## Contents

**CHAPTER 1**  
INTRODUCTION  
1.1 The Central Problems of Thermodynamics  4  
1.2 A System of Units  5  
1.3 The Equilibrium State  7  
1.4 Pressure, Temperature, and Equilibrium  10  
1.5 Heat, Work, and the Conservation of Energy  15  
1.6 Specification of the Equilibrium State; Intensive and Extensive Variables; Equations of State  18  
1.7 A Summary of Important Experimental Observations  21  
1.8 A Comment on the Development of Thermodynamics  23  
Problems  23  

**CHAPTER 2**  
CONSERVATION OF MASS  
2.1 A General Balance Equation and Conserved Quantities  26  
2.2 Conservation of Mass  30  
2.3 The Mass Balance Equations for a Multicomponent System with a Chemical Reaction  35  
2.4 The Microscopic Mass Balance Equations in Thermodynamics and Fluid Mechanics (Optional) (CD only)  
Problems  44  

**CHAPTER 3**  
CONSERVATION OF ENERGY  
3.1 Conservation of Energy  47  
3.2 Several Examples of Using the Energy Balance  54  
3.3 The Thermodynamic Properties of Matter  59  
3.4 Applications of the Mass and Energy Balances  69  
3.5 Conservation of Momentum  92  
3.6 The Microscopic Energy Balance (Optional) (CD only)  
Problems  93  

**CHAPTER 4**  
ENTROPY: AN ADDITIONAL BALANCE EQUATION  
4.1 Entropy: A New Concept  99  
4.2 The Entropy Balance and Reversibility  107  
4.3 Heat, Work, Engines, and Entropy  113  
4.4 Entropy Changes of Matter  124  
4.5 Applications of the Entropy Balance  127  
4.6 The Microscopic Entropy Balance (Optional) (CD only)  
Problems  139  

**CHAPTER 5**  
LIQUEFACTION, POWER CYCLES, AND EXPLOSIONS  
5.1 Liquefaction  147  
5.2 Power Generation and Refrigeration Cycles  152  
5.3 The Thermodynamics of Mechanical Explosions  173  
Problems  182  

**CHAPTER 6**  
THE THERMODYNAMIC PROPERTIES OF REAL SUBSTANCES  187  
6.1 Some Mathematical Preliminaries  188  
6.2 The Evaluation of Thermodynamic Partial Derivatives  192
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>The Ideal Gas and Absolute Temperature Scales</td>
<td>206</td>
</tr>
<tr>
<td>6.4</td>
<td>The Evaluation of Changes in the Thermodynamic Properties of Real Substances Accompanying a Change of State</td>
<td>207</td>
</tr>
<tr>
<td>6.5</td>
<td>An Example Involving the Change of State of a Real Gas</td>
<td>232</td>
</tr>
<tr>
<td>6.6</td>
<td>The Principle of Corresponding States</td>
<td>237</td>
</tr>
<tr>
<td>6.7</td>
<td>Generalized Equations of State</td>
<td>250</td>
</tr>
<tr>
<td>6.8</td>
<td>The Third Law of Thermodynamics</td>
<td>254</td>
</tr>
<tr>
<td>6.9</td>
<td>Estimation Methods for Critical and Other Properties</td>
<td>255</td>
</tr>
<tr>
<td>6.10</td>
<td>More About Thermodynamic Partial Derivatives (Optional) (CD only)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Problems</td>
<td>259</td>
</tr>
<tr>
<td>7.1</td>
<td>The Criteria for Equilibrium</td>
<td>269</td>
</tr>
<tr>
<td>7.2</td>
<td>Stability of Thermodynamic Systems</td>
<td>276</td>
</tr>
<tr>
<td>7.3</td>
<td>Phase Equilibria: Application of the Equilibrium and Stability Criteria to the Equation of State</td>
<td>283</td>
</tr>
<tr>
<td>7.4</td>
<td>The Molar Gibbs Energy and Fugacity of a Pure Component</td>
<td>290</td>
</tr>
<tr>
<td>7.5</td>
<td>The Calculation of Pure Fluid-Phase Equilibrium: The Computation of Vapor Pressure from an Equation of State</td>
<td>305</td>
</tr>
<tr>
<td>7.7</td>
<td>Thermodynamic Properties of Phase Transitions</td>
<td>317</td>
</tr>
<tr>
<td>7.8</td>
<td>Thermodynamic Properties of Small Systems, or Why Subcooling and Superheating Occur</td>
<td>324</td>
</tr>
<tr>
<td></td>
<td>Problems</td>
<td>327</td>
</tr>
<tr>
<td>8.1</td>
<td>The Thermodynamic Description of Mixtures</td>
<td>337</td>
</tr>
<tr>
<td>8.2</td>
<td>The Partial Molar Gibbs Energy and the Generalized Gibbs-Duhem Equation</td>
<td>346</td>
</tr>
<tr>
<td>8.3</td>
<td>A Notation for Chemical Reactions</td>
<td>350</td>
</tr>
<tr>
<td>8.4</td>
<td>The Equations of Change for a Multicomponent System</td>
<td>353</td>
</tr>
<tr>
<td>8.5</td>
<td>The Heat of Reaction and a Convention for the Thermodynamic Properties of Reacting Mixtures</td>
<td>361</td>
</tr>
<tr>
<td>8.6</td>
<td>The Experimental Determination of the Partial Molar Volume and Enthalpy</td>
<td>368</td>
</tr>
<tr>
<td>8.7</td>
<td>Criteria for Phase Equilibrium in Multicomponent Systems</td>
<td>378</td>
</tr>
<tr>
<td>8.8</td>
<td>Criteria for Chemical Equilibrium, and Combined Chemical and Phase Equilibrium</td>
<td>382</td>
</tr>
<tr>
<td>8.9</td>
<td>Specification of the Equilibrium Thermodynamic State of a Multicomponent, Multiphase System; the Gibbs Phase Rule</td>
<td>387</td>
</tr>
<tr>
<td>8.10</td>
<td>A Concluding Remark</td>
<td>391</td>
</tr>
<tr>
<td></td>
<td>Problems</td>
<td>391</td>
</tr>
<tr>
<td>9.1</td>
<td>The Ideal Gas Mixture</td>
<td>400</td>
</tr>
<tr>
<td>9.2</td>
<td>The Partial Molar Gibbs Energy and Fugacity</td>
<td>404</td>
</tr>
<tr>
<td>9.3</td>
<td>Ideal Mixture and Excess Mixture Properties</td>
<td>408</td>
</tr>
<tr>
<td>9.4</td>
<td>Fugacity of Species in Gaseous, Liquid, and Solid Mixtures</td>
<td>419</td>
</tr>
<tr>
<td>9.5</td>
<td>Several Correlative Liquid Mixture Activity Coefficient Models</td>
<td>429</td>
</tr>
<tr>
<td>9.6</td>
<td>Two Predictive Activity Coefficient Models</td>
<td>443</td>
</tr>
</tbody>
</table>
## Contents

9.7 Fugacity of Species in Nonsimple Mixtures  451  
9.8 Some Comments on Reference and Standard States  461  
9.9 Combined Equation-of-State and Excess Gibbs Energy Model  462  
9.10 Electrolyte Solutions  465  
9.11 Choosing the Appropriate Thermodynamic Model  473  
Appendix 9.1 A Statistical Mechanical Interpretation of the Entropy of Mixing in an Ideal Mixture (CD only)  476  
Appendix 9.2 Multicomponent Excess Gibbs Energy (Activity Coefficient) Models  476  
Appendix 9.3 The Activity Coefficient of a Solvent in an Electrolyte Solution  478  
Problems  482  

### CHAPTER 10  VAPOUR-LIQUID EQUILIBRIUM IN MIXTURES  489  
10.0 Introduction to Vapor-Liquid Equilibrium  490  
10.1 Vapor-Liquid Equilibrium in Ideal Mixtures  492  
Problems for Section 10.1  518  
10.2 Low-Pressure Vapor-Liquid Equilibrium in Nonideal Mixtures  519  
Problems for Section 10.2  548  
10.3 High-Pressure Vapor-Liquid Equilibria Using Equations of State (\(\gamma-\gamma\) Method)  556  
Problems for Section 10.3  572  

### CHAPTER 11  OTHER TYPES OF PHASE EQUILIBRIA IN FLUID MIXTURES  575  
11.1 The Solubility of a Gas in a Liquid  576  
Problems for Section 11.1  591  
11.2 Liquid-Liquid Equilibrium  593  
Problems for Section 11.2  621  
11.3 Vapor-Liquid-Liquid Equilibrium  625  
Problems for Section 11.3  633  
11.4 The Partitioning of a Solute Among Two Coexisting Liquid Phases; The Distribution Coefficient  636  
Problems for Section 11.4  646  
11.5 Osmotic Equilibrium and Osmotic Pressure  648  
Problems for Section 11.5  655  

### CHAPTER 12  MIXTURE PHASE EQUILIBRIA INVOLVING SOLIDS  658  
12.1 The Solubility of a Solid in a Liquid, Gas, or Supercritical Fluid  659  
Problems for Section 12.1  669  
12.2 Partitioning of a Solid Solute Between Two Liquid Phases  670  
Problem for Section 12.2  673  
12.3 Freezing-Point Depression of a Solvent Due to the Presence of a Solute; the Freezing Point of Liquid Mixtures  673  
Problems for Section 12.3  678  
12.4 Phase Behavior of Solid Mixtures  679  
Problems for Section 12.4  687  
12.5 The Phase Behavior Modeling of Chemicals in the Environment  689  
Problems for Section 12.5  695  
12.6 Process Design and Product Design  695  
Problem for Section 12.6  701  
12.7 Concluding Remarks on Phase Equilibria  701
CHAPTER 13  CHEMICAL EQUILIBRIUM  703
13.1 Chemical Equilibrium in a Single-Phase System  704
13.2 Heterogeneous Chemical Reactions  737
13.3 Chemical Equilibrium When Several Reactions Occur in a Single Phase  750
13.4 Combined Chemical and Phase Equilibrium  760
Problems  767

CHAPTER 14  THE BALANCE EQUATIONS FOR CHEMICAL REACTORS AND ELECTROCHEMISTRY  778
14.1 The Balance Equations for a Tank-Type Chemical Reactor  779
14.2 The Balance Equations for a Tubular Reactor  787
14.3 Overall Reactor Balance Equations and the Adiabatic Reaction Temperature  791
14.4 Thermodynamics of Chemical Explosions  799
14.5 Availability and Available Work in Chemically Reacting Systems  805
14.6 Introduction to Electrochemical Processes  810
Problems  819

CHAPTER 15  SOME BIOCHEMICAL APPLICATIONS OF THERMODYNAMICS  822
15.1 Acidity of Solutions  823
15.2 Ionization of Biochemicals  841
15.3 Solubilities of Weak Acids, Weak Bases, and Pharmaceuticals as a Function of pH  851
15.4 Binding of a Ligand to a Substrate  858
15.5 Some Other Examples of Biochemical Reactions  863
15.6 Protein Concentration in an Ultracentrifuge  870
15.7 Gibbs-Donnan Equilibrium and Membrane Potentials  873
15.8 Coupled Chemical Reactions: the ATP-ADP Energy Storage and Delivery Mechanism  880
15.9 Thermodynamic Analysis of Fermenters and Other Bioreactors  885
Problems  908

APPENDICES  913
Appendix A.I Conversion Factors to SI Units  913
Appendix A.II The Molar Heat Capacities of Gases in the Ideal Gas (Zero-Pressure) State  914
Appendix A.III The Thermodynamic Properties of Water and Steam  917
Appendix A.IV Enthalpies and Gibbs Energies of Formation  927
Appendix A.V Heats of Combustion  930
Appendix B Brief Descriptions of Computer Programs and Computer Aids for Use with This Book  931
Appendix B Descriptions of Computer Programs and Computer Aids for Use with This Book (CD only)  CDB1
B.I Windows-Based Visual Basic Programs  CDB1
B.II DOS-Based Basic Programs  CDB9
B.III MATHCAD Worksheets  CDB12
B.IV MATLAB Programs  CDB14
Appendix C Answers to Selected Problems  933

INDEX  936