



OXFORD

Third Edition

Atkins

The Elements of
Physical Chemistry

CONTENTS

Introduction	1
0.1 The states of matter	2
0.2 Physical state	2
0.3 Pressure	3
0.4 Temperature	6
0.5 Amount of substance	7

Chapter 1 The properties of gases	11
------------------------------------------	----

Equations of state	11
1.1 The perfect gas equation of state	12
Box 1.1 <i>The gas laws and the weather</i>	15
1.2 Using the perfect gas law	17
1.3 Mixtures of gases: partial pressures	18

The kinetic model of gases	20
1.4 The pressure of a gas according to the kinetic model	20
1.5 The average speed of gas molecules	21
1.6 The Maxwell distribution of speeds	22
1.7 Diffusion and effusion	23
1.8 Molecular collisions	25
Box 1.2 <i>The Sun as a ball of perfect gas</i>	27

Real gases	27
1.9 Intermolecular interactions	28
1.10 The critical temperature	28
1.11 The compression factor	30
1.12 The virial equation of state	31
1.13 The van der Waals equation of state	31
1.14 The liquefaction of gases	33

Chapter 2 Thermodynamics: the First Law	37
------------------------------------------------	----

The conservation of energy	38
2.1 Systems and surroundings	38
2.2 Work and heat	39
2.3 The measurement of work	41
2.4 The measurement of heat	44

Internal energy and enthalpy	47
2.5 The internal energy	47
2.6 The enthalpy	49
2.7 The temperature variation of the enthalpy	52

Chapter 3 Thermochemistry	57
----------------------------------	----

Physical change	57
3.1 The enthalpy of phase transition	58
3.2 Atomic and molecular change	61
Chemical change	66
3.3 Standard enthalpy changes	66
3.4 The combination of reaction enthalpies	68
3.5 Standard enthalpies of formation	69
Box 3.1 <i>Food and energy reserves</i>	71
3.6 The variation of reaction enthalpy with temperature	72

Chapter 4 Thermodynamics: the Second Law	77
-------------------------------------------------	----

Entropy	78	6.5 Ideal-dilute solutions	120
4.1 The direction of spontaneous change	78	Box 6.1 Gas solubility and breathing	122
4.2 Entropy and the Second Law	79	6.6 Real solutions: activities	124
4.3 Entropy changes for typical processes	80		
4.4 Entropy changes in the surroundings	84	Colligative properties	125
4.5 Absolute entropies and the Third Law of thermodynamics	85	6.7 The modification of boiling and freezing points	125
4.6 The standard reaction entropy	88	6.8 Osmosis	127
4.7 The spontaneity of chemical reactions	88	Box 6.2 Dialysis and protein binding	128
Box 4.1 The hydrophobic effect	89		
		Phase diagrams of mixtures	132
The Gibbs energy	90	6.9 Mixtures of volatile liquids	132
4.8 Focusing on the system	90	6.10 Liquid-liquid phase diagrams	135
4.9 Properties of the Gibbs energy	90	6.11 Liquid-solid phase diagrams	137
		6.12 Ultrapurity and controlled impurity	139
Chapter 5 Phase equilibria: pure substances	95	Chapter 7 Principles of chemical equilibrium	143
The thermodynamics of transition	95	Thermodynamic background	143
5.1 The condition of stability	95	7.1 The reaction Gibbs energy	144
5.2 The variation of Gibbs energy with pressure	96	7.2 The variation of $\Delta_r G$ with composition	146
5.3 The variation of Gibbs energy with temperature	97	7.3 Reactions at equilibrium	147
		7.4 The standard reaction Gibbs energy	149
		7.5 Coupled reactions	152
Phase diagrams	99	Box 7.1 Anaerobic and aerobic metabolism	154
5.4 Phase boundaries	99	7.6 The equilibrium composition	154
5.5 The location of phase boundaries	101	Box 7.2 Myoglobin and haemoglobin	156
5.6 Characteristic points	103		
5.7 The phase rule	105	The response of equilibria to the conditions	158
5.8 Phase diagrams of typical materials	106	7.7 The presence of a catalyst	158
		7.8 The effect of temperature	158
		7.9 The effect of compression	160
Chapter 6 The properties of mixtures	111		
		Chapter 8 Consequences of equilibrium	167
The thermodynamic description of mixtures	111	Proton transfer equilibria	167
6.1 Measures of concentration	112	8.1 Brønsted-Lowry theory	168
6.2 Partial molar properties	113	8.2 Protonation and deprotonation	168
6.3 Spontaneous mixing	116		
6.4 Ideal solutions	117		

8.3 Polyprotic acids	172
8.4 Amphiprotic systems	175

Salts in water	176
-----------------------	-----

8.5 Acid-base titrations	176
8.6 Buffer action	179
8.7 Indicators	180

Solubility equilibria	182
------------------------------	-----

8.8 The solubility constant	182
8.9 The common-ion effect	182

Chapter 9 Electrochemistry	187
-----------------------------------	-----

The migration of ions	188
------------------------------	-----

9.1 Conductivity	188
9.2 Ion mobility	190

Electrochemical cells	192
------------------------------	-----

9.3 Half-reactions and electrodes	193
9.4 Reactions at electrodes	194
9.5 Varieties of cell	197
Box 9.1 Action potentials	198
9.6 The cell reaction	199
9.7 The cell potential	199
Box 9.2 Chemiosmotic theory	201
9.8 Cells at equilibrium	202
9.9 Standard potentials	203
9.10 The variation of potential with pH	205
9.11 The determination of pH	206

Applications of standard potentials	207
--------------------------------------------	-----

9.12 The electrochemical series	207
Box 9.3 Cytochrome cascades	208
9.13 The determination of thermodynamic functions	209

Chapter 10 The rates of reactions	215
------------------------------------------	-----

Empirical chemical kinetics	216
------------------------------------	-----

10.1 Experimental techniques	216
10.2 Application of the techniques	216
Box 10.1 Ultrafast reactions: femtochemistry	218

Reaction rates	219
-----------------------	-----

10.3 The definition of rate	219
10.4 Rate laws and rate constants	220
10.5 Reaction order	220
10.6 The determination of the rate law	221
10.7 Integrated rate laws	223
10.8 Half-lives	227

The temperature dependence of reaction rates	229
-----------------------------------------------------	-----

10.9 The Arrhenius parameters	229
10.10 Collision theory	231
10.11 Activated complex theory	234
10.12 Catalysis	236

Chapter 11 Accounting for the rate laws	241
------------------------------------------------	-----

Reaction schemes	241
-------------------------	-----

11.1 The approach to equilibrium	242
11.2 Consecutive reactions	243

Reaction mechanisms	244
----------------------------	-----

11.3 Elementary reactions	244
11.4 The formulation of rate laws	246
11.5 The steady-state approximation	246
11.6 The rate-determining step	247
11.7 Reactions on surfaces	249
11.8 Unimolecular reactions	250

Enzyme reactions	251
-------------------------	-----

11.9 The mechanism of enzyme action	251
Box 11.1 Catalytic action and catalytic antibodies	253

11.10 Enzyme inhibition	256	13.2 The permitted energies of hydrogenic atoms	299
Chain reactions	259	13.3 Quantum numbers	301
11.11 The structure of chain reactions	259	13.4 The wavefunctions: <i>s</i> orbitals	302
11.12 The rate laws of chain reactions	260	13.5 The wavefunctions: <i>p</i> and <i>d</i> orbitals	304
11.13 Explosions	261	13.6 Electron spin	306
Photochemical processes	262	13.7 Spectral transitions and selection rules	307
11.14 Quantum yield	262	The structures of many-electron atoms	309
Box 11.2 <i>Photobiology</i>	264	13.8 The orbital approximation	310
11.15 Photochemical rate laws	266	13.9 The Pauli principle	310
Chapter 12 Quantum theory	269	13.10 Penetration and shielding	311
The failures of classical physics	270	13.11 The building-up principle	312
12.1 Black-body radiation	270	13.12 The occupation of <i>d</i> orbitals	313
12.2 Heat capacities	273	13.13 The configurations of cations and anions	313
12.3 The photoelectric effect	275	Periodic trends in atomic properties	314
12.4 The diffraction of electrons	277	13.14 Atomic radius	315
12.5 Atomic and molecular spectra	278	Box 13.1 <i>Atomic radius and respiration</i>	316
The dynamics of microscopic systems	279	13.15 Ionization energy and electron affinity	317
12.6 The Schrödinger equation	280	The spectra of complex atoms	319
12.7 The Born interpretation	281	13.16 Term symbols	319
12.8 The uncertainty principle	282	13.17 Spin-orbit coupling	321
Applications of quantum mechanics	285	Chapter 14 The chemical bond	325
12.9 Translation: a particle in a box	285	Introductory concepts	326
12.10 Rotation: a particle on a ring	287	14.1 The classification of bonds	326
12.11 Vibration: the harmonic oscillator	290	14.2 Potential energy curves	326
Box 12.1 <i>Scanning tunnelling microscopy</i>	292	Valence bond theory	327
Chapter 13 Atomic structure	297	14.3 Diatomic molecules	327
Hydrogenic atoms	298	14.4 Polyatomic molecules	329
13.1 The spectra of hydrogenic atoms	298	14.5 Promotion and hybridization	329
		14.6 Resonance	332

Molecular orbitals	333
14.7 Linear combinations of atomic orbitals	334
14.8 Bonding orbitals	335
14.9 Antibonding orbitals	335
14.10 The structures of diatomic molecules	336
14.11 Hydrogen and helium molecules	336
14.12 Period 2 diatomic molecules	338
14.13 Symmetry and overlap	340
14.14 The electronic structures of homonuclear diatomic molecules	343
14.15 Parity	344
14.16 Heteronuclear diatomic molecules	345
14.17 Polar covalent bonds	346
Box 14.1 <i>Computational chemistry</i>	348
14.18 The structures of polyatomic molecules	349
 Chapter 15 Metallic and ionic solids	 355
Bonding in solids	356
15.1 The band theory of solids	357
15.2 The occupation of bands	358
15.3 The ionic model of bonding	360
15.4 Lattice enthalpy	360
15.5 Coulombic contributions to lattice enthalpies	362
 Crystal structure	 364
15.6 Unit cells	364
15.7 The identification of crystal planes	365
15.8 The determination of structure	369
15.9 The Bragg law	371
15.10 Experimental techniques	371
 Typical structures	 373
15.11 Metal crystals	374
15.12 Ionic crystals	376

Chapter 16 Molecular substances	381
The origins of cohesion	381
16.1 Interactions between partial charges	382
16.2 Electric dipole moments	382
16.3 Interactions between dipoles	386
16.4 Induced dipole moments	388
16.5 Dispersion interactions	389
16.6 Hydrogen bonding	389
16.7 The total interaction	391
 Biopolymers	 394
16.8 Polypeptide structures	394
16.9 Denaturation	395
 Liquids	 396
Box 16.1 <i>The prediction of protein structure</i>	397
16.10 The relative positions of molecules	398
16.11 Molecular motion in liquids	399
 Mesophases and disperse systems	 403
16.12 Liquid crystals	403
16.13 Classification of disperse systems	404
16.14 Surface, structure, and stability	405
16.15 The electric double layer	407
Box 16.2 <i>Cell membranes</i>	408
 Chapter 17 Molecular rotations and vibrations	 415
General features of spectroscopy	416
17.1 Experimental techniques	417
17.2 Intensities and linewidths	418
 Rotational spectroscopy	 420
17.3 The rotational energy levels of molecules	420

xii CONTENTS

17.4	Rotational transitions: microwave spectroscopy	422
17.5	Rotational Raman spectra	424

Vibrational spectroscopy	424
---------------------------------	------------

17.6	The vibrations of molecules	425
17.7	Vibrational transitions	426
17.8	Vibrational Raman spectra of diatomic molecules	428
17.9	The vibrations of polyatomic molecules	428
17.10	Vibrational Raman spectra of polyatomic molecules	431

Chapter 18 Electronic transitions	437
------------------------------------------	------------

Ultraviolet and visible spectra	438
----------------------------------------	------------

18.1	The Franck–Condon principle	439
18.2	Measures of intensity	440
18.3	Circular dichroism	443
18.4	Specific types of transitions	444
	Box 18.1 <i>The photochemistry of vision</i>	446

Radiative decay	447
------------------------	------------

18.5	Fluorescence	448
18.6	Fluorescence quenching	449
18.7	Phosphorescence	451
18.8	Lasers	453

Photoelectron spectroscopy	454
-----------------------------------	------------

Chapter 19 Magnetic resonance	459
--------------------------------------	------------

Principles of magnetic resonance	460
-----------------------------------------	------------

19.1	Nuclei in magnetic fields	460
19.2	The technique	461

The information in NMR spectra	462
---------------------------------------	------------

19.3	The chemical shift	462
------	--------------------	-----

19.4	The fine structure	464
	Box 19.1 <i>Magnetic resonance imaging</i>	466
19.5	Spin relaxation	468
19.6	The nuclear Overhauser effect	470

Chapter 20 Statistical thermodynamics	475
----------------------------------------------	------------

The partition function	476
-------------------------------	------------

20.1	The Boltzmann distribution	476
20.2	The interpretation of the partition function	478
20.3	Examples of partition functions	481

Thermodynamic properties	482
---------------------------------	------------

20.4	The internal energy and the heat capacity	483
20.5	The entropy and the Gibbs energy	484
20.6	The statistical basis of equilibrium	487
	Box 20.1 <i>The helix–coil transition in polypeptides</i>	489

Further Information	493
----------------------------	------------

1 Mathematical techniques	493
----------------------------------	------------

1.1	Algebraic equations and graphs	493
1.2	Logarithms, exponentials, and powers	494
1.3	Differentiation and integration	495

2 Quantities and units	498
-------------------------------	------------

3 Energy and force	500
---------------------------	------------

4 The kinetic theory of gases	501
--------------------------------------	------------

5 The variation of Gibbs energy with the conditions	502
------------------------------------------------------------	------------

6 Concepts of electrostatics	503
-------------------------------------	------------

7 Electromagnetic radiation and photons	505	1.2 Thermodynamic data	515
8 Oxidation numbers	507	2 Standard potentials	522
9 The Lewis theory of covalent bonding	509	2.1a Standard potentials in electrochemical order	522
10 The VSEPR model	511	2.1b Standard potentials in alphabetical order	523
Appendices	514	3 The amino acids	525
1 Thermodynamic data	514	Answers to exercises	526
1.1 Thermodynamic data for organic compounds	514	Index	533