

# CONTENTS

|  |             |
|--|-------------|
| <b>PREFACE</b>   | <b>xvii</b> |
| Notes to Students  | xviii       |
| Acknowledgments  | xviii       |
| <b>ABOUT THE AUTHORS</b>   | <b>xix</b>  |
| <b>GLOSSARY</b>  | <b>xxi</b>  |
| <b>NOTATION</b>  | <b>xxv</b>  |
| <b>UNIT I FIRST AND SECOND LAWS</b>                                  | <b>1</b>    |
| <b>CHAPTER 1 BASIC CONCEPTS</b>                                      | <b>3</b>    |
| 1.1 Introduction   | 5           |
| 1.2 The Molecular Nature of Energy, Temperature, and Pressure        | 6           |
| <i>Example 1.1 The energy derived from intermolecular potentials</i> | 12          |
| <i>Example 1.2 Intermolecular potentials for mixtures</i>            | 14          |
| 1.3 The Molecular Nature of Entropy                                  | 15          |
| 1.4 Basic Concepts   | 15          |
| 1.5 Real Fluids and Tabulated Properties                             | 22          |
| <i>Example 1.3 Introduction to steam tables</i>                      | 25          |
| <i>Example 1.4 Interpolation</i>                                     | 27          |
| <i>Example 1.5 Double interpolation</i>                              | 27          |
| <i>Example 1.6 Double interpolation using different tables</i>       | 28          |
| <i>Example 1.7 Double interpolation using Excel</i>                  | 29          |
| <i>Example 1.8 Quality calculations</i>                              | 31          |
| <i>Example 1.9 Constant volume cooling</i>                           | 32          |
| 1.6 Summary  | 33          |
| 1.7 Practice Problems  | 34          |

**vi** Contents

|  |     |
|--|-----|
| 1.8 Homework Problems  | 35  |
| <b>CHAPTER 2 THE ENERGY BALANCE</b> <span style="float: right;">39</span>  |     |
| 2.1 Expansion/Contraction Work   | 40  |
| 2.2 Shaft Work   | 41  |
| 2.3 Work Associated with Flow  | 41  |
| 2.4 Lost Work versus Reversibility<br><i>Example 2.1 Isothermal reversible compression of an ideal gas</i>   | 42  |
| 2.5 Heat Flow  | 46  |
| 2.6 Path Properties and State Properties<br><i>Example 2.2 Work as a path function</i>   | 46  |
| 2.7 The Closed-System Energy Balance<br><i>Example 2.3 Internal energy and heat</i>  | 48  |
| 2.8 The Open-System, Steady-State Balance<br><i>Example 2.4 Pump work for compressing H<sub>2</sub>O</i>   | 51  |
| 2.9 The Complete Energy Balance  | 56  |
| 2.10 Internal Energy, Enthalpy, and Heat Capacities<br><i>Example 2.5 Enthalpy change of an ideal gas: Integrating C<sub>P</sub><sup>ig</sup>(T)</i><br><i>Example 2.6 Enthalpy of compressed liquid</i><br><i>Example 2.7 Adiabatic compression of an ideal gas in a piston/cylinder</i>  | 57  |
| 2.11 Reference States<br><i>Example 2.8 Acetone enthalpy using various reference states</i>  | 63  |
| 2.12 Kinetic and Potential Energy<br><i>Example 2.9 Comparing changes in kinetic energy, potential energy, internal energy, and enthalpy</i><br><i>Example 2.10 Transformation of kinetic energy into enthalpy</i>   | 66  |
| 2.13 Energy Balances for Process Equipment   | 68  |
| 2.14 Strategies for Solving Process Thermodynamics Problems  | 74  |
| 2.15 Closed and Steady-State Open Systems<br><i>Example 2.11 Adiabatic, reversible expansion of an ideal gas</i><br><i>Example 2.12 Continuous adiabatic, reversible compression of an ideal gas</i><br><i>Example 2.13 Continuous, isothermal, reversible compression of an ideal gas</i><br><i>Example 2.14 Heat loss from a turbine</i> | 75  |
| 2.16 Unsteady-State Open Systems<br><i>Example 2.15 Adiabatic expansion of an ideal gas from a leaky tank</i><br><i>Example 2.16 Adiabatically filling a tank with an ideal gas</i><br><i>Example 2.17 Adiabatic expansion of steam from a leaky tank</i>  | 80  |
| 2.17 Details of Terms in the Energy Balance  | 85  |
| 2.18 Summary   | 86  |
| 2.19 Practice Problems   | 88  |
| 2.20 Homework Problems   | 90  |
| <b>CHAPTER 3 ENERGY BALANCES FOR COMPOSITE SYSTEMS</b> <span style="float: right;">95</span>   |     |
| 3.1 Heat Engines and Heat Pumps – The Carnot Cycle<br><i>Example 3.1 Analyzing heat pumps for housing</i>  | 96  |
| 3.2 Distillation Columns<br><i>Example 3.2 Start-up for a distillation column</i>  | 101 |
| 3.3 Introduction to Mixture Properties   | 105 |
| 3.4 Ideal Gas Mixture Properties   | 106 |

|  |            |
|--|------------|
| 3.5 Mixture Properties for Ideal Solutions   | 106        |
| <i>Example 3.3 Condensation of a vapor stream</i>                                  | 107        |
| 3.6 Energy Balance for Reacting Systems  | 109        |
| <i>Example 3.4 Stoichiometry and the reaction coordinate</i>                       | 110        |
| <i>Example 3.5 Using the reaction coordinates for simultaneous reactions</i>       | 111        |
| <i>Example 3.6 Reactor energy balances</i>   | 116        |
| 3.7 Reactions in Biological Systems  | 119        |
| 3.8 Summary  | 121        |
| 3.9 Practice Problems  | 122        |
| 3.10 Homework Problems   | 122        |
| <b>CHAPTER 4 ENTROPY</b>   | <b>129</b> |
| 4.1 The Concept of Entropy   | 130        |
| 4.2 The Microscopic View of Entropy  | 132        |
| <i>Example 4.1 Entropy change and “lost work” in a gas expansion</i>               | 137        |
| <i>Example 4.2 Stirling’s approximation in the Einstein solid</i>                  | 141        |
| 4.3 The Macroscopic View of Entropy  | 142        |
| <i>Example 4.3 Adiabatic, reversible expansion of steam</i>                        | 144        |
| <i>Example 4.4 A Carnot cycle based on steam</i>                                   | 145        |
| <i>Example 4.5 Ideal gas entropy changes in an adiabatic, reversible expansion</i> | 149        |
| <i>Example 4.6 Ideal gas entropy change: Integrating <math>C_P^{ig}(T)</math></i>  | 151        |
| <i>Example 4.7 Entropy generation and “lost work”</i>                              | 151        |
| <i>Example 4.8 Entropy generation in a temperature gradient</i>                    | 152        |
| 4.4 The Entropy Balance  | 153        |
| <i>Example 4.9 Entropy balances for steady-state composite systems</i>             | 155        |
| 4.5 Internal Reversibility   | 158        |
| 4.6 Entropy Balances for Process Equipment   | 159        |
| <i>Example 4.10 Entropy generation by quenching</i>                                | 159        |
| <i>Example 4.11 Entropy in a heat exchanger</i>                                    | 160        |
| <i>Example 4.12 Isentropic expansion in a nozzle</i>                               | 162        |
| 4.7 Turbine, Compressor, and Pump Efficiency                                       | 164        |
| 4.8 Visualizing Energy and Entropy Changes   | 165        |
| 4.9 Turbine Calculations   | 166        |
| <i>Example 4.13 Various cases of turbine outlet conditions</i>                     | 168        |
| <i>Example 4.14 Turbine efficiency calculation</i>                                 | 171        |
| <i>Example 4.15 Turbine inlet calculation given efficiency and outlet</i>          | 172        |
| 4.10 Pumps and Compressors   | 173        |
| <i>Example 4.16 Isothermal reversible compression of steam</i>                     | 173        |
| <i>Example 4.17 Compression of R134a using P-H chart</i>                           | 174        |
| 4.11 Strategies for Applying the Entropy Balance                                   | 175        |
| 4.12 Optimum Work and Heat Transfer  | 177        |
| <i>Example 4.18 Minimum heat and work of purification</i>                          | 180        |
| 4.13 The Irreversibility of Biological Life  | 181        |
| 4.14 Unsteady-State Open Systems   | 182        |
| <i>Example 4.19 Entropy change in a leaky tank</i>                                 | 182        |
| <i>Example 4.20 An ideal gas leaking through a turbine (unsteady state)</i>        | 183        |
| 4.15 The Entropy Balance in Brief  | 185        |
| 4.16 Summary   | 185        |
| 4.17 Practice Problems   | 187        |

|   |            |
|---|------------|
| 4.18 Homework Problems  | 189        |
| <b>CHAPTER 5 THERMODYNAMICS OF PROCESSES</b>  | <b>199</b> |
| 5.1 The Carnot Steam Cycle  | 199        |
| 5.2 The Rankine Cycle   | 200        |
| <i>Example 5.1 Rankine cycle</i>  | 201        |
| 5.3 Rankine Modifications   | 203        |
| <i>Example 5.2 A Rankine cycle with reheat</i>  | 204        |
| <i>Example 5.3 Regenerative Rankine cycle</i>   | 206        |
| 5.4 Refrigeration   | 208        |
| <i>Example 5.4 Refrigeration by vapor compression cycle</i>                                 | 209        |
| 5.5 Liquefaction  | 212        |
| <i>Example 5.5 Liquefaction of methane by the Linde process</i>                             | 213        |
| 5.6 Engines   | 214        |
| 5.7 Fluid Flow  | 214        |
| 5.8 Problem-Solving Strategies  | 214        |
| 5.9 Summary   | 215        |
| 5.10 Practice Problems  | 215        |
| 5.11 Homework Problems  | 216        |
| <b>UNIT II GENERALIZED ANALYSIS OF FLUID PROPERTIES</b>                                     | <b>223</b> |
| <b>CHAPTER 6 CLASSICAL THERMODYNAMICS —<br/>GENERALIZATIONS FOR ANY FLUID</b>               | <b>225</b> |
| 6.1 The Fundamental Property Relation   | 226        |
| 6.2 Derivative Relations  | 229        |
| <i>Example 6.1 Pressure dependence of <math>H</math></i>                                    | 233        |
| <i>Example 6.2 Entropy change with respect to <math>T</math> at constant <math>P</math></i> | 234        |
| <i>Example 6.3 Entropy as a function of <math>T</math> and <math>P</math></i>               | 235        |
| <i>Example 6.4 Entropy change for an ideal gas</i>  | 237        |
| <i>Example 6.5 Entropy change for a simple nonideal gas</i>                                 | 237        |
| <i>Example 6.6 Accounting for <math>T</math> and <math>V</math> impacts on energy</i>       | 238        |
| <i>Example 6.7 The relation between Helmholtz energy and internal energy</i>                | 239        |
| <i>Example 6.8 A quantum explanation of low <math>T</math> heat capacity</i>                | 240        |
| <i>Example 6.9 Volumetric dependence of <math>C_V</math> for ideal gas</i>                  | 242        |
| <i>Example 6.10 Application of the triple product relation</i>                              | 243        |
| <i>Example 6.11 Master equation for an ideal gas</i>  | 243        |
| <i>Example 6.12 Relating <math>C_P</math> to <math>C_V</math></i>                           | 244        |
| 6.3 Advanced Topics   | 244        |
| 6.4 Summary   | 247        |
| 6.5 Practice Problems   | 248        |
| 6.6 Homework Problems   | 248        |
| <b>CHAPTER 7 ENGINEERING EQUATIONS OF STATE<br/>FOR PVT PROPERTIES</b>                      | <b>251</b> |
| 7.1 Experimental Measurements   | 252        |
| 7.2 Three-Parameter Corresponding States  | 253        |
| 7.3 Generalized Compressibility Factor Charts   | 256        |

|   |     |
|---|-----|
| <i>Example 7.1 Application of the generalized charts</i>                    | 258 |
| 7.4 The Virial Equation of State  | 258 |
| <i>Example 7.2 Application of the virial equation</i>                       | 259 |
| 7.5 Cubic Equations of State  | 260 |
| 7.6 Solving the Cubic Equation of State for Z                               | 263 |
| <i>Example 7.3 Peng-Robinson solution by hand calculation</i>               | 266 |
| <i>Example 7.4 The Peng-Robinson equation for molar volume</i>              | 266 |
| <i>Example 7.5 Application of the Peng-Robinson equation</i>                | 268 |
| 7.7 Implications of Real Fluid Behavior                                     | 269 |
| <i>Example 7.6 Derivatives of the Peng-Robinson equation</i>                | 269 |
| 7.8 Matching the Critical Point   | 270 |
| <i>Example 7.7 Critical parameters for the van der Waals equation</i>       | 271 |
| 7.9 The Molecular Basis of Equations of State: Concepts and Notation        | 271 |
| <i>Example 7.8 Estimating molecular size</i>                                | 273 |
| <i>Example 7.9 Characterizing molecular interactions</i>                    | 275 |
| 7.10 The Molecular Basis of Equations of State: Molecular Simulation        | 276 |
| <i>Example 7.10 Computing molecular collisions in 2D</i>                    | 279 |
| <i>Example 7.11 Equations of state from trends in molecular simulations</i> | 281 |
| 7.11 The Molecular Basis of Equations of State: Analytical Theories         | 282 |
| <i>Example 7.12 Deriving your own equation of state</i>                     | 288 |
| 7.12 Summary  | 289 |
| 7.13 Practice Problems  | 290 |
| 7.14 Homework Problems  | 291 |

## CHAPTER 8 DEPARTURE FUNCTIONS 301

|  |     |
|--|-----|
| 8.1 The Departure Function Pathway   | 302 |
| 8.2 Internal Energy Departure Function   | 304 |
| <i>Example 8.1 Internal energy departure from the van der Waals equation</i>                 | 306 |
| 8.3 Entropy Departure Function   | 307 |
| 8.4 Other Departure Functions  | 308 |
| 8.5 Summary of Density-Dependent Formulas  | 308 |
| 8.6 Pressure-Dependent Formulas  | 309 |
| 8.7 Implementation of Departure Formulas   | 310 |
| <i>Example 8.2 Real entropy in a combustion engine</i>                                       | 310 |
| <i>Example 8.3 Compression of methane using the virial equation</i>                          | 312 |
| <i>Example 8.4 Computing enthalpy and entropy departures from the Peng-Robinson equation</i> | 314 |
| <i>Example 8.5 Enthalpy departure for the Peng-Robinson equation</i>                         | 316 |
| <i>Example 8.6 Gibbs departure for the Peng-Robinson equation</i>                            | 317 |
| <i>Example 8.7 U and S departure for the Peng-Robinson equation</i>                          | 317 |
| 8.8 Reference States   | 318 |
| <i>Example 8.8 Enthalpy and entropy from the Peng-Robinson equation</i>                      | 320 |
| <i>Example 8.9 Liquefaction revisited</i>  | 320 |
| <i>Example 8.10 Adiabatically filling a tank with propane</i>                                | 322 |
| 8.9 Generalized Charts for the Enthalpy Departure  | 323 |
| 8.10 Summary   | 323 |
| 8.11 Practice Problems   | 325 |
| 8.12 Homework Problems   | 326 |

|   |            |
|---|------------|
| <b>CHAPTER 9 PHASE EQUILIBRIUM IN A PURE FLUID</b>                                      | <b>335</b> |
| 9.1 Criteria for Phase Equilibrium  | 336        |
| 9.2 The Clausius-Clapeyron Equation   | 337        |
| <i>Example 9.1 Clausius-Clapeyron equation near or below the boiling point</i>          | 338        |
| 9.3 Shortcut Estimation of Saturation Properties  | 339        |
| <i>Example 9.2 Vapor pressure interpolation</i>   | 339        |
| <i>Example 9.3 Application of the shortcut vapor pressure equation</i>                  | 341        |
| <i>Example 9.4 General application of the Clapeyron equation</i>                        | 342        |
| 9.4 Changes in Gibbs Energy with Pressure   | 342        |
| 9.5 Fugacity and Fugacity Coefficient   | 344        |
| 9.6 Fugacity Criteria for Phase Equilibria  | 346        |
| 9.7 Calculation of Fugacity (Gases)   | 347        |
| 9.8 Calculation of Fugacity (Liquids)   | 348        |
| <i>Example 9.5 Vapor and liquid fugacities using the virial equation</i>                | 352        |
| 9.9 Calculation of Fugacity (Solids)  | 353        |
| 9.10 Saturation Conditions from an Equation of State                                    | 353        |
| <i>Example 9.6 Vapor pressure from the Peng-Robinson equation</i>                       | 354        |
| <i>Example 9.7 Acentric factor for the van der Waals equation</i>                       | 356        |
| <i>Example 9.8 Vapor pressure using equal area rule</i>                                 | 359        |
| 9.11 Stable Roots and Saturation Conditions   | 359        |
| 9.12 Temperature Effects on $G$ and $f$   | 361        |
| 9.13 Summary  | 361        |
| 9.14 Practice Problems  | 362        |
| 9.15 Homework Problems  | 363        |
| <b>UNIT III FLUID PHASE EQUILIBRIA IN MIXTURES</b>                                      | <b>367</b> |
| <b>CHAPTER 10 INTRODUCTION TO MULTICOMPONENT SYSTEMS</b>                                | <b>369</b> |
| 10.1 Introduction to Phase Diagrams   | 370        |
| 10.2 Vapor-Liquid Equilibrium (VLE) Calculations  | 372        |
| 10.3 Binary VLE Using Raoult's Law  | 374        |
| 10.4 Multicomponent VLE Raoult's Law Calculations                                       | 381        |
| <i>Example 10.1 Bubble and dew temperatures and isothermal flash of ideal solutions</i> | 382        |
| <i>Example 10.2 Adiabatic flash</i>   | 385        |
| 10.5 Emissions and Safety   | 386        |
| 10.6 Relating VLE to Distillation   | 390        |
| 10.7 Nonideal Systems   | 393        |
| 10.8 Concepts for Generalized Phase Equilibria  | 397        |
| 10.9 Mixture Properties for Ideal Gases   | 401        |
| 10.10 Mixture Properties for Ideal Solutions  | 403        |
| 10.11 The Ideal Solution Approximation and Raoult's Law                                 | 404        |
| 10.12 Activity Coefficient and Fugacity Coefficient Approaches                          | 405        |
| 10.13 Summary   | 405        |
| 10.14 Practice Problems   | 407        |
| 10.15 Homework Problems   | 407        |
| <b>CHAPTER 11 AN INTRODUCTION TO ACTIVITY MODELS</b>                                    | <b>411</b> |
| 11.1 Modified Raoult's Law and Excess Gibbs Energy                                      | 412        |

|  |     |
|--|-----|
| <i>Example 11.1 Gibbs excess energy for system 2-propanol + water</i>                  | 414 |
| 11.2 Calculations Using Activity Coefficients  | 416 |
| <i>Example 11.2 VLE predictions from the Margules equation</i>                         | 417 |
| <i>Example 11.3 Gibbs excess characterization by matching the bubble point</i>         | 418 |
| <i>Example 11.4 Predicting the Margules parameter with the MAB model</i>               | 423 |
| 11.3 Deriving Modified Raoult's Law  | 423 |
| 11.4 Excess Properties   | 426 |
| 11.5 Modified Raoult's Law and Excess Gibbs Energy                                     | 427 |
| 11.6 Redlich-Kister and the Two-Parameter Margules Models                              | 429 |
| <i>Example 11.5 Fitting one measurement with the two-parameter Margules equation</i>   | 430 |
| <i>Example 11.6 Dew pressure using the two-parameter Margules equation</i>             | 431 |
| 11.7 Activity Coefficients at Special Compositions                                     | 432 |
| <i>Example 11.7 Azeotrope fitting with bubble-temperature calculations</i>             | 433 |
| 11.8 Preliminary Indications of VLLE   | 434 |
| 11.9 Fitting Activity Models to Multiple Data  | 435 |
| <i>Example 11.8 Fitting parameters using nonlinear least squares</i>                   | 436 |
| 11.10 Relations for Partial Molar Properties   | 439 |
| <i>Example 11.9 Heats of mixing with the Margules two-parameter model</i>              | 441 |
| 11.11 Distillation and Relative Volatility of Nonideal Solutions                       | 442 |
| <i>Example 11.10 Suspecting an azeotrope</i>   | 442 |
| 11.12 Lewis-Randall Rule and Henry's Law   | 443 |
| <i>Example 11.11 Solubility of CO<sub>2</sub> by Henry's Law</i>                       | 446 |
| <i>Example 11.12 Henry's constant for CO<sub>2</sub> with the MAB/SCVP+ model</i>      | 448 |
| 11.13 Osmotic Pressure   | 449 |
| <i>Example 11.13 Osmotic pressure of BSA</i>   | 451 |
| <i>Example 11.14 Osmotic pressure and electroporation of E. coli</i>                   | 453 |
| 11.14 Summary  | 454 |
| 11.15 Practice Problems  | 455 |
| 11.16 Homework Problems  | 455 |
| <b>CHAPTER 12 VAN DER WAALS ACTIVITY MODELS</b> <b>465</b>                             |     |
| 12.1 The van der Waals Perspective for Mixtures  | 466 |
| 12.2 The van Laar Model  | 469 |
| <i>Example 12.1 Infinite dilution activity coefficients from the van Laar theory</i>   | 471 |
| 12.3 Scatchard-Hildebrand Theory   | 471 |
| <i>Example 12.2 VLE predictions using the Scatchard-Hildebrand theory</i>              | 473 |
| 12.4 The Flory-Huggins Model   | 474 |
| <i>Example 12.3 Deriving activity models involving volume fractions</i>                | 475 |
| <i>Example 12.4 Scatchard-Hildebrand versus van Laar theory for methanol + benzene</i> | 476 |
| <i>Example 12.5 Polymer mixing</i>   | 478 |
| 12.5 MOSCED and SSced Theories   | 479 |
| <i>Example 12.6 Predicting VLE with the SSced model</i>                                | 482 |
| 12.6 Molecular Perspective and VLE Predictions   | 483 |
| 12.7 Multicomponent Extensions of van der Waals' Models                                | 486 |
| <i>Example 12.7 Multicomponent VLE using the SSced model</i>                           | 487 |
| <i>Example 12.8 Entrainer selection for gasohol production</i>                         | 490 |
| 12.8 Flory-Huggins and van der Waals Theories  | 491 |
| 12.9 Summary   | 492 |
| 12.10 Practice Problems  | 494 |

|  |            |
|--|------------|
| 12.11 Homework Problems  | 495        |
| <b>CHAPTER 13 LOCAL COMPOSITION ACTIVITY MODELS</b>                                  | <b>499</b> |
| <i>Example 13.1 VLE prediction using UNIFAC activity coefficients</i>                | 500        |
| 13.1 Local Composition Theory  | 501        |
| <i>Example 13.2 Local compositions in a two-dimensional lattice</i>                  | 503        |
| 13.2 Wilson's Equation   | 505        |
| <i>Example 13.3 Application of Wilson's equation to VLE</i>                          | 508        |
| 13.3 NRTL  | 508        |
| 13.4 UNIQUAC   | 509        |
| <i>Example 13.4 Combinatorial contribution to the activity coefficient</i>           | 512        |
| 13.5 UNIFAC  | 514        |
| <i>Example 13.5 Calculation of group mole fractions</i>                              | 518        |
| <i>Example 13.6 Detailed calculations of activity coefficients via UNIFAC</i>        | 518        |
| 13.6 COSMO-RS Methods  | 520        |
| <i>Example 13.7 Calculation of activity coefficients using COSMO-RS/SAC</i>          | 524        |
| 13.7 The Molecular Basis of Solution Models  | 526        |
| 13.8 Summary   | 532        |
| 13.9 Important Equations   | 533        |
| 13.10 Practice Problems  | 533        |
| 13.11 Homework Problems  | 534        |
| <b>CHAPTER 14 LIQUID-LIQUID AND SOLID-LIQUID PHASE EQUILIBRIA</b>                    | <b>539</b> |
| 14.1 The Onset of Liquid-Liquid Instability  | 539        |
| <i>Example 14.1 Simple vapor-liquid-liquid equilibrium (VLLE) calculations</i>       | 540        |
| <i>Example 14.2 LLE predictions using Flory-Huggins theory: Polymer mixing</i>       | 541        |
| 14.2 Stability and Excess Gibbs Energy   | 542        |
| 14.3 Binary LLE by Graphing the Gibbs Energy of Mixing                               | 543        |
| <i>Example 14.3 LLE predictions by graphing</i>                                      | 544        |
| 14.4 LLE Using Activities  | 545        |
| <i>Example 14.4 The binary LLE algorithm using MAB and SSCED models</i>              | 547        |
| 14.5 VLLE with Immiscible Components   | 548        |
| <i>Example 14.5 Steam distillation</i>   | 548        |
| 14.6 Binary Phase Diagrams   | 549        |
| 14.7 Plotting Ternary LLE Data   | 551        |
| 14.8 Critical Points in Binary Liquid Mixtures                                       | 552        |
| <i>Example 14.6 Liquid-liquid critical point of the Margules one-parameter model</i> | 553        |
| <i>Example 14.7 Liquid-liquid critical point of the Flory-Huggins model</i>          | 554        |
| 14.9 Numerical Procedures for Binary, Ternary LLE                                    | 556        |
| 14.10 Solid-Liquid Equilibria  | 556        |
| <i>Example 14.8 Variation of solid solubility with temperature</i>                   | 560        |
| <i>Example 14.9 Eutectic behavior of chloronitrobenzenes</i>                         | 561        |
| <i>Example 14.10 Eutectic behavior of benzene + phenol</i>                           | 562        |
| <i>Example 14.11 Precipitation by adding antisolvent</i>                             | 563        |
| <i>Example 14.12 Wax precipitation</i>   | 567        |
| 14.11 Summary  | 569        |
| 14.12 Practice Problems  | 570        |
| 14.13 Homework Problems  | 570        |

|  |            |
|--|------------|
| <b>CHAPTER 15 PHASE EQUILIBRIA IN MIXTURES<br/>BY AN EQUATION OF STATE</b> | <b>579</b> |
| 15.1 Mixing Rules for Equations of State                                   | 580        |
| <i>Example 15.1 The virial equation for vapor mixtures</i>                 | 581        |
| 15.2 Fugacity and Chemical Potential from an EOS                           | 582        |
| <i>Example 15.2 K-values from the Peng-Robinson equation</i>               | 587        |
| 15.3 Differentiation of Mixing Rules                                       | 588        |
| <i>Example 15.3 Fugacity coefficient from the virial equation</i>          | 590        |
| <i>Example 15.4 Fugacity coefficient from the van der Waals equation</i>   | 591        |
| <i>Example 15.5 Fugacity coefficient from the Peng-Robinson equation</i>   | 592        |
| 15.4 VLE Calculations by an Equation of State                              | 594        |
| <i>Example 15.6 Bubble-point pressure from the Peng-Robinson equation</i>  | 594        |
| <i>Example 15.7 Isothermal flash using the Peng-Robinson equation</i>      | 596        |
| <i>Example 15.8 Phase diagram for azeotropic methanol + benzene</i>        | 598        |
| <i>Example 15.9 Phase diagram for nitrogen + methane</i>                   | 599        |
| <i>Example 15.10 Ethane + heptane phase envelopes</i>                      | 601        |
| 15.5 Strategies for Applying VLE Routines                                  | 603        |
| 15.6 Summary   | 603        |
| 15.7 Practice Problems   | 604        |
| 15.8 Homework Problems   | 606        |
| <b>CHAPTER 16 ADVANCED PHASE DIAGRAMS</b>                                  | <b>613</b> |
| 16.1 Phase Behavior Sections of 3D Objects                                 | 613        |
| 16.2 Classification of Binary Phase Behavior                               | 617        |
| 16.3 Residue Curves  | 630        |
| 16.4 Practice Problems   | 636        |
| 16.5 Homework Problems   | 636        |
| <b>UNIT IV REACTION EQUILIBRIA</b>   | <b>639</b> |
| <b>CHAPTER 17 REACTION EQUILIBRIA</b>                                      | <b>641</b> |
| 17.1 Introduction  | 642        |
| <i>Example 17.1 Computing the reaction coordinate</i>                      | 643        |
| 17.2 Reaction Equilibrium Constraint                                       | 644        |
| 17.3 The Equilibrium Constant  | 646        |
| 17.4 The Standard State Gibbs Energy of Reaction                           | 647        |
| <i>Example 17.2 Calculation of standard state Gibbs energy of reaction</i> | 648        |
| 17.5 Effects of Pressure, Inerts, and Feed Ratios                          | 649        |
| <i>Example 17.3 Butadiene production in the presence of inerts</i>         | 650        |
| 17.6 Determining the Spontaneity of Reactions                              | 652        |
| 17.7 Temperature Dependence of $K_a$                                       | 652        |
| <i>Example 17.4 Equilibrium constant as a function of temperature</i>      | 653        |
| 17.8 Shortcut Estimation of Temperature Effects                            | 655        |
| <i>Example 17.5 Application of the shortcut van't Hoff equation</i>        | 656        |
| 17.9 Visualizing Multiple Equilibrium Constants                            | 656        |
| 17.10 Solving Equilibria for Multiple Reactions                            | 658        |
| <i>Example 17.6 Simultaneous reactions that can be solved by hand</i>      | 658        |
| <i>Example 17.7 Solving multireaction equilibria with Excel</i>            | 660        |

**xiv** Contents

|   |     |
|---|-----|
| 17.11 Driving Reactions by Chemical Coupling                            | 662 |
| <i>Example 17.8 Chemical coupling to induce conversion</i>              | 663 |
| 17.12 Energy Balances for Reactions                                     | 664 |
| <i>Example 17.9 Adiabatic reaction in an ammonia reactor</i>            | 665 |
| 17.13 Liquid Components in Reactions                                    | 667 |
| <i>Example 17.10 Oligomerization of lactic acid</i>                     | 668 |
| 17.14 Solid Components in Reactions                                     | 669 |
| <i>Example 17.11 Thermal decomposition of methane</i>                   | 670 |
| 17.15 Rate Perspectives in Reaction Equilibria                          | 671 |
| 17.16 Entropy Generation via Reactions                                  | 672 |
| 17.17 Gibbs Minimization  | 673 |
| <i>Example 17.12 Butadiene by Gibbs minimization</i>                    | 673 |
| <i>Example 17.13 Direct minimization of the Gibbs energy with Excel</i> | 675 |
| <i>Example 17.14 Pressure effects for Gibbs energy minimization</i>     | 676 |
| 17.18 Reaction Modeling with Limited Data                               | 677 |
| 17.19 Simultaneous Reaction and VLE                                     | 677 |
| <i>Example 17.15 The solvent methanol process</i>                       | 677 |
| <i>Example 17.16 NO<sub>2</sub> absorption</i>                          | 681 |
| 17.20 Summary   | 683 |
| 17.21 Practice Problems   | 684 |
| 17.22 Homework Problems   | 686 |

**CHAPTER 18 ELECTROLYTE SOLUTIONS**

|   |     |
|---|-----|
|   | 693 |
| 18.1 Introduction to Electrolyte Solutions                      | 693 |
| 18.2 Colligative Properties                                     | 695 |
| <i>Example 18.1 Freezing point depression</i>                   | 695 |
| <i>Example 18.2 Example of osmotic pressure</i>                 | 696 |
| <i>Example 18.3 Example of boiling point elevation</i>          | 697 |
| 18.3 Speciation and the Dissociation Constant                   | 697 |
| 18.4 Concentration Scales and Standard States                   | 699 |
| 18.5 The Definition of pH                                       | 701 |
| 18.6 Thermodynamic Network for Electrolyte Equilibria           | 702 |
| 18.7 Perspectives on Speciation                                 | 703 |
| 18.8 Acids and Bases  | 704 |
| <i>Example 18.4 Dissociation of fluconazole</i>                 | 709 |
| 18.9 Sillèn Diagram Solution Method                             | 712 |
| <i>Example 18.5 Sillèn diagram for HOAc and NaOAc</i>           | 713 |
| <i>Example 18.6 Phosphate salt and strong acid</i>              | 717 |
| <i>Example 18.7 Distribution of species in glycine solution</i> | 721 |
| 18.10 Applications  | 723 |
| <i>Example 18.8 Dissociation and solubility of fluconazole</i>  | 726 |
| 18.11 Redox Reactions   | 727 |
| <i>Example 18.9 Alkaline dry-cell battery</i>                   | 730 |
| 18.12 Biological Reactions                                      | 731 |
| <i>Example 18.10 ATP hydrolysis</i>                             | 737 |
| <i>Example 18.11 Biological fuel cell</i>                       | 738 |
| 18.13 Nonideal Electrolyte Solutions: Background                | 739 |
| 18.14 Overview of Model Development                             | 740 |
| 18.15 The Extended Debye-Hückel Activity Model                  | 742 |

|   |            |
|---|------------|
| 18.16 Gibbs Energies for Electrolytes   | 743        |
| 18.17 Transformed Biological Gibbs Energies and Apparent Equilibrium Constants        | 745        |
| <i>Example 18.12 Gibbs energy of formation for ATP</i>                                | 748        |
| 18.18 Coupled Multireaction and Phase Equilibria                                      | 749        |
| <i>Example 18.13 Chlorine + water electrolyte solutions</i>                           | 750        |
| 18.19 Mean Ionic Activity Coefficients  | 753        |
| 18.20 Extending Activity Calculations to High Concentrations                          | 755        |
| 18.21 Summary   | 755        |
| 18.22 Supplement 1: Interconversion of Concentration Scales                           | 757        |
| 18.23 Supplement 2: Relation of Apparent Chemical Potential to Species Potentials     | 758        |
| 18.24 Supplement 3: Standard States   | 759        |
| 18.25 Supplement 4: Conversion of Equilibrium Constants                               | 760        |
| 18.26 Practice Problems   | 761        |
| 18.27 Homework Problems   | 761        |
| <b>CHAPTER 19 MOLECULAR ASSOCIATION AND SOLVATION</b>                                 | <b>767</b> |
| 19.1 Introducing the Chemical Contribution  | 768        |
| 19.2 Equilibrium Criteria   | 772        |
| 19.3 Balance Equations for Binary Systems   | 775        |
| 19.4 Ideal Chemical Theory for Binary Systems   | 776        |
| <i>Example 19.1 Compressibility factors in associating/solvating systems</i>          | 777        |
| <i>Example 19.2 Dimerization of carboxylic acids</i>                                  | 778        |
| <i>Example 19.3 Activity coefficients in a solvated system</i>                        | 779        |
| 19.5 Chemical-Physical Theory   | 779        |
| 19.6 Wertheim's Theory for Complex Mixtures   | 782        |
| <i>Example 19.4 The chemical contribution to the equation of state</i>                | 788        |
| 19.7 Mass Balances for Chain Association  | 792        |
| <i>Example 19.5 Molecules of H<sub>2</sub>O in a 100 ml beaker</i>                    | 793        |
| 19.8 The Chemical Contribution to the Fugacity Coefficient and Compressibility Factor | 793        |
| 19.9 Wertheim's Theory of Polymerization  | 795        |
| <i>Example 19.6 Complex fugacity for the van der Waals model</i>                      | 796        |
| <i>Example 19.7 More complex fugacity for the van der Waals model</i>                 | 798        |
| 19.10 Statistical Associating Fluid Theory (The SAFT Model)                           | 799        |
| <i>Example 19.8 The SAFT model</i>  | 800        |
| 19.11 Fitting the Constants for an Associating Equation of State                      | 802        |
| 19.12 Summary   | 804        |
| 19.13 Practice Problems   | 806        |
| 19.14 Homework Problems   | 806        |
| <b>APPENDIX A SUMMARY OF COMPUTER PROGRAMS</b>  | <b>811</b> |
| A.1 Programs for Pure Component Properties  | 811        |
| A.2 Programs for Mixture Phase Equilibria   | 812        |
| A.3 Reaction Equilibria   | 813        |
| A.4 Notes on Excel Spreadsheets   | 813        |
| A.5 Notes on MATLAB   | 814        |
| A.6 Disclaimer  | 815        |

|  |            |
|--|------------|
| <b>APPENDIX B MATHEMATICS</b>  | <b>817</b> |
| B.1 Important Relations  | 817        |
| B.2 Solutions to Cubic Equations                                     | 822        |
| B.3 The Dirac Delta Function   | 825        |
| <i>Example B.1 The hard-sphere equation of state</i>                 | 828        |
| <i>Example B.2 The square-well equation of state</i>                 | 829        |
| <b>APPENDIX C STRATEGIES FOR SOLVING VLE PROBLEMS</b>                | <b>831</b> |
| C.1 Modified Raoult's Law Methods                                    | 832        |
| C.2 EOS Methods  | 835        |
| C.3 Activity Coefficient (Gamma-Phi) Methods                         | 838        |
| <b>APPENDIX D MODELS FOR PROCESS SIMULATORS</b>                      | <b>839</b> |
| D.1 Overview   | 839        |
| D.2 Equations of State   | 839        |
| D.3 Solution Models  | 840        |
| D.4 Hybrid Models  | 840        |
| D.5 Recommended Decision Tree  | 841        |
| <b>APPENDIX E THEMODYNAMIC PROPERTIES</b>                            | <b>843</b> |
| E.1 Thermochemical Data  | 843        |
| E.2 Latent Heats   | 846        |
| E.3 Antoine Constants  | 847        |
| E.4 Henry's Constant with Water as Solvent                           | 847        |
| E.5 Dielectric Constant for Water                                    | 848        |
| E.6 Dissociation Constants of Polyprotic Acids                       | 849        |
| E.7 Standard Reduction Potentials                                    | 849        |
| E.8 Biochemical Data   | 852        |
| E.9 Properties of Water  | 854        |
| E.10 Pressure-Enthalpy Diagram for Methane                           | 865        |
| E.11 Pressure-Enthalpy Diagram for Propane                           | 866        |
| E.12 Pressure-Enthalpy Diagram for R134a (1,1,1,2-Tetraflouroethane) | 867        |
| <b>INDEX</b>   | <b>869</b> |