Natural Waters.....	311
6.3	The Air Environment.....	313
6.3.1	F&T Models.....	313
6.3.1.1	Box Models.....	313
6.3.1.2	Dispersion Models.....	319
6.3.2	Air Pollution Control.....	324
6.3.2.1	Adsorption.....	324
6.3.2.2	Thermal Destruction.....	327
6.3.3	Atmospheric Processes.....	330
6.3.3.1	Reactions in Aqueous Droplets.....	330
6.3.3.2	Global Warming and Greenhouse Effect.....	337
6.3.3.3	Ozone in the Stratosphere and Troposphere.....	347
6.4	Soil and Sediment Environments.....	357
6.4.1	F&T Modeling.....	357
6.4.1.1	Transport in Groundwater.....	358
6.4.1.2	Sediment–Water Exchange of Chemicals.....	364
6.4.1.3	Soil–Air Exchange of Chemicals.....	366
6.4.2	Soil and Groundwater Treatment.....	369
6.4.2.1	P&T for NAPL Removal from Groundwater.....	370
6.4.2.2	<i>In Situ</i> Soil Vapor Stripping in the Vadose Zone.....	373
6.4.2.3	Incineration for <i>ex Situ</i> Treatment of Soils and Solid Waste.....	375
6.5	Applications of Chemical Kinetics in Environmental Bioengineering.....	376
6.5.1	Enzyme Reactors.....	380
6.5.1.1	Batch Reactor.....	381
6.5.1.2	Plug-Flow Enzyme Reactor.....	382
6.5.1.3	Continuous Stirred Tank Enzyme Reactor.....	383
6.5.1.4	Immobilized Enzyme or Cell Reactor.....	387
6.5.1.5	<i>In Situ</i> Subsoil Bioremediation.....	391
6.5.2	Kinetics of Bioaccumulation of Chemicals in the Aquatic Food Chain.....	393
6.6	Applications in Green Engineering.....	398
6.6.1	Environmental Impact Analysis.....	399
6.6.2	Life Cycle Assessment.....	405
	Problems.....	406
	References.....	420
Appendix 1	Properties of Selected Chemicals of Environmental Significance.....	425
Appendix 2	Standard Free Energy, Enthalpy, and Entropy of Formation for Compounds of Environmental Significance.....	431

Appendix 3	Selected Fragment (b_j) and Structural Factors (B_k) for Octanol–Water Partition Constant Estimation.....	433
Appendix 4	Concentration Units for Compartments in Environmental Engineering	435
Appendix 5	Dissociation Constants for Environmentally Significant Acids and Bases	437
Appendix 6	Bond Contributions to Log K_{aw} for the Meylan and Howard Model.....	439
Appendix 7	Regression Analysis (the Linear Least-Squares Methodology).....	441
Appendix 8	Error Function and Complementary Error Function Definitions	445
Appendix 9	Cancer Slope Factor and Inhalation Unit Risk for Selected Carcinogens	447
Appendix 10	U.S. National Ambient Air Quality Standards	449
Index	451