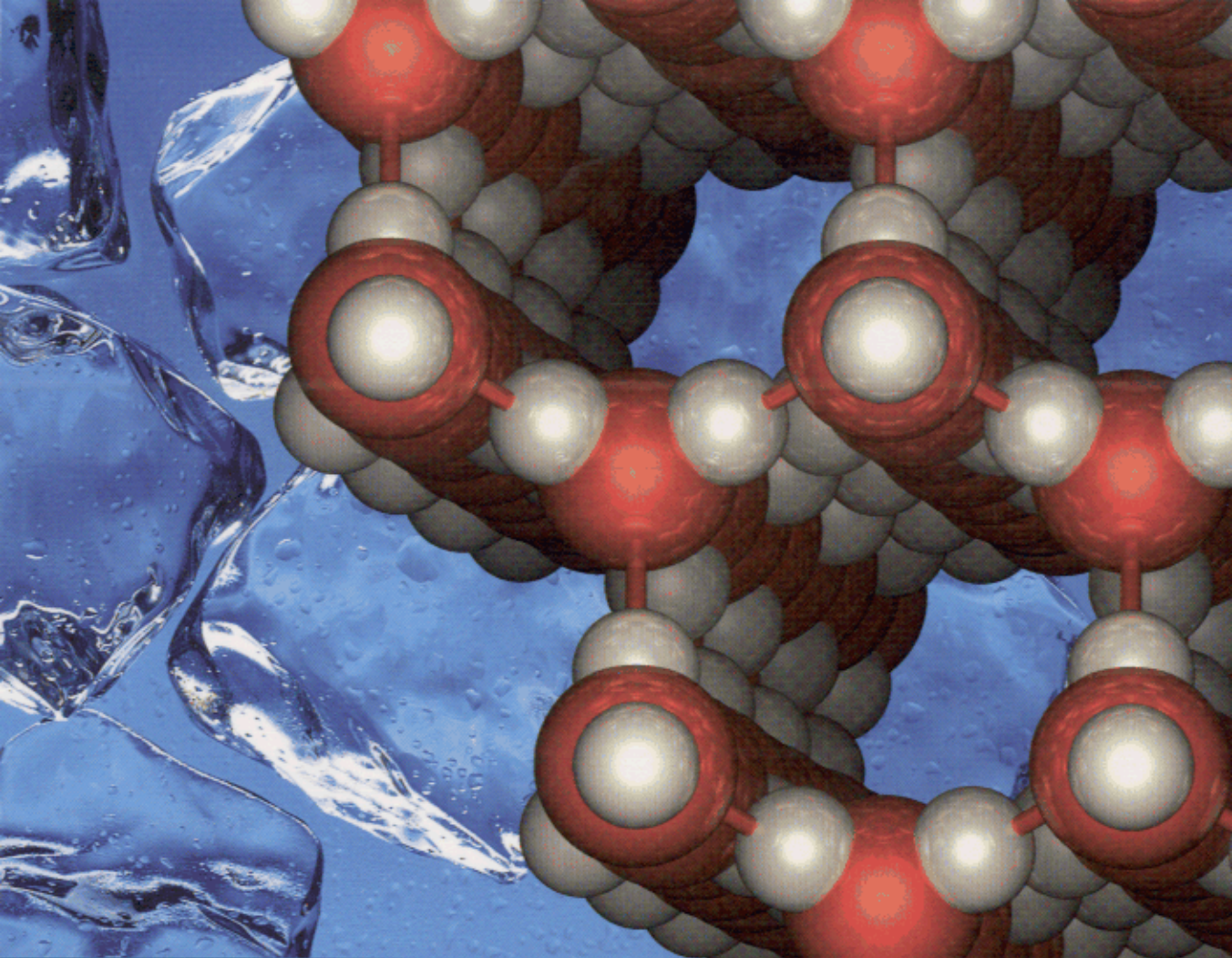




ELEMENTS OF
**PHYSICAL
CHEMISTRY**

Peter Atkins • Julio de Paula

FOURTH EDITION



Contents

Introduction	1	1.14 The liquefaction of gases	35
0.1 The states of matter	1	CHECKLIST OF KEY IDEAS	36
0.2 Physical state	2	FURTHER INFORMATION 1.1	36
0.3 Force	3	DISCUSSION QUESTIONS	38
0.4 Energy	3	EXERCISES	38
0.5 Pressure	4		
0.6 Temperature	7	Chapter 2	
0.7 Amount of substance	8	Thermodynamics: the First Law	40
0.8 Extensive and intensive properties	9		
CHECKLIST OF KEY IDEAS	10	The conservation of energy	41
DISCUSSION QUESTIONS	10	2.1 Systems and surroundings	41
EXERCISES	10	2.2 Work and heat	42
		2.3 The measurement of work	44
Chapter 1		2.4 The measurement of heat	48
The properties of gases	12	2.5 Heat influx during expansion	50
		Internal energy and enthalpy	51
Equations of state	12	2.6 The internal energy	51
1.1 The perfect gas equation of state	13	2.7 The enthalpy	54
1.2 Using the perfect gas law	15	Box 2.1 Differential scanning calorimetry	57
Box 1.1 The gas laws and the weather	16	2.8 The temperature variation of the enthalpy	58
1.3 Mixtures of gases: partial pressures	19	CHECKLIST OF KEY IDEAS	60
		DISCUSSION QUESTIONS	60
The kinetic model of gases	21	EXERCISES	60
1.4 The pressure of a gas according to the kinetic model	21		
1.5 The average speed of gas molecules	22	Chapter 3	
1.6 The Maxwell distribution of speeds	22	Thermochemistry	63
1.7 Diffusion and effusion	25		
1.8 Molecular collisions	26	Physical change	63
		3.1 The enthalpy of phase transition	64
Real gases	27	3.2 Atomic and molecular change	67
Box 1.2 The Sun as a ball of perfect gas	28	Chemical change	72
1.9 Molecular interactions	28	3.3 Enthalpies of combustion	73
1.10 The critical temperature	29	Box 3.1 Fuels, food, and energy reserves	74
1.11 The compression factor	31	3.4 The combination of reaction enthalpies	76
1.12 The virial equation of state	32	3.5 Standard enthalpies of formation	76
1.13 The van der Waals equation of state	32	3.6 Enthalpies of formation and molecular modelling	79

3.7 The variation of reaction enthalpy with temperature	79	5.6 Characteristic points	117
CHECKLIST OF KEY IDEAS	81	Box 5.1 Supercritical fluids	118
DISCUSSION QUESTIONS	82	5.7 The phase rule	119
EXERCISES	82	5.8 Phase diagrams of typical materials	120
		5.9 The molecular structure of liquids	122
Chapter 4		CHECKLIST OF KEY IDEAS	124
Thermodynamics: the Second Law	85	DISCUSSION QUESTIONS	124
		EXERCISES	124
Entropy	86	Chapter 6	
4.1 The direction of spontaneous change	86	The properties of mixtures	126
4.2 Entropy and the Second Law	87		
4.3 The entropy change accompanying expansion	88	The thermodynamic description of mixtures	126
Box 4.1 Heat engines, refrigerators, and heat pumps	89	6.1 Measures of concentration	127
4.4 The entropy change accompanying heating	91	6.2 Partial molar properties	128
4.5 The entropy change accompanying a phase transition	93	6.3 Spontaneous mixing	131
4.6 Entropy changes in the surroundings	95	6.4 Ideal solutions	132
4.7 Absolute entropies and the Third Law of thermodynamics	96	6.5 Ideal-dilute solutions	135
4.8 The standard reaction entropy	99	Box 6.1 Gas solubility and breathing	138
4.9 The spontaneity of chemical reactions	99	6.6 Real solutions: activities	139
The Gibbs energy	100	Colligative properties	140
4.10 Focusing on the system	100	6.7 The modification of boiling and freezing points	140
4.11 Properties of the Gibbs energy	100	6.8 Osmosis	142
CHECKLIST OF KEY IDEAS	103	Phase diagrams of mixtures	145
DISCUSSION QUESTIONS	103	6.9 Mixtures of volatile liquids	145
EXERCISES	104	6.10 Liquid-liquid phase diagrams	148
		6.11 Liquid-solid phase diagrams	151
Chapter 5		Box 6.2 Ultrapurity and controlled impurity	152
Phase equilibria: pure substances	106	CHECKLIST OF KEY IDEAS	153
		DISCUSSION QUESTIONS	154
The thermodynamics of transition	106	EXERCISES	154
5.1 The condition of stability	107	Chapter 7	
5.2 The variation of Gibbs energy with pressure	107	Principles of chemical equilibrium	157
5.3 The variation of Gibbs energy with temperature	109		
Phase diagrams	111	Thermodynamic background	157
5.4 Phase boundaries	111	7.1 The reaction Gibbs energy	158
5.5 The location of phase boundaries	113	7.2 The variation of $\Delta_r G$ with composition	159
		7.3 Reactions at equilibrium	161
		7.4 The standard reaction Gibbs energy	162

CONTENTS

7.5	The equilibrium composition	165	Electrochemical cells	209
7.6	The equilibrium constant in terms of concentration	167	9.3	Half-reactions and electrodes 210
7.7	Coupled reactions	168		Box 9.2 Fuel cells 211
The response of equilibria to the conditions	169		9.4	Reactions at electrodes 213
7.8	The presence of a catalyst	170	9.5	Varieties of cell 215
7.9	The effect of temperature	170	9.6	The cell reaction 216
7.10	The effect of compression	172	9.7	The electromotive force 216
	Box 7.1 Binding of oxygen to myoglobin and haemoglobin	172	9.8	Cells at equilibrium 218
CHECKLIST OF KEY IDEAS	175		9.9	Standard potentials 219
DISCUSSION QUESTIONS	175		9.10	The variation of potential with pH 219
EXERCISES	176		9.11	The determination of pH 221
 Chapter 8			Applications of standard potentials	222
Consequences of equilibrium	179		9.12	The electrochemical series 222
 Proton transfer equilibria	179		9.13	The determination of thermodynamic functions 222
8.1	Brønsted–Lowry theory	179	CHECKLIST OF KEY IDEAS	224
8.2	Protonation and deprotonation	180	DISCUSSION QUESTIONS	225
8.3	Polyprotic acids	184	EXERCISES	225
8.4	Amphiprotic systems	187	 Chapter 10	
Salts in water	188		The rates of reactions	229
8.5	Acid–base titrations	188	 Empirical chemical kinetics	230
8.6	Buffer action	191	10.1	Spectrophotometry 230
	Box 8.1 Buffer action in blood	192	10.2	Applications of spectrophotometry 232
8.7	Indicators	193	Reaction rates	233
Solubility equilibria	195		10.3	The definition of rate 233
8.8	The solubility constant	195	10.4	Rate laws and rate constants 234
8.9	The common-ion effect	196	10.5	Reaction order 235
CHECKLIST OF KEY IDEAS	197		10.6	The determination of the rate law 236
DISCUSSION QUESTIONS	197		10.7	Integrated rate laws 238
EXERCISES	197		10.8	Half-lives and time constants 242
 Chapter 9			The temperature dependence of reaction rates	244
Electrochemistry	200		10.9	The Arrhenius parameters 244
 Ions in solution	201		10.10	Collision theory 246
9.1	The Debye–Hückel theory	201	10.11	Transition state theory 249
9.2	The migration of ions	204		Box 10.1 Femtochemistry 250
	Box 9.1 Ion channels and pumps	207		

CHECKLIST OF KEY IDEAS	253	12.3 The photoelectric effect	292
DISCUSSION QUESTIONS	253	12.4 The diffraction of electrons	293
EXERCISES	254	12.5 Atomic and molecular spectra	295
 Chapter 11		 The dynamics of microscopic systems	296
Accounting for the rate laws	257	12.6 The Schrödinger equation	296
		12.7 The Born interpretation	297
Reaction schemes	257	12.8 The uncertainty principle	298
11.1 The approach to equilibrium	257	 Applications of quantum mechanics	300
11.2 Relaxation methods	259	12.9 Translation: motion in one dimension	301
Box 11.1 Kinetics of protein unfolding	260	(a) A particle in a box	301
11.3 Consecutive reactions	262	(b) Tunnelling	304
Reaction mechanisms	263	12.10 Rotation: a particle on a ring	304
11.4 Elementary reactions	263	12.11 Vibration: the harmonic oscillator	307
11.5 The formulation of rate laws	264	CHECKLIST OF KEY IDEAS	309
11.6 The steady-state approximation	265	FURTHER INFORMATION 12.1	310
11.7 The rate-determining step	266	DISCUSSION QUESTIONS	311
11.8 Kinetic control	267	EXERCISES	311
11.9 Unimolecular reactions	267	 Chapter 13	
Reactions in solution	268	Atomic structure	313
11.10 Activation control and diffusion control	268		
11.11 Diffusion	270	Hydrogenic atoms	313
Catalysis	273	13.1 The spectra of hydrogenic atoms	314
11.12 Homogeneous catalysis	273	13.2 The permitted energies of hydrogenic atoms	315
11.13 Enzymes	274	13.3 Quantum numbers	317
Chain reactions	277	13.4 The wavefunctions: <i>s</i> orbitals	319
11.14 The structure of chain reactions	277	13.5 The wavefunctions: <i>p</i> and <i>d</i> orbitals	323
11.15 The rate laws of chain reactions	277	13.6 Electron spin	325
Box 11.2 Explosions	278	13.7 Spectral transitions and selection rules	326
CHECKLIST OF KEY IDEAS	280	 The structures of many-electron atoms	327
FURTHER INFORMATION 11.1	280	13.8 The orbital approximation	327
DISCUSSION QUESTIONS	282	13.9 The Pauli exclusion principle	328
EXERCISES	282	13.10 Penetration and shielding	328
 Chapter 12		13.11 The building-up principle	329
Quantum theory	285	13.12 The occupation of <i>d</i> orbitals	330
		13.13 The configurations of cations and anions	331
The failures of classical physics	286	 Periodic trends in atomic properties	331
12.1 Black-body radiation	286	13.14 Atomic radius	332
12.2 Heat capacities	290	13.15 Ionization energy and electron affinity	333

CONTENTS

The spectra of complex atoms	335	Chapter 15	
13.16 Term symbols	335	Metallic, ionic, and covalent solids	375
Box 13.1 Spectroscopy of stars	336		
13.17 Spin-orbit coupling	338	Bonding in solids	375
13.18 Selection rules	338	15.1 The band theory of solids	376
CHECKLIST OF KEY IDEAS	339	15.2 The occupation of bands	377
FURTHER INFORMATION 13.1	340	15.3 The optical properties of junctions	379
DISCUSSION QUESTIONS	340	15.4 Superconductivity	379
EXERCISES	340	15.5 The ionic model of bonding	380
		15.6 Lattice enthalpy	381
Chapter 14		15.7 The origin of lattice enthalpy	383
The chemical bond	343	15.8 Covalent networks	384
		15.9 Magnetic properties of solids	385
Introductory concepts	344	Box 15.1 Nanowires	386
14.1 The classification of bonds	344	Crystal structure	388
14.2 Potential energy curves	344	15.10 Unit cells	389
Valence bond theory	345	15.11 The identification of crystal planes	390
14.3 Diatomic molecules	345	15.12 The determination of structure	393
14.4 Polyatomic molecules	347	15.13 The Bragg law	394
14.5 Promotion and hybridization	348	15.14 Experimental techniques	395
14.6 Resonance	351	15.15 Metal crystals	397
Molecular orbitals	352	15.16 Ionic crystals	399
14.7 Linear combinations of atomic orbitals	352	CHECKLIST OF KEY IDEAS	401
14.8 Bonding and antibonding orbitals	354	DISCUSSION QUESTIONS	402
14.9 The structures of diatomic molecules	355	EXERCISES	402
14.10 Hydrogen and helium molecules	355		
14.11 Period 2 diatomic molecules	357	Chapter 16	
14.12 Symmetry and overlap	359	Solid surfaces	404
14.13 The electronic structures of homonuclear diatomic molecules	361		
14.14 Heteronuclear diatomic molecules	363	The growth and structure of surfaces	405
14.15 The structures of polyatomic molecules	366	16.1 Surface growth	405
Computational chemistry	367	16.2 Surface composition and structure	405
14.16 Semi-empirical methods	368	The extent of adsorption	410
14.17 <i>Ab initio</i> methods and density functional theory	369	16.3 Physisorption and chemisorption	411
14.18 Graphical output	370	16.4 Adsorption isotherms	412
14.19 Applications of computational chemistry	371	16.5 The rates of surface processes	416
CHECKLIST OF KEY IDEAS	372	Catalytic activity at surfaces	418
DISCUSSION QUESTIONS	373	16.6 Mechanisms of heterogeneous catalysis	419
EXERCISES	373	16.7 Examples of catalysis	420

Processes at electrodes	423	18.6	Classification of disperse systems	468
16.8 The electrode–solution interface	424	18.7	Surface, structure, and stability	469
16.9 The rate of electron transfer	425		Box 18.2 Biological membranes	471
16.10 Voltammetry	427	18.8	The electric double layer	473
16.11 Electrolysis	429		CHECKLIST OF KEY IDEAS	474
CHECKLIST OF KEY IDEAS	429		DISCUSSION QUESTIONS	475
DISCUSSION QUESTIONS	430		EXERCISES	476
EXERCISES	431			
 Chapter 17			Chapter 19	
Molecular interactions	433		Molecular rotations and vibrations	478
van der Waals interactions	433		General features of spectroscopy	478
17.1 Interactions between partial charges	434	19.1	Experimental techniques	479
17.2 Electric dipole moments	435		(a) Absorption spectroscopy	479
17.3 Interactions between dipoles	438		(b) Raman spectroscopy	481
17.4 Induced dipole moments	440	19.2	Measures of intensity	482
17.5 Dispersion interactions	441	19.3	Selection rules	483
		19.4	Linewidths	484
The total interaction	442		Rotational spectroscopy	486
17.6 Hydrogen bonding	442	19.5	The rotational energy levels of molecules	486
17.7 The hydrophobic effect	443	19.6	The populations of rotational states	489
Box 17.1 Molecular recognition	444	19.7	Rotational transitions: microwave spectroscopy	491
17.8 Modelling the total interaction	445	19.8	Rotational Raman spectra	493
17.9 Molecules in motion	447		Vibrational spectra	494
CHECKLIST OF KEY IDEAS	448	19.9	The vibrations of molecules	494
DISCUSSION QUESTIONS	448	19.10	Vibrational transitions	495
EXERCISES	449	19.11	Anharmonicity	497
 Chapter 18		19.12	Vibrational Raman spectra of diatomic molecules	497
Macromolecules and aggregates	452	19.13	The vibrations of polyatomic molecules	498
			Box 19.1 Global warming	500
Synthetic and biological macromolecules	453	19.14	Vibration–rotation spectra	502
18.1 Determination of size and shape	453	19.15	Vibrational Raman spectra of polyatomic molecules	503
18.2 Models of structure: random coils	456		CHECKLIST OF KEY IDEAS	504
18.3 Models of structure: polypeptides and polynucleotides	458		FURTHER INFORMATION 19.1	505
18.4 Mechanical properties of polymers	462		FURTHER INFORMATION 19.2	507
Box 18.1 The prediction of protein structure	463		DISCUSSION QUESTIONS	507
			EXERCISES	508
Mesophases and disperse systems	467			
18.5 Liquid crystals	467			

CONTENTS

Chapter 20			
Electronic transitions and photochemistry	510	The information in EPR spectra	559
Ultraviolet and visible spectra	511	21.10 The g -value	560
20.1 The Franck–Condon principle	512	21.11 Hyperfine structure	560
20.2 Circular dichroism	513	CHECKLIST OF KEY IDEAS	563
20.3 Specific types of transitions	514	DISCUSSION QUESTIONS	564
		EXERCISES	564
Radiative and non-radiative decay	515	Chapter 22	
Box 20.1 Vision	516	Statistical thermodynamics	566
20.4 Fluorescence	518	The partition function	566
20.5 Phosphorescence	518	22.1 The Boltzmann distribution	567
20.6 Lasers	519	22.2 The interpretation of the partition function	569
20.7 Applications of lasers in chemistry	524	22.3 Examples of partition functions	571
Photoelectron spectroscopy	526	22.4 The molecular partition function	573
Photochemistry	528	Thermodynamic properties	573
20.8 Quantum yield	528	22.5 The internal energy and the heat capacity	573
Box 20.2 Photosynthesis	529	22.6 The entropy and the Gibbs energy	575
20.9 Mechanisms of photochemical reactions	531	22.7 The statistical basis of chemical equilibrium	578
20.10 The kinetics of decay of excited states	531	22.8 The calculation of the equilibrium constant	579
20.11 Fluorescence quenching	533	CHECKLIST OF KEY IDEAS	580
CHECKLIST OF KEY IDEAS	536	FURTHER INFORMATION 22.1	581
DISCUSSION QUESTIONS	537	FURTHER INFORMATION 22.2	582
EXERCISES	538	DISCUSSION QUESTIONS	582
		EXERCISES	583
Chapter 21		Appendix 1 Quantities and units	585
Magnetic resonance	540	Appendix 2 Mathematical techniques	587
Principles of magnetic resonance	540	Basic procedures	587
21.1 Electrons and nuclei in magnetic fields	541	A2.1 Algebraic equations and graphs	587
21.2 The technique	544	A2.2 Logarithms, exponentials, and powers	588
The information in NMR spectra	545	A2.3 Vectors	589
21.3 The chemical shift	545	Calculus	591
Box 21.1 Magnetic resonance imaging	547	A2.4 Differentiation	591
21.4 The fine structure	550	A2.5 Power series and Taylor expansions	592
21.5 Spin relaxation	554	A2.6 Integration	592
21.6 Proton decoupling	555	A2.7 Differential equations	593
21.7 Conformational conversion and chemical exchange	556		
21.8 The nuclear Overhauser effect	557		
21.9 Two-dimensional NMR	559		

3 Concepts of physics	594	4 Review of chemical principles	599
Classical mechanics	594	A4.1 Oxidation numbers	599
A3.1 Energy	594	A4.2 The Lewis theory of covalent bonding	599
A3.2 Force	594	A4.3 The VSEPR model	601
Electrostatics	595	Data section	604
A3.3 The Coulomb interaction	595		
A3.4 The Coulomb potential	596	1 Thermodynamic data	604
A3.5 Current, resistance, and Ohm's law	596	2 Standard potentials	612
Electromagnetic radiation	596	Answers to exercises	614
A3.6 The electromagnetic field	597	Index	615
A3.7 Features of electromagnetic radiation	597		