

Contents

Preface to the SI Edition vi

Preface vii

Acknowledgments xi

About the Authors xxi

Chapter 1 Introduction 1

1.1 The Role of Thermodynamics in Chemical Engineering 2

1.2 Motivational Example: The Conversion of Fuel into Electricity 3

1.2.1 Generation of Electricity 3

1.2.2 Forms of Energy and Energy Conversion 4

1.2.3 The Rankine Cycle 7

1.3 Systems and Processes 10

1.3.1 Fundamental Definitions for Describing Systems 13

1.3.2 Equilibrium and Steady State 16

1.4 The Forms of Energy 19

1.4.1 Force 19

1.4.2 Pressure 19

1.4.3 Work 22

1.4.4 Kinetic Energy 28

1.4.5 Potential Energy 29

1.4.6 Internal Energy 31

1.4.7 Heat 33

1.4.8 Temperature 35

1.4.9 Overview of the Forms of Energy 37

1.5 Summary of Chapter One 38

1.6 Exercises 39

1.7 Problems 40

1.8 Glossary of Symbols 42

1.9 References 43

Chapter 2 The Physical Properties of Pure Compounds 45

2.1 Motivational Example: Vapor Pressure of Water and Its Effect on the Rankine Cycle 46

2.2 Physical Properties of Pure Chemical Compounds 47

2.2.1 The P - V - T Behavior of Real Compounds 47

2.2.2 Forms and Sources of Physical Property Data 51

2.2.3 State Properties and Path-Dependent Properties 52

2.2.4	Intensive and Extensive Material Properties	54
2.2.5	State Properties of Multiphase Mixtures	56
2.3	Thermodynamic Models of Physical Properties	59
2.3.1	Enthalpy	59
2.3.2	Heat Capacity	60
2.3.3	Ideal Gases	64
2.3.4	Equations of State	72
2.3.5	Simple Models of Liquids and Solids	75
2.3.6	Summary of Simple Thermodynamic Models for Materials	76
2.4	Summary of Chapter Two	76
2.5	Exercises	77
2.6	Problems	78
2.7	Glossary of Symbols	81
2.8	References	81

Chapter 3 Material and Energy Balances 83

3.1	Motivational Example: Rockets	83
3.2	Material Balances	85
3.2.1	Mathematical Formulation of the Material Balance	86
3.2.2	Examples of Material Balances	87
3.3	Mathematical Expression of the First Law of Thermodynamics	93
3.4	Applications of the Generalized Energy Balance Equation	96
3.5	Combining the Energy Balance with Simple Thermodynamic Models	108
3.6	Energy Balances for Common Chemical Process Equipment	119
3.6.1	Valves	121
3.6.2	Nozzles	121
3.6.3	Pumps, Compressors, and Turbines	121
3.6.4	Heat Exchangers	123
3.7	Summary of Chapter Three	125
3.8	Exercises	125
3.9	Problems	126
3.10	Glossary of Symbols	129
3.11	References	130

Chapter 4 Entropy 131

4.1	Motivational Example: Turbines	131
4.2	Reversible Processes	134
4.3	Defining and Describing Entropy	141
4.3.1	Mathematical Definition of Entropy	142
4.3.2	Qualitative Perspectives on Entropy	146
4.3.3	Relating Entropy to Spontaneity and Directionality	147
4.3.4	Spontaneity and Reversibility	152

4.3.5	Relating Entropy to Disorder	152
4.3.6	The Microscopic Definition of Entropy	154
4.4	The Entropy Balance	158
4.4.1	Applying the Entropy Balance to a Reversible Nozzle	160
4.4.2	Entropy and Efficiency	165
4.4.3	Unsteady-State Entropy Balances	170
4.5	The Carnot Heat Engine	177
4.6	Summary of Chapter Four	185
4.7	Exercises	186
4.8	Problems	186
4.9	Glossary of Symbols	190
4.10	References	190

Chapter 5 Thermodynamic Processes and Cycles 191

5.1	Motivational Example: Chemical Process Design	191
5.2	Real Heat Engines	194
5.2.1	Comparing and Contrasting the Rankine Cycle with the Carnot Cycle	194
5.2.2	Complete Design of a Rankine Heat Engine	197
5.2.3	Design Variations in the Rankine Heat Engine	202
5.3	Refrigeration—The Vapor-Compression Cycle	208
5.3.1	A Household Refrigerator	208
5.3.2	Coefficient of Performance	213
5.3.3	The Carnot Refrigerator	213
5.3.4	Analyzing a Refrigeration Cycle with Simple Models	215
5.4	Liquefaction	219
5.4.1	Simple Liquefaction of Nitrogen	219
5.4.2	Energy-Efficient Compression Processes	221
5.4.3	Linde Liquefaction	224
5.5	Summary of Chapter Five	230
5.6	Exercises	231
5.7	Problems	232
5.8	Glossary of Symbols	236
5.9	References	236

Chapter 6 Thermodynamic Models of Real, Pure Compounds 237

6.1	Motivational Example: Joule-Thomson Expansion	237
6.1.1	The Total Derivative	240
6.2	Mathematical Models of Thermodynamic Properties	245
6.2.1	The Triple Product Rule	246
6.2.2	Fundamental Property Relationships	247
6.2.3	The Expansion Rule	249

6.2.4	Maxwell's Equations	250
6.2.5	Coefficient of Thermal Expansion and Isothermal Compressibility	252
6.2.6	Additional Applications of Thermodynamic Partial Derivatives	254
6.2.7	Summary of Useful Partial Differential Expressions	263
6.3	Heat Capacity and Residual Properties	264
6.3.1	Distinction between Real and Ideal Gas Heat Capacity	264
6.3.2	Motivation for the Residual Property	266
6.3.3	Definition of Residual Properties	270
6.3.4	Mathematical Expressions for Residual Properties	271
6.3.5	Summary of Residual Properties	273
6.3.6	Application of Residual Properties	274
6.4	Summary of Chapter Six	283
6.5	Exercises	284
6.6	Problems	284
6.7	Glossary of Symbols	287
6.8	Reference	287

Chapter 7 Equations of State (EOS) 289

7.1	Motivational Examples: Transportation of Natural Gas	289
7.2	Cubic Equations of State	295
7.2.1	The Rationale for Cubic Equations of State	295
7.2.2	Modern Cubic Equations of State	298
7.2.3	Solving Cubic Equations of State	299
7.2.4	Interpreting Solutions to Cubic Equations of State	302
7.2.5	Fitting Parameters to Cubic Equations of State	304
7.2.6	Vapor Pressure Curves and the Acentric Factor	310
7.2.7	Summary of Cubic Equations of State	312
7.2.8	Residual Properties from Cubic Equations of State	312
7.3	The Principle of Corresponding States	316
7.3.1	Illustrations of the Principle of Corresponding States	317
7.3.2	Generalized Correlations and Aggregated Data	324
7.3.3	Group Additivity Methods	330
7.4	Beyond the Cubic Equations of State	333
7.4.1	The Virial Equation of State	335
7.4.2	Microstates and Macrostates	338
7.4.3	Radial Distribution Functions	340
7.4.4	The Lennard-Jones Potential	344
7.5	Summary of Chapter Seven	347
7.6	Exercises	348
7.7	Problems	348
7.8	Glossary of Symbols	351
7.9	References	351

Chapter 8 Modeling Phase Equilibrium for Pure Components 353

- 8.1 Motivational Example: VLE Curves for Refrigerants 353**
- 8.2 Mathematical Models of Phase Equilibrium 356**
 - 8.2.1 Qualitative Discussion of Phase Transitions 356**
 - 8.2.2 Mathematical Expression of the Equilibrium Criterion 357**
 - 8.2.3 Chemical Potential 359**
 - 8.2.4 The Clapeyron Equation 360**
 - 8.2.5 The Shortcut Equation 364**
 - 8.2.6 The Antoine Equation 368**
- 8.3 Fugacity and Its Use in Modeling Phase Equilibrium 370**
 - 8.3.1 Calculating Changes in Gibbs Energy 371**
 - 8.3.2 Mathematical Definition of Fugacity 374**
 - 8.3.3 Poynting Method of Estimating Liquid and Solid Fugacity 381**
- 8.4 Summary of Chapter Eight 388**
- 8.5 Exercises 389**
- 8.6 Problems 389**
- 8.7 Glossary of Symbols 392**
- 8.8 References 392**

Chapter 9 An Introduction to Mixtures 393

- 9.1 Motivational Example: Mixing Chemicals—Intuition 393**
- 9.2 Ideal Solutions 396**
- 9.3 Properties of Mixing 400**
- 9.4 Mathematical Framework for Solutions 407**
- 9.5 Ideal Gas Mixtures 418**
- 9.6 Summary of Chapter Nine 422**
- 9.7 Exercises 423**
- 9.8 Problems 423**
- 9.9 Glossary of Symbols 426**
- 9.10 References 427**

Chapter 10 Vapor–Liquid Equilibrium 429

- 10.1 Motivational Example 429**
- 10.2 Raoult’s Law and the Presentation of Data 431**
 - 10.2.1 Distribution Coefficients, Relative Volatility, and xy Diagrams 441**
- 10.3 Mixture Critical Points 444**
- 10.4 Lever Rule and the Flash Problem 447**
 - 10.4.1 Ternary Systems 457**
- 10.5 Summary of Chapter Ten 461**

- 10.6** Exercises 462
- 10.7** Problems 462
- 10.8** Glossary of Symbols 466
- 10.9** References 466

Chapter 11 Theories and Models for Vapor–Liquid Equilibrium of Mixtures: Modified Raoult’s Law Approaches 469

- 11.1** Motivational Example 469
- 11.2** Phase Equilibrium for Mixtures 470
- 11.3** Fugacity in Mixtures 473
- 11.4** Gamma-Phi Modeling 478
 - 11.4.1** Raoult’s Law Revisited 478
 - 11.4.2** Henry’s Law 479
- 11.5** Modified Raoult’s Law 483
- 11.6** Excess Molar Gibbs Free Energy Models: An Introduction 485
- 11.7** Excess Molar Gibbs Free Energy Models: Usage 488
 - 11.7.1** Temperature and Pressure Dependence of the Activity Coefficient 499
 - 11.7.2** Excess Molar Gibbs Free Energy Models and the Flash Problem 502
- 11.8** Predictive Excess Molar Gibbs Free Energy Models 506
 - 11.8.1** Van Laar Equation and Regular Solution Theory 507
- 11.9** Thermodynamic Consistency 516
 - 11.9.1** Integral (Area) Test 517
 - 11.9.2** Direct Test 521
- 11.10** Summary of Chapter Eleven 525
- 11.11** Exercises 526
- 11.12** Problems 527
- 11.13** Glossary of Symbols 532
- 11.14** References 533

Chapter 12 Theories and Models for Vapor–Liquid Equilibrium of Mixtures: Using Equations of State 535

- 12.1** Motivational Example 535
- 12.2** Deviations from the Ideal Gas Model for the Vapor Phase 536
 - 12.2.1** Mixture Fugacity Coefficients 536
 - 12.2.2** Incorporating the Mixture Fugacity Coefficient 539
 - 12.2.3** Gamma-Phi Modeling: Application Example 540
- 12.3** Phi-Phi Modeling 549
 - 12.3.1** Equality of Mixture Fugacities 549
 - 12.3.2** Mixture Fugacity Coefficients when Pressure Is a Dependent Variable 550
- 12.4** Ideal Solution for the Vapor Phase 560
- 12.5** Summary of Chapter Twelve 566

12.6	Exercises	566
12.7	Problems	567
12.8	Glossary of Symbols	573
12.9	References	574

Chapter 13 Liquid–Liquid, Vapor–Liquid–Liquid, and Solid–Liquid Equilibrium 575

13.1	Motivational Example	575
13.2	Liquid–Liquid Equilibrium	576
13.2.1	Impact of Pressure on Liquid–Liquid Equilibrium	579
13.2.2	LLE—Components of the Gibbs Free Energy	580
13.3	Various Types of LLE	581
13.4	Miscibility Gaps from a ΔG of Mixing Perspective	583
13.5	Stability Criterion for Liquid Mixtures	586
13.6	Modeling Liquid–Liquid Equilibrium	589
13.6.1	Modeling Liquid–Liquid Equilibrium— Immiscible Systems	594
13.7	Vapor–Liquid–Liquid Equilibrium (VLLE)	595
13.8	Modeling of Vapor–Liquid–Liquid Equilibrium (VLLE)	599
13.9	Solid–Liquid Equilibrium (SLE)	601
13.10	Modeling Solid–Liquid Equilibrium (SLE)	604
13.10.1	Modeling Solid–Liquid Equilibrium (SLE): Simplifications	606
13.11	Summary of Chapter Thirteen	610
13.12	Exercises	611
13.13	Problems	614
13.14	Glossary of Symbols	616
13.15	References	616

Chapter 14 Fundamentals of Chemical Reaction Equilibrium 619

14.1	Motivational Example: Ethylene from Ethane	620
14.2	Chemical Reaction Stoichiometry	625
14.2.1	Extent of Reaction and Time-Independent Mole Balances	626
14.2.2	Extent of Reaction and Time-Dependent Material Balances	629
14.3	The Equilibrium Criterion Applied to a Chemical Reaction	630
14.3.1	The Equilibrium Constant	631
14.3.2	Accounting for the Effects of Pressure	635
14.3.3	Accounting for Changes in Temperature	650
14.3.4	Reference States and Nomenclature	659
14.4	Multiple Reaction Equilibrium	660
14.5	Summary of Chapter Fourteen	665
14.6	Exercises	665

- 14.7** Problems 667
- 14.8** Glossary of Symbols 668
- 14.9** References 669

Chapter 15 Synthesis of Thermodynamic Principles 671

- 15.1** Motivational Example: Reactive Distillation 671
- 15.2** Energy Balances on Chemical Reactors 674
- 15.3** Simultaneous Reaction and Phase Equilibrium 682
- 15.4** A Complete Chemical Process 689
- 15.5** Summary of Chapter Fifteen 699
- 15.6** Problems 699
- 15.7** Glossary of Symbols 701
- 15.8** References 702

Appendix 703

- Appendix A: Steam Tables 703
- Appendix B: Mathematical Techniques 733
- Appendix C: Physical Properties 735
- Appendix D: Heat Capacity 739
- Appendix E: Antoine Coefficients 741
- Appendix F: Thermodynamic Diagrams 743
- Appendix G: The Joback Group Additivity Method 748

Index 753