Detailed Contents

THERMODYNAMICS, STATISTICAL THERMODYNAMICS, AND KINETICS

Preface 10

Math Essential 1 Units, Significant Figures, and Solving End of Chapter Problems

1 Fundamental Concepts of Thermodynamics 21

- 1.1 What Is Thermodynamics and Why Is It Useful? 21
- 1.2 The Macroscopic Variables Volume, Pressure, and Temperature 22
- 1.3 Basic Definitions Needed to Describe Thermodynamic Systems 26
- 1.4 Equations of State and the Ideal Gas Law 28
- 1.5 A Brief Introduction to Real Gases 30

Math Essential 2 Differentiation and Integration

2 Heat, Work, Internal Energy, Enthalpy, and the First Law of Thermodynamics 45

- 2.1 Internal Energy and the First Law of Thermodynamics 45
- 2.2 Heat 46
- 2.3 Work 47
- 2.4 Equilibrium, Change, and Reversibility 49
- 2.5 The Work of Reversible Compression or Expansion of an Ideal Gas 50
- 2.6 The Work of Irreversible Compression or Expansion of an Ideal Gas 52
- 2.7 Other Examples of Work 53
- 2.8 State Functions and Path Functions 55
- 2.9 Comparing Work for Reversible and Irreversible Processes 57
- 2.10 Changing the System Energy from a Molecular-Level Perspective 61
- 2.11 Heat Capacity 63
- 2.12 Determining ΔU and Introducing the State Function Enthalpy 66
- 2.13 Calculating q, w, ΔU , and ΔH for Processes Involving Ideal Gases 67
- 2.14 Reversible Adiabatic Expansion and Compression of an Ideal Gas 71

Math Essential 3 Partial Derivatives

3 The Importance of State Functions: Internal Energy and Enthalpy 81

- 3.1 Mathematical Properties of State Functions 81
- 3.2 Dependence of U on V and T 84
- 3.3 Does the Internal Energy Depend More Strongly on *V* or *T*? 86
- 3.4 Variation of Enthalpy with Temperature at Constant Pressure 90
- 3.5 How are C_P and C_V Related? 92
- 3.6 Variation of Enthalpy with Pressure at Constant Temperature 93
- 3.7 The Joule–Thomson Experiment 95
- 3.8 Liquefying Gases Using an Isenthalpic Expansion 97

4 Thermochemistry 103

- 4.1 Energy Stored in Chemical Bonds Is Released or Absorbed in Chemical Reactions 103
- 4.2 Internal Energy and Enthalpy Changes Associated with Chemical Reactions 104
- 4.3 Hess's Law Is Based on Enthalpy Being a State Function 107
- 4.4 Temperature Dependence of Reaction Enthalpies 109
- 4.5 Experimental Determination of ΔU and ΔH for Chemical Reactions 111
- 4.6 Differential Scanning Calorimetry 113

5 Entropy and the Second and Third Laws of Thermodynamics 123

- 5.1 What Determines the Direction of Spontaneous Change in a Process? 123
- 5.2 The Second Law of Thermodynamics, Spontaneity, and the Sign of ΔS 125
- 5.3 Calculating Changes in Entropy as *T*, *P*, or *V* Change 126
- 5.4 Understanding Changes in Entropy at the Molecular Level 130
- 5.5 The Clausius Inequality 132

- 5.6 The Change of Entropy in the Surroundings and $\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{sur}}$ 133
- 5.7 Absolute Entropies and the Third Law of Thermodynamics 135
- 5.8 Standard States in Entropy Calculations 139
- 5.9 Entropy Changes in Chemical Reactions 139
- 5.10 Heat Engines and the Carnot Cycle 141
- 5.11 How Does S Depend on V and T? 146
- 5.12 Dependence of S on T and P 147
- 5.13 Energy Efficiency, Heat Pumps, Refrigerators, and Real Engines 148

6 Chemical Equilibrium 163

- 6.1 Gibbs Energy and Helmholtz Energy 163
- 6.2 Differential Forms of U, H, A, and G 167
- 6.3 Dependence of Gibbs and Helmholtz Energies on *P*, *V*, and *T* 169
- 6.4 Gibbs Energy of a Reaction Mixture 171
- 6.5 Calculating the Gibbs Energy of Mixing for Ideal Gases 173
- 6.6 Calculating the Equilibrium Position for a Gas-Phase Chemical Reaction 175
- 6.7 Introducing the Equilibrium Constant for a Mixture of Ideal Gases 178
- 6.8 Calculating the Equilibrium Partial Pressures in a Mixture of Ideal Gases 182
- 6.9 Variation of K_P with Temperature 183
- 6.10 Equilibria Involving Ideal Gases and Solid or Liquid Phases 185
- 6.11 Expressing the Equilibrium Constant in Terms of Mole Fraction or Molarity 187
- 6.12 Expressing *U*, *H*, and Heat Capacities Solely in Terms of Measurable Quantities 188
- 6.13 A Case Study: The Synthesis of Ammonia 192
- 6.14 Measuring ΔG for the Unfolding of Single RNA Molecules 196

7 The Properties of Real Gases 205

- 7.1 Real Gases and Ideal Gases 205
- 7.2 Equations of State for Real Gases and Their Range of Applicability 206
- 7.3 The Compression Factor 210
- 7.4 The Law of Corresponding States 213
- 7.5 Fugacity and the Equilibrium Constant for Real Gases 216

8 Phase Diagrams and the Relative Stability of Solids, Liquids, and Gases 223

- 8.1 What Determines the Relative Stability of the Solid, Liquid, and Gas Phases? 223
- 8.2 The Pressure–Temperature Phase Diagram 226
- 8.3 The Phase Rule 233
- 8.4 Pressure–Volume and Pressure–Volume– Temperature Phase Diagrams 233
- 8.5 Providing a Theoretical Basis for the *P*–*T* Phase Diagram 235
- 8.6 Using the Clausius–Clapeyron Equation to Calculate Vapor Pressure as a Function of *T* 237
- 8.7 Dependence of Vapor Pressure of a Pure Substance on Applied Pressure 239
- 8.8 Surface Tension 240
- 8.9 Chemistry in Supercritical Fluids 243
- 8.10 Liquid Crystal Displays 244

9 Ideal and Real Solutions 253

- 9.1 Defining the Ideal Solution 253
- 9.2 The Chemical Potential of a Component in the Gas and Solution Phases 255
- 9.3 Applying the Ideal Solution Model to Binary Solutions 256
- 9.4 The Temperature–Composition Diagram and Fractional Distillation 260
- 9.5 The Gibbs–Duhem Equation 262
- 9.6 Colligative Properties 263
- 9.7 Freezing Point Depression and Boiling Point Elevation 264
- 9.8 Osmotic Pressure 266
- 9.9 Deviations from Raoult's Law in Real Solutions 268
- 9.10 The Ideal Dilute Solution 270
- 9.11 Activities are Defined with Respect to Standard States 272
- 9.12 Henry's Law and the Solubility of Gases in a Solvent 276
- 9.13 Chemical Equilibrium in Solutions 277
- 9.14 Solutions Formed from Partially Miscible Liquids 280
- 9.15 Solid–Solution Equilibrium 282

10 Electrolyte Solutions 289

- 10.1 Enthalpy, Entropy, and Gibbs Energy of Ion Formation in Solutions 289
- 10.2 Understanding the Thermodynamics of Ion Formation and Solvation 291
- 10.3 Activities and Activity Coefficients for Electrolyte Solutions 294
- 10.4 Calculating γ_{\pm} Using the Debye–Hückel Theory 296
- 10.5 Chemical Equilibrium in Electrolyte Solutions 300

11 Electrochemical Cells, Batteries, and Fuel Cells 307

- 11.1 The Effect of an Electrical Potential on the Chemical Potential of Charged Species 307
- 11.2 Conventions and Standard States in Electrochemistry 309
- 11.3 Measurement of the Reversible Cell Potential 312
- 11.4 Chemical Reactions in Electrochemical Cells and the Nernst Equation 312
- 11.5 Combining Standard Electrode Potentials to Determine the Cell Potential 314
- 11.6 Obtaining Reaction Gibbs Energies and Reaction Entropies from Cell Potentials 316
- 11.7 Relationship Between the Cell EMF and the Equilibrium Constant 316
- 11.8 Determination of E^{\oplus} and Activity Coefficients Using an Electrochemical Cell 318
- 11.9 Cell Nomenclature and Types of Electrochemical Cells 319
- 11.10 The Electrochemical Series 320
- 11.11 Thermodynamics of Batteries and Fuel Cells 321
- 11.12 Electrochemistry of Commonly Used Batteries 322
- 11.13 Fuel Cells 326
- 11.14 Electrochemistry at the Atomic Scale 328
- 11.15 Using Electrochemistry for Nanoscale Machining 331

12 Probability 337

- 12.1 Why Probability? 337
- 12.2 Basic Probability Theory 338
- 12.3 Stirling's Approximation 346
- 12.4 Probability Distribution Functions 347
- 12.5 Probability Distributions Involving Discrete and Continuous Variables 349
- 12.6 Characterizing Distribution Functions 352

Math Essential 4 Lagrange Multipliers

13 The Boltzmann Distribution 365

- 13.1 Microstates and Configurations 365
- 13.2 Derivation of the Boltzmann Distribution 371
- 13.3 Dominance of the Boltzmann Distribution 376
- 13.4 Physical Meaning of the Boltzmann Distribution Law 378
- 13.5 The Definition of β 379

14 Ensemble and Molecular Partition Functions 389

- 14.1 The Canonical Ensemble 389
- 14.2 Relating Q to q for an Ideal Gas 391
- 14.3 Molecular Energy Levels 393
- 14.4 Translational Partition Function 394
- 14.5 Rotational Partition Function: Diatomic Molecules 396
- 14.6 Rotational Partition Function: Polyatomic Molecules 404
- 14.7 Vibrational Partition Function 406
- 14.8 The Equipartition Theorem 411
- 14.9 Electronic Partition Function 412
- 14.10 Review 416

15 Statistical Thermodynamics 423

- 15.1 Energy 423
- 15.2 Energy and Molecular Energetic Degrees of Freedom 427
- 15.3 Heat Capacity 432
- 15.4 Entropy 437
- 15.5 Residual Entropy 442
- 15.6 Other Thermodynamic Functions 443
- 15.7 Chemical Equilibrium 447

16 Kinetic Theory of Gases 457

- 16.1 Kinetic Theory of Gas Motion and Pressure 457
- 16.2 Velocity Distribution in One Dimension 458
- 16.3 The Maxwell Distribution of Molecular Speeds 462
- 16.4 Comparative Values for Speed Distributions 465
- 16.5 Gas Effusion 467
- 16.6 Molecular Collisions 469
- 16.7 The Mean Free Path 473

17 Transport Phenomena 479

- 17.1 What Is Transport? 479
- 17.2 Mass Transport: Diffusion 481
- 17.3 Time Evolution of a Concentration Gradient 485
- 17.4 Statistical View of Diffusion 487
- 17.5 Thermal Conduction 489
- 17.6 Viscosity of Gases 492
- 17.7 Measuring Viscosity 495
- 17.8 Diffusion and Viscosity of Liquids 496
- 17.9 Ionic Conduction 498

18 Elementary Chemical Kinetics 509

- 18.1 Introduction to Kinetics 509
- 18.2 Reaction Rates 510
- 18.3 Rate Laws 512
- 18.4 Reaction Mechanisms 517
- 18.5 Integrated Rate Law Expressions 518
- 18.6 Numerical Approaches 523
- 18.7 Sequential First-Order Reactions 524
- 18.8 Parallel Reactions 529
- 18.9 Temperature Dependence of Rate Constants 531
- 18.10 Reversible Reactions and Equilibrium 533
- 18.11 Perturbation-Relaxation Methods 537
- 18.12 The Autoionization of Water: A Temperature-Jump Example 539
- 18.13 Potential Energy Surfaces 540
- 18.14 Activated Complex Theory 542
- 18.15 Diffusion-Controlled Reactions 546

19 Complex Reaction Mechanisms 557

- 19.1 Reaction Mechanisms and Rate Laws 557
- 19.2 The Preequilibrium Approximation 559
- 19.3 The Lindemann Mechanism 561
- 19.4 Catalysis 563
- 19.5 Radical-Chain Reactions 574
- 19.6 Radical-Chain Polymerization 577
- 19.7 Explosions 578
- 19.8 Feedback, Nonlinearity, and Oscillating Reactions 580
- 19.9 Photochemistry 583
- 19.10 Electron Transfer 595

20 Macromolecules 609

- 20.1 What Are Macromolecules? 609
- 20.2 Macromolecular Structure 610
- 20.3 Random-Coil Model 612
- 20.4 Biological Polymers 615
- 20.5 Synthetic Polymers 623
- 20.6 Characterizing Macromolecules 626
- 20.7 Self-Assembly, Micelles, and Biological Membranes 633

APPENDIX A Data Tables 641

Credits 659

Index 660