

Contents

Notation, xix

1

INTRODUCTION

1

- 1.1 The Central Problems of Thermodynamics, 1
- 1.2 A System of Units, 3
- 1.3 The Equilibrium State, 5
- 1.4 Pressure, Temperature, and Equilibrium, 8
- 1.5 Heat, Work, and the Conservation of Energy, 13
- 1.6 Specification of the Equilibrium State; Intensive and Extensive Variables; Equations of State, 17
- 1.7 A Summary of Important Experimental Observations, 20
- 1.8 A Comment on the Development of Thermodynamics Problems, 22

2

CONSERVATION OF MASS AND ENERGY

24

- 2.1 A General Balance Equation and Conserved Quantities, 25
- 2.2 Conservation of Mass, 28
- 2.3 Conservation of Energy, 30
- 2.4 The Thermodynamic Properties of Matter, 42
- 2.5 Applications of the Mass and Energy Balances, 50
- 2.6 Conservation of Momentum, 70
- 2.7 The Microscopic Equations of Change for Thermodynamics and Fluid Mechanics (Optional), 71
- Problems, 77

3

ENTROPY: AN ADDITIONAL BALANCE EQUATION

84

- 3.1 Entropy—A New Concept, 85
- 3.2 The Entropy Balance and Reversibility, 90
- 3.3 Heat, Work, Engines, and Entropy, 96
- 3.4 Entropy Changes of Matter, 103
- 3.5 Applications of the Entropy Balance, 104
- 3.6 The Microscopic Entropy Balance (Optional), 117
Problems, 118

4

THE THERMODYNAMIC PROPERTIES OF REAL SUBSTANCES

131

- 4.1 Some Mathematical Preliminaries, 131
- 4.2 The Evaluation of Thermodynamic Partial Derivatives, 134
- 4.3 The Ideal Gas and Absolute Temperature Scales, 145
- 4.4 The Evaluation of Changes in the Thermodynamic
Properties of Real Substances Accompanying a Change of
State, 146
- 4.5 An Example, 163
- 4.6 The Principle of Corresponding States, 167
- 4.7 Generalized Equations of State, 181
- 4.8 More About Thermodynamic Partial Derivatives
(Optional), 185
- Appendix A4.1 A BASIC Language Program for
Thermodynamic Properties Calculations
Using the Peng–Robinson Cubic Equation
of State, PR1.BAS, 193
- Problems, 194

5

EQUILIBRIUM AND STABILITY IN ONE-COMPONENT SYSTEMS

202

- 5.1 The Criteria for Equilibrium, 202
- 5.2 Stability of Thermodynamic Systems, 206
- 5.3 Phase Equilibria: Application of the Equilibrium and
Stability Criteria to the Equation of State, 212
- 5.4 The Molar Gibbs Free Energy and Fugacity of a Pure
Component, 219
- 5.5 The Calculation of Pure Fluid Phase Equilibrium. The
Computation of Vapor Pressure from an Equation of
State, 227

- 5.6 The Specification of the Equilibrium Thermodynamic State of a System of Several Phases. The Gibbs Phase Rule for a One-Component System, 232
- 5.7 Thermodynamic Properties of Phase Transitions, 237 Problems, 241

6

THE THERMODYNAMICS OF MULTICOMPONENT MIXTURES

251

- 6.1 The Thermodynamic Description of Mixtures, 251
- 6.2 The Partial Molar Gibbs Free Energy and the Generalized Gibbs–Duhem Equation, 259
- 6.3 A Notation for Chemical Reactions, 263
- 6.4 The Equations of Change for a Multicomponent System, 266
- 6.5 The Heat of Reaction and a Convention for the Thermodynamic Properties of Reacting Mixtures, 274
- 6.6 The Experimental Determination of the Partial Molar Volume and Enthalpy, 279
- 6.7 Criteria for Phase Equilibrium in Multicomponent Systems, 287
- 6.8 The Criteria for Chemical Equilibrium, and Combined Chemical and Phase Equilibrium, 290
- 6.9 The Specification of the Equilibrium Thermodynamic State of a Multicomponent, Multiphase System; The Gibbs Phase Rule, 295
- 6.10 Some Concluding Remarks, 298 Problems, 298

7

THE ESTIMATION OF THE GIBBS FREE ENERGY AND FUGACITY OF A COMPONENT IN A MIXTURE

305

- 7.1 The Ideal Gas Mixture, 305
- 7.2 The Partial Molar Gibbs Free Energy and Fugacity, 308
- 7.3 The Ideal Mixture and Excess Mixture Properties, 311
- 7.4 The Fugacity of a Species in Gaseous, Liquid, and Solid Mixtures, 316
- 7.5 Several Correlative Liquid Mixture (Activity Coefficient) Models, 322
- 7.6 Two Predictive Activity Coefficient Models, 336
- 7.7 A Corresponding States Principle for Mixtures; The Pseudocritical Constant Method, 346
- 7.8 The Fugacity of Species in Nonsimple Mixtures, 351

- 7.9 Electrolyte Solutions, 359
- 7.10 Concluding Remarks, 363
 - Appendix A7.1 A Statistical Mechanical Interpretation of the Entropy of Mixing in an Ideal Mixture, 366
 - Appendix A7.2 A BASIC Language Program for Multicomponent Phase Equilibrium Calculations Using the Peng–Robinson Equation of State, VLMU.BAS, 369
 - Appendix A7.3 Multicomponent Excess Gibbs Free Energy (Activity Coefficient) Models, 371
 - Appendix A7.4 A BASIC Language Program for the Prediction of Activity Coefficients and Low Pressure Vapor–Liquid Equilibrium Using the UNIFAC Model UNIFAC.BAS, 373
- Problems, 374

8

PHASE EQUILIBRIUM IN MIXTURES

381

- 8.1 Vapor–Liquid Equilibria Using Activity Coefficient Models, 381
 - Problems for Section 8.1, 411
- 8.2 Vapor–Liquid Equilibria Using Equations of State, 416
 - Problems for Section 8.2, 428
- 8.3 The Solubility of a Gas in a Liquid, 430
 - Problems for Section 8.3, 441
- 8.4 The Solubility of a Liquid in a Liquid and Liquid–Liquid–Vapor Equilibrium, 443
 - Problems for Section 8.4, 456
- 8.5 The Solubility of a Solid in a Liquid, Gas, or Supercritical Fluid, 460
 - Problems for Section 8.5, 468
- 8.6 The Partitioning of a Solute Among Two Coexisting Liquid Phases; The Distribution Coefficient, 469
 - Problems for Section 8.6, 477
- 8.7 Freezing Point Depression of a Solvent Due to the Presence of a Solute; The Freezing Point of Liquid Mixtures, 478
 - Problems for Section 8.7, 482
- 8.8 Osmotic Equilibrium and Osmotic Pressure, 482
 - Problems for Section 8.8, 485
- 8.9 Concluding Remarks, 487
 - Additional Phase Equilibrium Problems, 488

9**CHEMICAL EQUILIBRIUM AND THE BALANCE EQUATIONS
FOR CHEMICALLY REACTING SYSTEMS****494**

- 9.1 Chemical Equilibrium in a Single-Phase System, 494
- 9.2 Heterogeneous Chemical Reactions, 523
- 9.3 Chemical Equilibrium When Several Reactions Occur in a Single Phase, 531
- 9.4 Combined Chemical and Phase Equilibrium, 538
- 9.5 The Balance Equations for a Tank-Type Chemical Reactor, 545
- 9.6 The Balance Equations for a Tubular Reactor, 554
- 9.7 Overall Reactor Balance Equations and the Adiabatic Reaction Temperature, 557
- Appendix A9.1 A BASIC Language Program for the Calculation of Chemical Equilibrium Constants as a Function of Temperature, CHEMEQ.BAS, 567
- Problems, 567

APPENDIXES**579**

- Appendix I Conversion Factors to SI Units, 579
- Appendix II The Molar Heat Capacities of Gases in the Ideal Gas (Zero Pressure) State, 580
- Appendix III The Thermodynamic Properties of Water and Steam, 584
- Appendix IV Heats and Free Energies of Formation, 599
- Appendix V Heats of Combustion, 607

INDEX**611**