CONTENTS

Preface v

Chapter 1
THERMODYNAMIC PRINCIPLES AND FUNCTIONS

1.1 Introduction 1
1.2 Systems, Processes, and Properties 2
1.3 Exact and Inexact Differentials 4
1.4 Zeroth Law, Temperature, and the Ideal Gas 10
1.5 First Law and Internal Energy 13
1.6 Second Law and Entropy 17
1.7 Energy Functions 26
1.8 Shaft Work 35
1.9 Criteria of Equilibrium and Stability 42
1.10 Chemical Potential 55
1.11 Integrated Forms and the Gibbs-Duhem Relation 62
Appendix A Partial Molal Quantities from Total Molal Quantities 69
Appendix B Derivations by Jacobians 73
Appendix C Thermodynamic Identities 80
Problems 82
References 87

Chapter 2
PARTITION FUNCTIONS, INTERMOLECULAR FORCES, AND CONFIGURATIONAL PROPERTIES

2.1 Introduction 89
2.2 Micro and Macro States and Partition Functions 90
2.3 Micro Partition Function 100

2.4 Canonical Partition Function 116
2.5 Grand Partition Function 131
2.6 Intermolecular Forces 139
2.7 Configurational and Molecular Partition Functions 155
Problems 164
References 168

Chapter 3
GASES AND GAS MIXTURES

3.1 Introduction 171
3.2 Pressure-Volume-Temperature Behavior of Pure Fluids 173
3.3 Principle of Corresponding States and Generalized Compressibility-Factor Correlations 182
3.4 Generalized Fugacity and Energy Functions 197
3.5 Equations of State 208
3.6 Fugacity, Energy Functions, and Vapor Pressure from Equations of State 232
3.7 Ideal-Gas Mixtures 244
3.8 Equations of State for Mixtures 253
3.9 Principle of Corresponding States for Mixtures 277
3.10 Amagat's Law and Dalton's Law 285
3.11 Sublimation Equilibrium 291
Appendix A Pure-Component Constants 297
Appendix B Generalized Thermodynamic Properties of Pure Fluids 299
Problems 314
References 316

Chapter 4
LIQUID SOLUTIONS

4.1 Introduction 321
4.2 Ideal and Dilute Solutions 336
4.3 Real Solutions 339
4.4 Empirical Representation of Excess Free Energy: Composition Dependence 355

4.5 Empirical Representation of Real Solutions: Group Contributions 367
4.6 Nearly Ideal Solutions 390
4.7 Regular Solutions 401
4.8 Polymer Solutions 411
Problems 424
References 425

Chapter 5
PHASE AND CHEMICAL EQUILIBRIA

5.1 Introduction 429
5.2 Degrees of Freedom of Heterogeneous Systems, Process Elements, and Processes 431
5.3 The Phase Behavior and the Critical States of Mixtures 440
5.4 Vapor-Liquid Equilibria: Low-Pressure Systems 450
5.5 Vaporization Equilibrium Ratios 463
5.6 Gas-Solid Adsorption Equilibrium 484
5.7 The Third Law of Thermodynamics 506
5.8 Chemical Reaction Equilibrium 513
Problems 536
References 541

List of Symbols 545
Index 549