

Contents

Preface	xv
About the companion website	xvii
1 Introduction	1
1.1 Atoms and molecules	1
1.2 Phases	2
1.3 Energy	3
1.4 Chemical reactions	4
1.5 Problem solving	5
1.6 Some conventions	7
Exercises	11
Further reading	14
2 Ideal gases	15
2.1 Ideal gas equation of state	16
2.2 Molecular degrees of freedom	18
2.3 Translational energy: Distribution and relation to pressure	21
2.4 Maxwell distribution of molecular speeds	23
2.5 Principle of equipartition of energy	24
2.6 Temperature and the zeroth law of thermodynamics	25
2.7 Mixtures of gases	27
2.8 Molecular collisions	27
Exercises	29
Further reading	30
3 Non-ideal gases and intermolecular interactions	31
3.1 Non-ideal behavior	31
3.2 Interactions of matter with matter	32
3.3 Intermolecular interactions	34
3.4 Real gases	39
3.5 Corresponding states	42
3.6 Supercritical fluids	43
Exercises	43
Further reading	44
4 Liquids, liquid crystals, and ionic liquids	45
4.1 Liquid formation	45
4.2 Properties of liquids	45
4.3 Intermolecular interaction in liquids	47
4.4 Structure of liquids	50
4.5 Internal energy and equation of state of a rigid sphere liquid	52
4.6 Concentration units	53
4.7 Diffusion	55
4.8 Viscosity	57

4.9 Migration	59
4.10 Interface formation	60
4.11 Liquid crystals	62
4.12 Ionic liquids	64
Exercises	66
Further reading	67
5 Solids, nanoparticles, and interfaces	68
5.1 Solid formation	68
5.2 Electronic structure of solids	70
5.3 Geometrical structure of solids	72
5.4 Interface formation	76
5.5 Glass formation	78
5.6 Clusters and nanoparticles	78
5.7 The carbon family: Diamond, graphite, graphene, fullerenes, and carbon nanotubes	80
5.8 Porous solids	83
5.9 Polymers and macromolecules	84
Exercises	86
Endnotes	86
Further reading	86
6 Statistical mechanics	87
6.1 The initial state of the universe	88
6.2 Microstates and macrostates of molecules	89
6.3 The connection of entropy to microstates	91
6.4 The constant α : Introducing the partition function	93
6.5 Using the partition function to derive thermodynamic functions	94
6.6 Distribution functions for gases	96
6.7 Quantum statistics for particle distributions	98
6.8 The Maxwell–Boltzmann speed distribution	102
6.9 Derivation of the ideal gas law	103
6.10 Deriving the Sackur–Tetrode equation for entropy of a monatomic gas	104
6.11 The partition function of a diatomic molecule	106
6.12 Contributions of each degree of freedom to thermodynamic functions	106
6.13 The total partition function and thermodynamic functions	111
6.14 Polyatomic molecules	113
Exercises	115
Endnotes	116
Further reading	116
7 First law of thermodynamics	117
7.1 Some definitions and fundamental concepts in thermodynamics	118
7.2 Laws of thermodynamics	118
7.3 Internal energy and the first law	119
7.4 Work	121
7.5 Intensive and extensive variables	121
7.6 Heat	123
7.7 Non-ideal behavior changes the work	124
7.8 Heat capacity	125
7.9 Temperature dependence of C_p	126
7.10 Internal energy change at constant volume	127
7.11 Enthalpy	129
	130

7.12	Relationship between C_V and C_p and partial differentials	131
7.13	Reversible adiabatic expansion/compression	133
	Exercises	136
	Endnotes	138
	Further reading	138
8	Second law of thermodynamics	139
8.1	The second law of thermodynamics	140
8.2	Thermodynamics of a hurricane	141
8.3	Heat engines, refrigeration, and heat pumps	145
8.4	Definition of entropy	148
8.5	Calculating changes in entropy	150
8.6	Maxwell's relations	152
8.7	Calculating the natural direction of change	154
	Exercises	157
	Endnotes	159
	Further reading	159
9	Third law of thermodynamics and temperature dependence of heat capacity, enthalpy and entropy	160
9.1	When and why does a system change?	160
9.2	Natural variables of internal energy	161
9.3	Helmholtz and Gibbs energies	162
9.4	Standard molar Gibbs energies	163
9.5	Properties of the Gibbs energy	164
9.6	The temperature dependence of $\Delta_r C_p$ and H	168
9.7	Third law of thermodynamics	170
9.8	The unattainability of absolute zero	171
9.9	Absolute entropies	172
9.10	Entropy changes in chemical reactions	173
9.11	Calculating $\Delta_r S^\circ$ at any temperature	175
	Exercises	177
	Further reading	180
10	Thermochemistry: The role of heat in chemical and physical changes	181
10.1	Stoichiometry and extent of reaction	181
10.2	Standard enthalpy change	182
10.3	Calorimetry	184
10.4	Phase transitions	187
10.5	Bond dissociation and atomization	190
10.6	Solution	191
10.7	Enthalpy of formation	192
10.8	Hess's law	192
10.9	Reaction enthalpy from enthalpies of formation	193
10.10	Calculating enthalpy of reaction from enthalpies of combustion	194
10.11	The magnitude of reaction enthalpy	195
	Exercises	196
	Further reading	200
11	Chemical equilibrium	201
11.1	Chemical potential and Gibbs energy of a reaction mixture	201
11.2	The Gibbs energy and equilibrium composition	202
11.3	The response of equilibria to change	204

11.4	Equilibrium constants and associated calculations	209
11.5	Acid–base equilibria	212
11.6	Dissolution and precipitation of salts	216
11.7	Formation constants of complexes	219
11.8	Thermodynamics of self-assembly	222
	Exercises	224
	Endnote	228
	Further reading	228
12	Phase stability and phase transitions	229
12.1	Phase diagrams and the relative stability of solids, liquids, and gases	229
12.2	What determines relative phase stability?	232
12.3	The p – T phase diagram	234
12.4	The Gibbs phase rule	237
12.5	Theoretical basis for the p – T phase diagram	238
12.6	Clausius–Clapeyron equation	240
12.7	Surface tension	242
12.8	Nucleation	246
12.9	Construction of a liquid–vapor phase diagram at constant pressure	250
12.10	Polymers: Phase separation and the glass transition	252
	Exercises	254
	Endnotes	255
	Further reading	256
13	Solutions and mixtures: Nonelectrolytes	257
13.1	Ideal solution and the standard state	258
13.2	Partial molar volume	258
13.3	Partial molar Gibbs energy = chemical potential	259
13.4	The chemical potential of a mixture and $\Delta_{\text{mix}}G$	261
13.5	Activity	263
13.6	Measurement of activity	264
13.7	Classes of solutions and their properties	269
13.8	Colligative properties	273
13.9	Solubility of polymers	277
13.10	Supercritical CO_2	279
	Exercises	281
	Endnote	282
	Further reading	282
14	Solutions of electrolytes	283
14.1	Why salts dissolve	283
14.2	Ions in solution	284
14.3	The thermodynamic properties of ions in solution	287
14.4	The activity of ions in solution	289
14.5	Debye–Hückel theory	290
14.6	Use of activities in equilibrium calculations	292
14.7	Charge transport	295
	Exercises	295
	Further reading	298
		299

15	Electrochemistry: The chemistry of free charge exchange	300
15.1	Introduction to electrochemistry	301
15.2	The electrochemical potential	306
15.3	Electrochemical cells	310
15.4	Potential difference of an electrochemical cell	312
15.5	Surface charge and potential	318
15.6	Relating work functions to the electrochemical series	319
15.7	Applications of standard potentials	321
15.8	Biological oxidation and proton-coupled electron transfer	326
	Exercises	329
	Endnotes	331
	Further reading	332
16	Empirical chemical kinetics	333
16.1	What is chemical kinetics?	333
16.2	Rates of reaction and rate equations	335
16.3	Elementary versus composite reactions	336
16.4	Kinetics and thermodynamics	337
16.5	Kinetics of specific orders	338
16.6	Reaction rate determination	345
16.7	Methods of determining reaction order	346
16.8	Reversible reactions and the connection of rate constants to equilibrium constants	348
16.9	Temperature dependence of rates and the rate constant	350
16.10	Microscopic reversibility and detailed balance	353
16.11	Rate-determining step (RDS)	354
	Exercises	355
	Endnotes	359
	Further reading	359
17	Reaction dynamics I: Mechanisms and rates	360
17.1	Linking empirical kinetics to reaction dynamics	360
17.2	Hard-sphere collision theory	361
17.3	Activation energy and the transition state	364
17.4	Transition-state theory (TST)	366
17.5	Composite reactions and mechanisms	368
17.6	The rate of unimolecular reactions	372
17.7	Desorption kinetics	374
17.8	Langmuir (direct) adsorption	378
17.9	Precursor-mediated adsorption	380
17.10	Adsorption isotherms	381
17.11	Surmounting activation barriers	382
	Exercises	386
	Endnotes	389
	Further reading	390
18	Reaction dynamics II: Catalysis, photochemistry and charge transfer	391
18.1	Catalysis	392
18.2	Heterogeneous catalysis	393
18.3	Acid–base catalysis	402
18.4	Enzyme catalysis	403
18.5	Chain reactions	407
18.6	Explosions	410

18.7	Photochemical reactions	411
18.8	Charge transfer and electrochemical dynamics	415
	Exercises	428
	Endnotes	431
	Further reading	431
19	Developing quantum mechanical intuition	433
19.1	Classical electromagnetic waves	434
19.2	Classical mechanics to quantum mechanics	443
19.3	Necessity for an understanding of quantum mechanics	444
19.4	Quantum nature of light	448
19.5	Wave-particle duality	449
19.6	The Bohr atom	453
	Exercises	458
	Endnotes	460
	Further reading	461
20	The quantum mechanical description of nature	462
20.1	What determines if a quantum description is necessary?	463
20.2	The postulates of quantum mechanics	463
20.3	Wavefunctions	464
20.4	The Schrödinger equation	467
20.5	Operators and eigenvalues	469
20.6	Solving the Schrödinger equation	471
20.7	Expectation values	475
20.8	Orthonormality and superposition	477
20.9	Dirac notation	480
20.10	Developing quantum intuition	481
	Exercises	486
	Endnotes	488
	Further reading	488
21	Model quantum systems	489
21.1	Particle in a box	490
21.2	Quantum tunneling	495
21.3	Vibrational motion	497
21.4	Angular momentum	500
	Exercises	511
	Endnotes	513
	Further reading	513
22	Atomic structure	514
22.1	The hydrogen atom	515
22.2	How do you make it better? the Dirac equation	518
22.3	Atomic orbitals	520
22.4	Many-electron atoms	524
22.5	Ground and excited states of He	528
22.6	Slater-Condon theory for approximating atomic energy levels	530
22.7	Electron configurations	533
	Exercises	536
	Endnotes	538
	Further reading	538

23	Introduction to spectroscopy and atomic spectroscopy	539
23.1	Fundamentals of spectroscopy	540
23.2	Time-dependent perturbation theory and spectral transitions	544
23.3	The Beer–Lambert law	547
23.4	Electronic spectra of atoms	550
23.5	Spin–orbit coupling	551
23.6	Russell–Saunders (<i>LS</i>) coupling	554
23.7	<i>jj</i> -coupling	559
23.8	Selection rules for atomic spectroscopy	560
23.9	Photoelectron spectroscopy	561
	Exercises	566
	Endnotes	569
	Further reading	569
24	Molecular bonding and structure	570
24.1	Born–Oppenheimer approximation	571
24.2	Valence bond theory	573
24.3	Molecular orbital theory	576
24.4	The hydrogen molecular ion H_2^+	577
24.5	Solving the H_2 Schrödinger equation	580
24.6	Homonuclear diatomic molecules	585
24.7	Heteronuclear diatomic molecules	588
24.8	The variational principle in molecular orbital calculations	591
24.9	Polyatomic molecules: The Hückel approximation	593
24.10	Density functional theory (DFT)	597
	Exercises	598
	Endnotes	601
	Further reading	601
25	Molecular spectroscopy and excited-state dynamics: Diatomics	602
25.1	Introduction to molecular spectroscopy	603
25.2	Pure rotational spectra of molecules	604
25.3	Rovibrational spectra of molecules	609
25.4	Raman spectroscopy	614
25.5	Electronic spectra of molecules	617
25.6	Excited-state population dynamics	622
25.7	Electron collisions with molecules	628
	Exercises	629
	Endnotes	632
	Further reading	633
26	Polyatomic molecules and group theory	634
26.1	Absorption and emission by polyatomics	635
26.2	Electronic and vibronic selection rules	637
26.3	Molecular symmetry	641
26.4	Point groups	645
26.5	Character tables	647
26.6	Dipole moments	650
26.7	Rovibrational spectroscopy of polyatomic molecules	652
26.8	Excited-state dynamics	656
	Exercises	665

Endnotes	667
Further reading	667
27 Light–matter interactions: Lasers, laser spectroscopy, and photodynamics	668
27.1 Lasers	669
27.2 Harmonic generation (SHG and SFG)	673
27.3 Multiphoton absorption spectroscopy	675
27.4 Cavity ring-down spectroscopy	682
27.5 Femtochemistry	685
27.6 Beyond perturbation theory limit: High harmonic generation	688
27.7 Attosecond physics	690
27.8 Photosynthesis	691
27.9 Color and vision	694
Exercises	697
Endnotes	698
Further reading	699
Appendix 1 Basic calculus and trigonometry	700
Appendix 2 The method of undetermined multipliers	703
Appendix 3 Stirling’s theorem	705
Appendix 4 Density of states of a particle in a box	706
Appendix 5 Black-body radiation: Treating radiation as a photon gas	708
Appendix 6 Definitions of symbols used in quantum mechanics and quantum chemistry	710
Appendix 7 Character tables	712
Appendix 8 Periodic behavior	714
Appendix 9 Thermodynamic parameters	717
Index	719