Contents

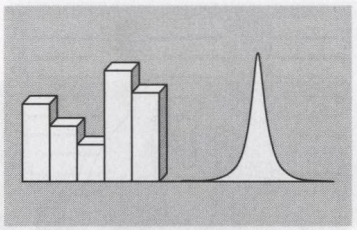
Preface xvii
Acknowledgements xx

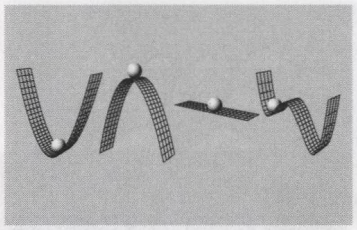
1 Principles of Probability **1**
Principles of Probability Are the Foundations of Entropy 1
What Is Probability? 2
Rules of Probability 3
Correlated Events/Conditional Probabilities 7
Combinatorics 9
Distribution Functions 13
Averages, Standard Deviations 17
Summary 21
Problems 24
Suggested Reading 26

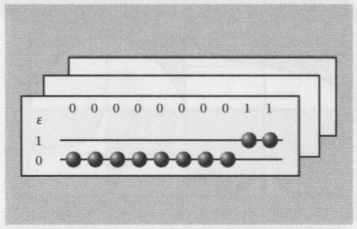
2 Extremum Principles Predict Equilibria **27**
What Are Extremum Principles? 27
What Is a State of Equilibrium? 28
Maximizing Multiplicity 30
Simple Models 31
Summary 35
Problems 36
Suggested Reading 36

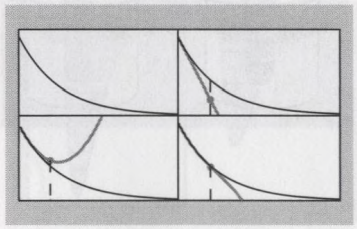
3 Heat, Work & Energy **37**
Heat Flows to Maximize Entropy 37
Conservation Laws 37
Heat Was Thought to Be a Fluid 40
Atoms and Molecules Have Energies 42
Why Does Heat Flow? 44
Summary 46
Problems 48
Suggested Reading 48

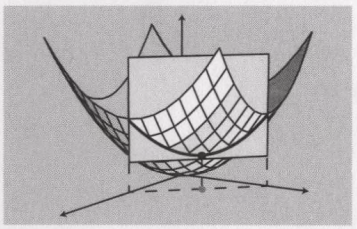
4 Math Tools: Series and Approximations **49**
Physical Modelling Involves Series Expansions 49
Making Approximations Involves Truncating Series' 53
Gaussian Distribution/Random Walk 57
Summary 59
Problems 60
Suggested Reading 60





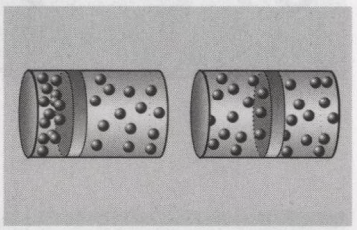




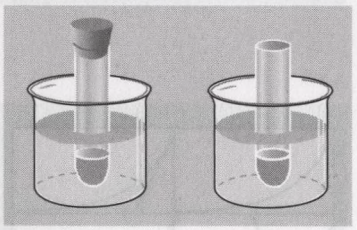


5 Multivariate Calculus **61**
Functions of Multiple Variables 61
Partial Derivatives 62
Extrema of Multivariate Functions 65
Integrating Multivariate Functions 73
The Chain Rule 77
Rearranging Dependent and Independent Variables 78
Summary 79
Problems 80
Suggested Reading 80

6 Entropy & the Boltzmann Distribution Law **81**
What Is Entropy? 81
Flat Distributions if there Are No Constraints 85
Exponential Distributions if there Are Constraints 86
Principle of Fair Apportionment 89
Philosophical Foundations 99
Summary 101
Problems 102
Suggested Reading 103

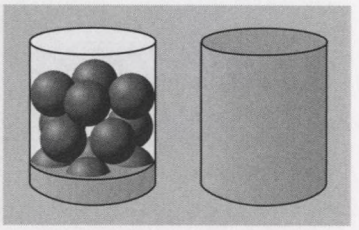


7 Thermodynamic Driving Forces **105**
Thermodynamics Is Two Laws 105
The Fundamental Thermodynamic Equations 107
Defining the Thermodynamic Driving Forces 108
Homogeneous Functions 111
Thermal, Mechanical, and Chemical Equilibria 111
Thermodynamic Logic 119
The First Law Interrelates Heat, Work, and Energy 122
Why Is There an Absolute Temperature Scale? 126
Other Statements of the Second Law 127
Summary 127
Problems 128
Suggested Reading 128

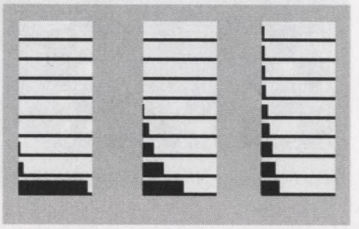


8 Free Energies **131**
Switching from Entropy to Free Energy 131
Free Energy Defines Another Extremum Principle 132
Using the Heat Capacity 142
Using Thermodynamic Cycles 146
Summary 150
Problems 151
Suggested Reading 152

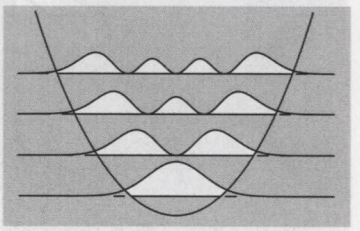
9 Maxwell's Relations & Mixtures **153**
Predicting Unmeasurable Quantities 153
Maxwell's Relations Interrelate Partial Derivatives 155
Multicomponent Systems/Partial Molar Quantities 163
Linkage Relations 166
Summary 168
Problems 169
Suggested Reading 169



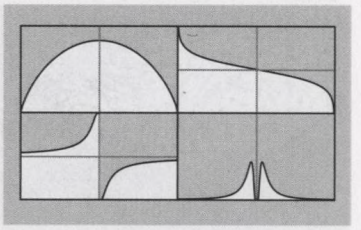
10 Boltzmann Distribution Law **171**
Probability Distributions for Atoms and Molecules 171
The Boltzmann Law Describes Equilibria 173
What Does a Partition Function Tell You? 177
Thermodynamic Properties from Partition Functions 183
What Is an Ensemble? 188
Summary 189
Problems 190
Suggested Reading 191



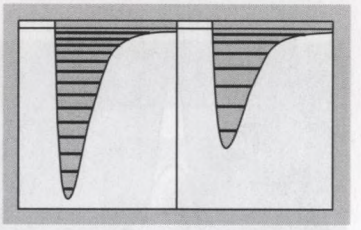
11 Statistical Mechanics of Simple Gases and Solids **193**
Macroscopic Properties from Atomic Structures 193
Translational Motion 195
Harmonic Oscillator Model 201
Rigid Rotor Model 203
Ideal Gas Properties 206
The Equipartition Theorem 212
Summary 216
Problems 217
Suggested Reading 219

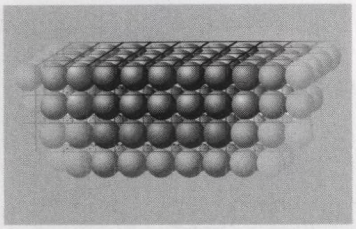


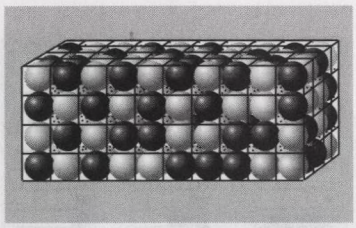
12 Temperature, Heat Capacity **221**
A Microscopic Perspective 221
A Graphical Pricedure, from S to C_v 225
What Drives Heat Exchange? 227
The Heat Capacity Reflects Energy Fluctuations 228
Summary 232
Problems 233
Suggested Reading 234

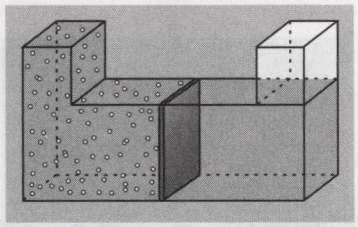


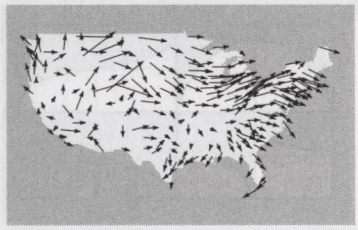
13 Chemical Equilibria **235**
Chemical Equilibria from Atomic Structures 235
Le Chatelier's Principle 243
Temperature Dependence of Equilibrium 244
Summary 248
Problems 249
Suggested Reading 249

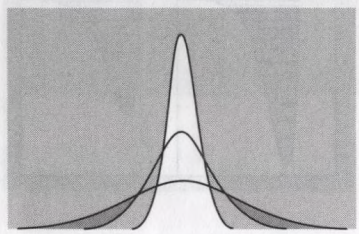












14 Equilibria Between Liquids, Solids, and Gases 251
Phase Equilibria 251
The Clapeyron Equation 256
How Do Refrigerators and Heat Pumps Work? 259
Surface Tension 262
Summary 264
Problems 265
Suggested Reading 265

15 Solutions and Mixtures 267
A Lattice Model Describes Mixtures 267
Interfacial Tension 273
What Have We Left Out? 275
Summary 276
Problems 277
Suggested Reading 277

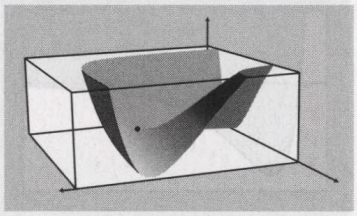
16 Solvation and Transfers of Molecules Between Phases 279
The Chemical Potential 279
Solvation 280
Activity and Activity Coefficient 282
Boiling Point Elevation 285
Freezing Point Depression 288
Osmotic Pressure 289
Solutes Can Transfer and Partition 291
Dimerization in Solution 294
Summary 297
Problems 298

17 Vector Calculus 301
Vectors Describe Forces and Flows 301
Vectors Add and Subtract by Components 301
The Dot Product 302
Scalar and Vector Fields 303
The Flux of a Vector Field 308
Gauss's Theorem 310
Summary 311
Problems 314

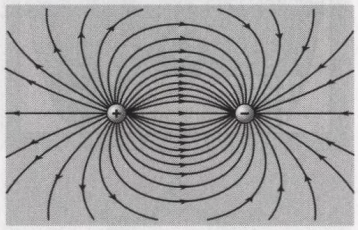
18 Physical Kinetics 315
Forces Drive Molecules to Flow 315
Linear Laws Relate Forces to Flows 316
The Diffusion Equation 318
Sources and Sinks: Examples from Population Biology 324
Additional Forces 326
The Einstein–Smoluchowski Equation 327
Brownian Ratchets 330
The Fluctuation–Dissipation Theorem 333

Onsager Reciprocal Relations Describe Coupled Flows 335
Summary 337
Problems 338
Suggested Reading 339

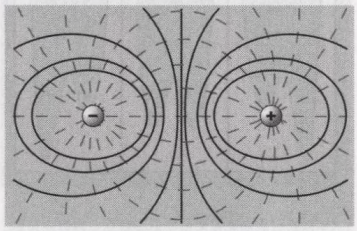
19 Chemical Kinetics & Transition States **341**
Rates Depend on Temperature 341
Rates Are Proportional to Concentrations 341
At Equilibrium, Rates Obey Detailed Balance 342
Mass Action Laws Describe Mechanisms 344
Reaction Rates Depend on Temperature 345
Activated Processes and Transition State Theory 348
Catalysts Speed Up Chemical Reactions 356
The Brønsted Law 359
Funnel Landscapes and Diffusional Processes 363
Summary 364
Problems 366
Suggested Reading 367



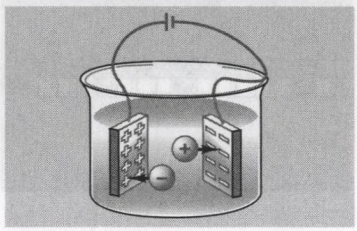
20 Coulomb's Law **369**
Charges and Coulomb's Law 369
Charge Interactions are Long-Ranged 370
Charge Interactions Are Weaker in Media: Dielectric Constants 373
Electrostatic Forces Add Like Vectors 375
What Is an Electrostatic Field? 376
Electric Fields Have Fluxes 378
Summary 384
Problems 385
Suggested Reading 385

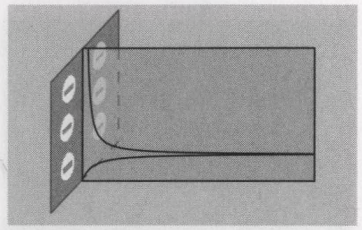


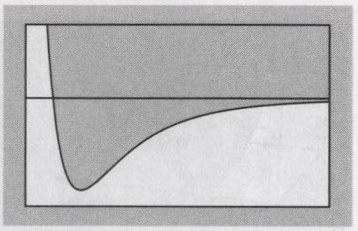
21 The Electrostatic Potential **387**
Electrostatic Potentials with Electrostatic Fields 387
Dipoles Are Separated Charges 392
The Poisson Equation 395
Method of Image Charges 399
Summary 406
Problems 407
Suggested Reading 407

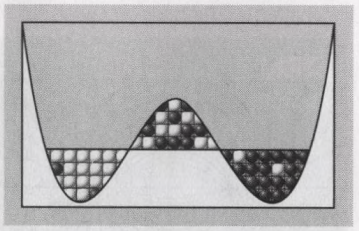


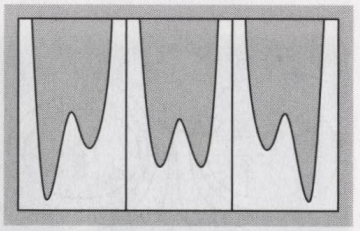
22 Electrochemical Equilibria **409**
Electrochemical Potentials in Ionic Solutions 409
The Nernst Equation 410
Voltage-Gated Ion Channels 417
Acid–Base Equilibria Are Shifted by Electrostatic Fields 418
Electrostatic Gradients Cause Ion Flows 420
Creating Charge Distribution Costs Free Energy 423
Summary 430
Problems 431
Suggested Reading 432

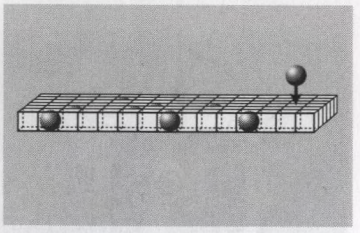












23 Salt Ions Shield Charged Objects **433**
Salts Dissociate and Shield Other Charges 433
Strong and Weak Electrolytes 440
Summary 444
Problems 446
Suggested Reading 447

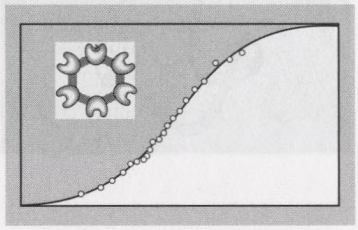
24 Intermolecular Interactions **449**
Short-ranged Repulsions and Long-ranged Attractions 449
Short-ranged Attractions Are Electrostatic 450
The van der Waals Gas Model 457
The Lattice Model Contact Energy 462
Summary 463
Problems 464
Suggested Reading 465

25 Phase Transitions **467**
Two States Can Be Stable at the Same Time 467
Liquids or Solids Mix at High Temperatures 468
Phase Separations Are Driven to Lower the Free Energy 471
The Spinodal Curve 477
The Critical Point 478
The Principles of Boiling 479
Boiling a Liquid Mixture Involves Two Transitions 485
Summary 487
Problems 488
Suggested Reading 491

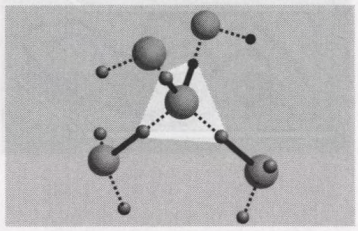
26 Cooperativity **493**
Abrupt Transitions Occur in Many Different Systems 493
Transitions and Critical Points Are Universal 493
The Landau Model 496
Helix–Coil Transitions 499
The Ising Model Describes Magnetization 508
The Kinetics of Phase Transitions and Nucleation 509
Summary 511
Problems 512

27 Adsorption, Binding & Catalysis **515**
Binding and Adsorption Processes Are Saturable 515
The Langmuir Model 515
Binding and Saturation in Solution 519
The Principle of Adsorption Chromatography 521
Michaelis–Menten Model 522
Sabatier's Principle for Stabilizing Transition States 527
Summary 529
Problems 530
Suggested Reading 531

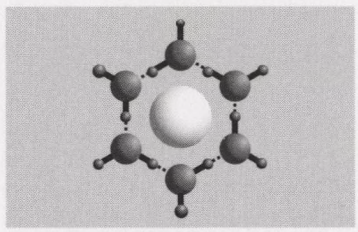
28 Multi-site Cooperative Ligand Binding 533
Binding Polynomials 534
The Two-site Model of Binding Cooperativity 536
Binding Intermediate States 539
Constructing Binding Polynomials from Rules of Probability 541
Oxygen Binding to Hemoglobin 546
Inhibitors 550
Model of McGhee and von Hippel 552
Rates Can Often Be Treated by Using Binding Polynomials 556
Grand Canonical Ensemble 556
Summary 558
Problems 559
Suggested Reading 562



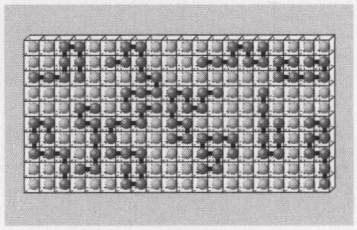
29 Water 563
Water Is an Unusual Liquid 563
Water Has Hydrogen Bonded Structure 563
Pure Water Has Anomalous Properties 568
Summary 575
Problems 576
Suggested Reading 576

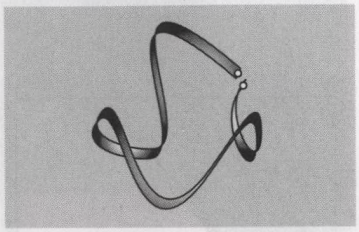


30 Water as a Solvent 577
Oil and Water Don't Mix: The Hydrophobic Effect 577
Signature of Hydrophobicity: Its Temperature Dependence 578
Water Is Structured Near Cavities and Planar Surfaces 582
Alcohols Constrict the Volumes of Aqueous Mixtures 585
Ions Can Make or Break Water Structure 586
Ion Pairing Preferences 588
Summary 589
Problems 590
Suggested Reading 591



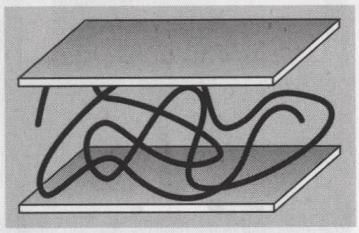
31 Polymer Solutions 593
Polymers Are Governed by Statistics 593
Polymers Have Distributions of Conformations 593
Polymer Solutions Differ from Small Molecule Solutions 594
The Flory–Huggins Model 596
Nonideal Colligative Properties 601
The Phase Behavior of Polymers 601
Dilution Entropy Drives Solute Partitioning into Polymers 605
The Flory Theorem 606
Summary 607
Problems 608





32 Polymer Elasticity 609
Polymeric Materials Are Elastic 609
Random-flight Chains Are Gaussian 613
Polymer Elasticity Follows Hooke's Law 614
Elasticity of Rubbery Materials 619
Polymer Collapse and Expansion 621
Summary 626
Problems 627
Suggested Reading 627

33 Polymers Resist Confinement & Deformation 629
Excluded Volume 629
Chain Conformations Are Perturbed Near Surfaces 631
Polymer Conformations by a Diffusion Equation Method 634
Polymers Tend to Avoid Confined Spaces 636
The Rouse–Zimm Model of Polymer Dynamics 638
The Reptation Model 640
Summary 642
Problems 643
Suggested Reading 643



Appendix A Table of Constants 645

Appendix B Table of Units 646

Appendix C Useful Taylor Series Expansions 647

Appendix D Useful Integrals 648

Appendix E Multiples of Units, Their Names, and Symbols 649

Index 651