

BRIEF CONTENTS

PROLOGUE	1	FOCUS 12 Magnetic resonance	487
FOCUS 1 The properties of gases	3	FOCUS 13 Statistical thermodynamics	531
FOCUS 2 The First Law	33	FOCUS 14 Molecular interactions	583
FOCUS 3 The Second and Third Laws	77	FOCUS 15 Solids	639
FOCUS 4 Physical transformations of pure substances	119	FOCUS 16 Molecules in motion	689
FOCUS 5 Simple mixtures	141	FOCUS 17 Chemical kinetics	721
FOCUS 6 Chemical equilibrium	203	FOCUS 18 Reaction dynamics	779
FOCUS 7 Quantum theory	235	FOCUS 19 Processes at solid surfaces	823
FOCUS 8 Atomic structure and spectra	303	Resource section	
FOCUS 9 Molecular structure	341	1 Common integrals	862
FOCUS 10 Molecular symmetry	387	2 Units	864
FOCUS 11 Molecular spectroscopy	417	3 Data	865
		4 Character tables	895
		Index	899

FULL CONTENTS

Conventions	xxv
List of tables	xxvi
List of <i>The chemist's toolkits</i>	xxviii
List of material provided as <i>A deeper look</i>	xxix
List of <i>Impacts</i>	xxx

PROLOGUE Energy, temperature, and chemistry 1

FOCUS 1 The properties of gases 3

TOPIC 1A The perfect gas 4

1A.1 Variables of state 4

- (a) Pressure 4
- (b) Temperature 5

1A.2 Equations of state 6

- (a) The empirical basis 7
- (b) Mixtures of gases 9

Checklist of concepts 10

Checklist of equations 10

TOPIC 1B The kinetic model 11

1B.1 The model 11

- (a) Pressure and molecular speeds 12
- (b) The Maxwell–Boltzmann distribution of speeds 13
- (c) Mean values 15

1B.2 Collisions 17

- (a) The collision frequency 17
- (b) The mean free path 18

Checklist of concepts 18

Checklist of equations 18

TOPIC 1C Real gases 19

1C.1 Deviations from perfect behaviour 19

- (a) The compression factor 20
- (b) Virial coefficients 20
- (c) Critical constants 22

1C.2 The van der Waals equation 23

- (a) Formulation of the equation 23
- (b) The features of the equation 24
- (c) The principle of corresponding states 26

Checklist of concepts 27

Checklist of equations 27

FOCUS 2 The First Law 33

TOPIC 2A Internal energy 34

2A.1 Work, heat, and energy 34

- (a) Operational definitions 34

- (b) The molecular interpretation of heat and work 36

2A.2 The definition of internal energy 37

- (a) Molecular interpretation of internal energy 37

- (b) The formulation of the First Law 38

2A.3 Expansion work 38

- (a) The general expression for work 39

- (b) Expansion against constant pressure 39

- (c) Reversible expansion 40

- (d) Isothermal reversible expansion of a perfect gas 41

2A.4 Heat transactions 42

- (a) Calorimetry 42

- (b) Heat capacity 43

Checklist of concepts 45

Checklist of equations 45

TOPIC 2B Enthalpy 46

2B.1 The definition of enthalpy 46

- (a) Enthalpy change and heat transfer 46

- (b) Calorimetry 47

2B.2 The variation of enthalpy with temperature 48

- (a) Heat capacity at constant pressure 48

- (b) The relation between heat capacities 49

Checklist of concepts 50

Checklist of equations 50

TOPIC 2C Thermochemistry 51

2C.1 Standard enthalpy changes 51

- (a) Enthalpies of physical change 51

- (b) Enthalpies of chemical change 52

- (c) Hess's law 53

2C.2 Standard enthalpies of formation 54

2C.3 The temperature dependence of reaction enthalpies 55

2C.4 Experimental techniques 56

- (a) Differential scanning calorimetry 56

- (b) Isothermal titration calorimetry 57

Checklist of concepts 57

Checklist of equations 58

TOPIC 2D State functions and exact differentials 59

2D.1 Exact and inexact differentials 59

2D.2 Changes in internal energy 60

- (a) General considerations 60

- (b) Changes in internal energy at constant pressure 62

2D.3 Changes in enthalpy 63

2D.4 The Joule–Thomson effect 64

- (a) The observation of the Joule–Thomson effect 64

- (b) The molecular interpretation of the Joule–Thomson effect 65

Checklist of concepts 66

Checklist of equations 66

TOPIC 2E Adiabatic changes	67	3E.2 Properties of the Gibbs energy	106
2E.1 The change in temperature	67	(a) General considerations	106
2E.2 The change in pressure	68	(b) The variation of the Gibbs energy with temperature	108
Checklist of concepts	69	(c) The variation of the Gibbs energy with pressure	108
Checklist of equations	69	Checklist of concepts	110
		Checklist of equations	110
FOCUS 3 The Second and Third Laws	77	FOCUS 4 Physical transformations of pure substances	119
TOPIC 3A Entropy	78	TOPIC 4A Phase diagrams of pure substances	120
3A.1 The Second Law	78	4A.1 The stabilities of phases	120
3A.2 The definition of entropy	80	(a) The number of phases	120
(a) The thermodynamic definition of entropy	80	(b) Phase transitions	120
(b) The statistical definition of entropy	81	(c) Thermodynamic criteria of phase stability	121
3A.3 The entropy as a state function	82	4A.2 Phase boundaries	122
(a) The Carnot cycle	82	(a) Characteristic properties related to phase transitions	122
(b) The thermodynamic temperature	85	(b) The phase rule	123
(c) The Clausius inequality	85	4A.3 Three representative phase diagrams	125
Checklist of concepts	86	(a) Carbon dioxide	125
Checklist of equations	87	(b) Water	125
		(c) Helium	126
TOPIC 3B Entropy changes accompanying specific processes	88	Checklist of concepts	127
3B.1 Expansion	88	Checklist of equations	127
3B.2 Phase transitions	89	TOPIC 4B Thermodynamic aspects of phase transitions	128
3B.3 Heating	90	4B.1 The dependence of stability on the conditions	128
3B.4 Composite processes	90	(a) The temperature dependence of phase stability	128
Checklist of concepts	91	(b) The response of melting to applied pressure	129
Checklist of equations	91	(c) The vapour pressure of a liquid subjected to pressure	130
TOPIC 3C The measurement of entropy	92	4B.2 The location of phase boundaries	131
3C.1 The calorimetric measurement of entropy	92	(a) The slopes of the phase boundaries	131
3C.2 The Third Law	93	(b) The solid–liquid boundary	132
(a) The Nernst heat theorem	93	(c) The liquid–vapour boundary	132
(b) Third-Law entropies	94	(d) The solid–vapour boundary	134
(c) The temperature dependence of reaction entropy	95	Checklist of concepts	134
Checklist of concepts	96	Checklist of equations	134
Checklist of equations	96		
TOPIC 3D Concentrating on the system	97	FOCUS 5 Simple mixtures	141
3D.1 The Helmholtz and Gibbs energies	97	TOPIC 5A The thermodynamic description of mixtures	143
(a) Criteria of spontaneity	97	5A.1 Partial molar quantities	143
(b) Some remarks on the Helmholtz energy	98	(a) Partial molar volume	143
(c) Maximum work	98	(b) Partial molar Gibbs energies	145
(d) Some remarks on the Gibbs energy	99	(c) The wider significance of the chemical potential	146
(e) Maximum non-expansion work	100	(d) The Gibbs–Duhem equation	146
3D.2 Standard molar Gibbs energies	100	5A.2 The thermodynamics of mixing	147
(a) Gibbs energies of formation	101	(a) The Gibbs energy of mixing of perfect gases	147
(b) The Born equation	102	(b) Other thermodynamic mixing functions	149
Checklist of concepts	103	5A.3 The chemical potentials of liquids	150
Checklist of equations	103	(a) Ideal solutions	150
TOPIC 3E Combining the First and Second Laws	104	(b) Ideal–dilute solutions	152
3E.1 Properties of the internal energy	104	Checklist of concepts	153
(a) The Maxwell relations	104	Checklist of equations	154
(b) The variation of internal energy with volume	106		

TOPIC 5B The properties of solutions	155	FOCUS 6 Chemical equilibrium	203
5B.1 Liquid mixtures	155	TOPIC 6A The equilibrium constant	204
(a) Ideal solutions	155	6A.1 The Gibbs energy minimum	204
(b) Excess functions and regular solutions	156	(a) The reaction Gibbs energy	204
5B.2 Colligative properties	158	(b) Exergonic and endergonic reactions	205
(a) The common features of colligative properties	158	6A.2 The description of equilibrium	205
(b) The elevation of boiling point	159	(a) Perfect gas equilibria	205
(c) The depression of freezing point	161	(b) The general case of a reaction	206
(d) Solubility	161	(c) The relation between equilibrium constants	209
(e) Osmosis	162	(d) Molecular interpretation of the equilibrium constant	210
Checklist of concepts	164	Checklist of concepts	211
Checklist of equations	165	Checklist of equations	211
TOPIC 5C Phase diagrams of binary systems: liquids	166	TOPIC 6B The response of equilibria to the conditions	212
5C.1 Vapour pressure diagrams	166	6B.1 The response to pressure	212
5C.2 Temperature–composition diagrams	168	6B.2 The response to temperature	213
(a) The construction of the diagrams	168	(a) The van 't Hoff equation	213
(b) The interpretation of the diagrams	169	(b) The value of K at different temperatures	215
5C.3 Distillation	170	Checklist of concepts	216
(a) Simple and fractional distillation	170	Checklist of equations	216
(b) Azeotropes	171	TOPIC 6C Electrochemical cells	217
(c) Immiscible liquids	172	6C.1 Half-reactions and electrodes	217
5C.4 Liquid–liquid phase diagrams	172	6C.2 Varieties of cells	218
(a) Phase separation	172	(a) Liquid junction potentials	218
(b) Critical solution temperatures	173	(b) Notation	219
(c) The distillation of partially miscible liquids	175	6C.3 The cell potential	219
Checklist of concepts	176	(a) The Nernst equation	219
Checklist of equations	176	(b) Cells at equilibrium	221
TOPIC 5D Phase diagrams of binary systems: solids	177	6C.4 The determination of thermodynamic functions	221
5D.1 Eutectics	177	Checklist of concepts	223
5D.2 Reacting systems	178	Checklist of equations	223
5D.3 Incongruent melting	179	TOPIC 6D Electrode potentials	224
Checklist of concepts	179	6D.1 Standard potentials	224
TOPIC 5E Phase diagrams of ternary systems	180	(a) The measurement procedure	225
5E.1 Triangular phase diagrams	180	(b) Combining measured values	226
5E.2 Ternary systems	181	6D.2 Applications of standard potentials	226
(a) Partially miscible liquids	181	(a) The electrochemical series	226
(b) Ternary solids	182	(b) The determination of activity coefficients	226
Checklist of concepts	182	(c) The determination of equilibrium constants	227
TOPIC 5F Activities	183	Checklist of concepts	227
5F.1 The solvent activity	183	Checklist of equations	228
5F.2 The solute activity	183	FOCUS 7 Quantum theory	235
(a) Ideal–dilute solutions	184	TOPIC 7A The origins of quantum mechanics	237
(b) Real solutes	184	7A.1 Energy quantization	237
(c) Activities in terms of molalities	185	(a) Black-body radiation	237
5F.3 The activities of regular solutions	185	(b) Heat capacity	240
5F.4 The activities of ions	187	(c) Atomic and molecular spectra	241
(a) Mean activity coefficients	187	7A.2 Wave–particle duality	242
(b) The Debye–Hückel limiting law	187	(a) The particle character of electromagnetic radiation	242
(c) Extensions of the limiting law	188	(b) The wave character of particles	244
Checklist of concepts	189		
Checklist of equations	190		

Checklist of concepts	245	Checklist of concepts	290
Checklist of equations	245	Checklist of equations	290
TOPIC 7B Wavefunctions	246	FOCUS 8 Atomic structure and spectra	303
7B.1 The Schrödinger equation	246	TOPIC 8A Hydrogenic atoms	304
7B.2 The Born interpretation	247	8A.1 The structure of hydrogenic atoms	304
(a) Normalization	248	(a) The separation of variables	304
(b) Constraints on the wavefunction	249	(b) The radial solutions	305
(c) Quantization	250	8A.2 Atomic orbitals and their energies	308
Checklist of concepts	250	(a) The specification of orbitals	308
Checklist of equations	250	(b) The energy levels	308
TOPIC 7C Operators and observables	251	(c) Ionization energies	309
7C.1 Operators	251	(d) Shells and subshells	309
(a) Eigenvalue equations	251	(e) s Orbitals	310
(b) The construction of operators	252	(f) Radial distribution functions	311
(c) Hermitian operators	253	(g) p Orbitals	313
(d) Orthogonality	254	(h) d Orbitals	314
7C.2 Superpositions and expectation values	255	Checklist of concepts	314
7C.3 The uncertainty principle	257	Checklist of equations	315
7C.4 The postulates of quantum mechanics	259	TOPIC 8B Many-electron atoms	316
Checklist of concepts	260	8B.1 The orbital approximation	316
Checklist of equations	260	8B.2 The Pauli exclusion principle	317
TOPIC 7D Translational motion	261	(a) Spin	317
7D.1 Free motion in one dimension	261	(b) The Pauli principle	318
7D.2 Confined motion in one dimension	262	8B.3 The building-up principle	319
(a) The acceptable solutions	263	(a) Penetration and shielding	319
(b) The properties of the wavefunctions	264	(b) Hund's rules	321
(c) The properties of the energy	265	(c) Atomic and ionic radii	323
7D.3 Confined motion in two and more dimensions	266	(d) Ionization energies and electron affinities	324
(a) Energy levels and wavefunctions	266	8B.4 Self-consistent field orbitals	325
(b) Degeneracy	267	Checklist of concepts	325
7D.4 Tunnelling	268	Checklist of equations	326
Checklist of concepts	271	TOPIC 8C Atomic spectra	327
Checklist of equations	272	8C.1 The spectra of hydrogenic atoms	327
TOPIC 7E Vibrational motion	273	8C.2 The spectra of many-electron atoms	328
7E.1 The harmonic oscillator	273	(a) Singlet and triplet terms	328
(a) The energy levels	274	(b) Spin-orbit coupling	329
(b) The wavefunctions	275	(c) Term symbols	332
7E.2 Properties of the harmonic oscillator	277	(d) Hund's rules	335
(a) Mean values	277	(e) Selection rules	335
(b) Tunnelling	278	Checklist of concepts	336
Checklist of concepts	279	Checklist of equations	336
Checklist of equations	280	FOCUS 9 Molecular structure	341
TOPIC 7F Rotational motion	281	PROLOGUE The Born–Oppenheimer approximation	343
7F.1 Rotation in two dimensions	281	TOPIC 9A Valence-bond theory	344
(a) The solutions of the Schrödinger equation	283	9A.1 Diatomic molecules	344
(b) Quantization of angular momentum	284	9A.2 Resonance	346
7F.2 Rotation in three dimensions	285	9A.3 Polyatomic molecules	346
(a) The wavefunctions and energy levels	285	(a) Promotion	347
(b) Angular momentum	288	(b) Hybridization	347
(c) The vector model	288		

Checklist of concepts	350	(e) The cubic groups	393
Checklist of equations	350	(f) The full rotation group	394
TOPIC 9B Molecular orbital theory: the hydrogen molecule-ion	351	10A.3 Some immediate consequences of symmetry	394
9B.1 Linear combinations of atomic orbitals	351	(a) Polarity	394
(a) The construction of linear combinations	351	(b) Chirality	395
(b) Bonding orbitals	353	Checklist of concepts	395
(c) Antibonding orbitals	354	Checklist of operations and elements	396
9B.2 Orbital notation	356	TOPIC 10B Group theory	397
Checklist of concepts	356	10B.1 The elements of group theory	397
Checklist of equations	356	10B.2 Matrix representations	398
TOPIC 9C Molecular orbital theory: homonuclear diatomic molecules	357	(a) Representatives of operations	398
9C.1 Electron configurations	357	(b) The representation of a group	399
(a) σ Orbitals and π orbitals	357	(c) Irreducible representations	400
(b) The overlap integral	359	(d) Characters	401
(c) Period 2 diatomic molecules	360	10B.3 Character tables	401
9C.2 Photoelectron spectroscopy	362	(a) The symmetry species of atomic orbitals	402
Checklist of concepts	363	(b) The symmetry species of linear combinations of orbitals	403
Checklist of equations	364	(c) Character tables and degeneracy	404
TOPIC 9D Molecular orbital theory: heteronuclear diatomic molecules	365	Checklist of concepts	405
9D.1 Polar bonds and electronegativity	365	Checklist of equations	405
9D.2 The variation principle	366	TOPIC 10C Applications of symmetry	406
(a) The procedure	367	10C.1 Vanishing integrals	406
(b) The features of the solutions	369	(a) Integrals of the product of functions	407
Checklist of concepts	370	(b) Decomposition of a representation	408
Checklist of equations	370	10C.2 Applications to molecular orbital theory	409
TOPIC 9E Molecular orbital theory: polyatomic molecules	371	(a) Orbital overlap	409
9E.1 The Hückel approximation	371	(b) Symmetry-adapted linear combinations	409
(a) An introduction to the method	371	10C.3 Selection rules	411
(b) The matrix formulation of the method	372	Checklist of concepts	411
9E.2 Applications	375	Checklist of equations	411
(a) π -Electron binding energy	375	FOCUS 11 Molecular spectroscopy	417
(b) Aromatic stability	376	TOPIC 11A General features of molecular spectroscopy	419
9E.3 Computational chemistry	377	11A.1 The absorption and emission of radiation	420
(a) Semi-empirical and <i>ab initio</i> methods	378	(a) Stimulated and spontaneous radiative processes	420
(b) Density functional theory	379	(b) Selection rules and transition moments	421
(c) Graphical representations	379	(c) The Beer–Lambert law	421
Checklist of concepts	380	11A.2 Spectral linewidths	423
Checklist of equations	380	(a) Doppler broadening	423
FOCUS 10 Molecular symmetry	387	(b) Lifetime broadening	425
TOPIC 10A Shape and symmetry	388	11A.3 Experimental techniques	425
10A.1 Symmetry operations and symmetry elements	388	(a) Sources of radiation	426
10A.2 The symmetry classification of molecules	390	(b) Spectral analysis	426
(a) The groups C_1 , C_p , and C_s	392	(c) Detectors	428
(b) The groups C_n , C_{nv} , and C_{nh}	392	(d) Examples of spectrometers	428
(c) The groups D_n , D_{nh} , and D_{nd}	393	Checklist of concepts	429
(d) The groups S_n	393	Checklist of equations	429
		TOPIC 11B Rotational spectroscopy	430
		11B.1 Rotational energy levels	430
		(a) Spherical rotors	432

(b) Symmetric rotors	432	TOPIC 11G Decay of excited states	470
(c) Linear rotors	434	11G.1 Fluorescence and phosphorescence	470
(d) Centrifugal distortion	434	11G.2 Dissociation and predissociation	472
11B.2 Microwave spectroscopy	435	11G.3 Lasers	473
(a) Selection rules	435	Checklist of concepts	474
(b) The appearance of microwave spectra	436		
11B.3 Rotational Raman spectroscopy	437		
11B.4 Nuclear statistics and rotational states	439	FOCUS 12 Magnetic resonance	487
Checklist of concepts	441	TOPIC 12A General principles	488
Checklist of equations	441	12A.1 Nuclear magnetic resonance	488
TOPIC 11C Vibrational spectroscopy of diatomic molecules	442	(a) The energies of nuclei in magnetic fields	488
11C.1 Vibrational motion	442	(b) The NMR spectrometer	490
11C.2 Infrared spectroscopy	443	12A.2 Electron paramagnetic resonance	491
11C.3 Anharmonicity	444	(a) The energies of electrons in magnetic fields	491
(a) The convergence of energy levels	444	(b) The EPR spectrometer	492
(b) The Birge–Sponer plot	445	Checklist of concepts	493
11C.4 Vibration–rotation spectra	446	Checklist of equations	493
(a) Spectral branches	447		
(b) Combination differences	448	TOPIC 12B Features of NMR spectra	494
11C.5 Vibrational Raman spectra	448	12B.1 The chemical shift	494
Checklist of concepts	449	12B.2 The origin of shielding constants	496
Checklist of equations	450	(a) The local contribution	496
		(b) Neighbouring group contributions	497
TOPIC 11D Vibrational spectroscopy of polyatomic molecules	451	(c) The solvent contribution	498
11D.1 Normal modes	451	12B.3 The fine structure	499
11D.2 Infrared absorption spectra	452	(a) The appearance of the spectrum	499
11D.3 Vibrational Raman spectra	453	(b) The magnitudes of coupling constants	501
Checklist of concepts	454	(c) The origin of spin–spin coupling	502
Checklist of equations	454	(d) Equivalent nuclei	503
		(e) Strongly coupled nuclei	504
TOPIC 11E Symmetry analysis of vibrational spectra	455	12B.4 Exchange processes	505
11E.1 Classification of normal modes according to symmetry	455	12B.5 Solid-state NMR	506
11E.2 Symmetry of vibrational wavefunctions	457	Checklist of concepts	507
(a) Infrared activity of normal modes	457	Checklist of equations	508
(b) Raman activity of normal modes	458		
(c) The symmetry basis of the exclusion rule	458	TOPIC 12C Pulse techniques in NMR	509
Checklist of concepts	458	12C.1 The magnetization vector	509
TOPIC 11F Electronic spectra	459	(a) The effect of the radiofrequency field	510
11F.1 Diatomic molecules	459	(b) Time- and frequency-domain signals	511
(a) Term symbols	459	12C.2 Spin relaxation	513
(b) Selection rules	461	(a) The mechanism of relaxation	513
(c) Vibrational fine structure	462	(b) The measurement of T_1 and T_2	514
(d) Rotational fine structure	465	12C.3 Spin decoupling	515
11F.2 Polyatomic molecules	466	12C.4 The nuclear Overhauser effect	516
(a) d-Metal complexes	467	Checklist of concepts	518
(b) $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions	468	Checklist of equations	518
Checklist of concepts	469		
Checklist of equations	469	TOPIC 12D Electron paramagnetic resonance	519
		12D.1 The g -value	519
		12D.2 Hyperfine structure	520
		(a) The effects of nuclear spin	520
		(b) The McConnell equation	521
		(c) The origin of the hyperfine interaction	522

Checklist of concepts	523	(e) Residual entropies	565
Checklist of equations	523	Checklist of concepts	566
		Checklist of equations	566
FOCUS 13 Statistical thermodynamics	531	TOPIC 13F Derived functions	567
TOPIC 13A The Boltzmann distribution	532	13F.1 The derivations	567
13A.1 Configurations and weights	532	13F.2 Equilibrium constants	570
(a) Instantaneous configurations	532	(a) The relation between K and the partition function	570
(b) The most probable distribution	533	(b) A dissociation equilibrium	570
(c) The values of the constants	535	(c) Contributions to the equilibrium constant	571
13A.2 The relative population of states	536	Checklist of concepts	573
Checklist of concepts	536	Checklist of equations	573
Checklist of equations	537		
TOPIC 13B Molecular partition functions	538	FOCUS 14 Molecular interactions	583
13B.1 The significance of the partition function	538	TOPIC 14A The electric properties of molecules	585
13B.2 Contributions to the partition function	540	14A.1 Electric dipole moments	585
(a) The translational contribution	540	14A.2 Polarizabilities	587
(b) The rotational contribution	542	14A.3 Polarization	588
(c) The vibrational contribution	546	(a) The frequency dependence of the polarization	588
(d) The electronic contribution	547	(b) Molar polarization	590
Checklist of concepts	548	Checklist of concepts	592
Checklist of equations	548	Checklist of equations	592
TOPIC 13C Molecular energies	549	TOPIC 14B Interactions between molecules	593
13C.1 The basic equations	549	14B.1 The interactions of dipoles	593
13C.2 Contributions of the fundamental modes of motion	550	(a) Charge–dipole interactions	593
(a) The translational contribution	550	(b) Dipole–dipole interactions	594
(b) The rotational contribution	550	(c) Dipole–induced dipole interactions	597
(c) The vibrational contribution	551	(d) Induced dipole–induced dipole interactions	597
(d) The electronic contribution	552	14B.2 Hydrogen bonding	598
(e) The spin contribution	552	14B.3 The total interaction	599
Checklist of concepts	553	Checklist of concepts	601
Checklist of equations	553	Checklist of equations	601
TOPIC 13D The canonical ensemble	554	TOPIC 14C Liquids	602
13D.1 The concept of ensemble	554	14C.1 Molecular interactions in liquids	602
(a) Dominating configurations	555	(a) The radial distribution function	602
(b) Fluctuations from the most probable distribution	555	(b) The calculation of $g(r)$	603
13D.2 The mean energy of a system	556	(c) The thermodynamic properties of liquids	604
13D.3 Independent molecules revisited	556	14C.2 The liquid–vapour interface	605
13D.4 The variation of the energy with volume	557	(a) Surface tension	605
Checklist of concepts	558	(b) Curved surfaces	606
Checklist of equations	558	(c) Capillary action	606
TOPIC 13E The internal energy and the entropy	559	14C.3 Surface films	608
13E.1 The internal energy	559	(a) Surface pressure	608
(a) The calculation of internal energy	559	(b) The thermodynamics of surface layers	609
(b) Heat capacity	560	14C.4 Condensation	611
13E.2 The entropy	561	Checklist of concepts	612
(a) Entropy and the partition function	561	Checklist of equations	612
(b) The translational contribution	563		
(c) The rotational contribution	563	TOPIC 14D Macromolecules	613
(d) The vibrational contribution	564	14D.1 Average molar masses	613
		14D.2 The different levels of structure	614

14D.3 Random coils	615	TOPIC 15D The mechanical properties of solids	666
(a) Measures of size	615	Checklist of concepts	667
(b) Constrained chains	618	Checklist of equations	668
(c) Partly rigid coils	618	TOPIC 15E The electrical properties of solids	669
14D.4 Mechanical properties	619	15E.1 Metallic conductors	669
(a) Conformational entropy	619	15E.2 Insulators and semiconductors	670
(b) Elastomers	620	15E.3 Superconductors	672
14D.5 Thermal properties	621	Checklist of concepts	673
Checklist of concepts	622	Checklist of equations	673
Checklist of equations	622	TOPIC 15F The magnetic properties of solids	674
TOPIC 14E Self-assembly	623	15F.1 Magnetic susceptibility	674
14E.1 Colloids	623	15F.2 Permanent and induced magnetic moments	675
(a) Classification and preparation	623	15F.3 Magnetic properties of superconductors	676
(b) Structure and stability	624	Checklist of concepts	676
(c) The electrical double layer	624	Checklist of equations	677
14E.2 Micelles and biological membranes	626	TOPIC 15G The optical properties of solids	678
(a) The hydrophobic interaction	626	15G.1 Excitons	678
(b) Micelle formation	627	15G.2 Metals and semiconductors	679
(c) Bilayers, vesicles, and membranes	628	(a) Light absorption	679
Checklist of concepts	630	(b) Light-emitting diodes and diode lasers	680
Checklist of equations	630	15G.3 Nonlinear optical phenomena	680
FOCUS 15 Solids	639	Checklist of concepts	681
TOPIC 15A Crystal structure	641	FOCUS 16 Molecules in motion	689
15A.1 Periodic crystal lattices	641	TOPIC 16A Transport properties of a perfect gas	690
15A.2 The identification of lattice planes	643	16A.1 The phenomenological equations	690
(a) The Miller indices	643	16A.2 The transport parameters	692
(b) The separation of neighbouring planes	644	(a) The diffusion coefficient	693
Checklist of concepts	645	(b) Thermal conductivity	694
Checklist of equations	645	(c) Viscosity	696
TOPIC 15B Diffraction techniques	646	(d) Effusion	697
15B.1 X-ray crystallography	646	Checklist of concepts	697
(a) X-ray diffraction	646	Checklist of equations	698
(b) Bragg's law	648	TOPIC 16B Motion in liquids	699
(c) Scattering factors	649	16B.1 Experimental results	699
(d) The electron density	649	(a) Liquid viscosity	699
(e) The determination of structure	652	(b) Electrolyte solutions	700
15B.2 Neutron and electron diffraction	654	16B.2 The mobilities of ions	701
Checklist of concepts	655	(a) The drift speed	701
Checklist of equations	655	(b) Mobility and conductivity	703
TOPIC 15C Bonding in solids	656	(c) The Einstein relations	704
15C.1 Metals	656	Checklist of concepts	705
(a) Close packing	656	Checklist of equations	705
(b) Electronic structure of metals	658	FOCUS 16C Diffusion	706
15C.2 Ionic solids	660	16C.1 The thermodynamic view	706
(a) Structure	660	16C.2 The diffusion equation	708
(b) Energetics	661	(a) Simple diffusion	708
15C.3 Covalent and molecular solids	663		
Checklist of concepts	664		
Checklist of equations	665		

(b) Diffusion with convection	710	(a) Stepwise polymerization	755
(c) Solutions of the diffusion equation	710	(b) Chain polymerization	756
16C.3 The statistical view	712	17F.3 Enzyme-catalysed reactions	758
Checklist of concepts	713	Checklist of concepts	761
Checklist of equations	714	Checklist of equations	761
FOCUS 17 Chemical kinetics	721	TOPIC 17G Photochemistry	762
TOPIC 17A The rates of chemical reactions	723	17G.1 Photochemical processes	762
17A.1 Monitoring the progress of a reaction	723	17G.2 The primary quantum yield	763
(a) General considerations	723	17G.3 Mechanism of decay of excited singlet states	764
(b) Special techniques	724	17G.4 Quenching	765
17A.2 The rates of reactions	725	17G.5 Resonance energy transfer	767
(a) The definition of rate	725	Checklist of concepts	768
(b) Rate laws and rate constants	726	Checklist of equations	768
(c) Reaction order	727	FOCUS 18 Reaction dynamics	779
(d) The determination of the rate law	728	TOPIC 18A Collision theory	780
Checklist of concepts	729	18A.1 Reactive encounters	780
Checklist of equations	730	(a) Collision rates in gases	781
TOPIC 17B Integrated rate laws	731	(b) The energy requirement	781
17B.1 Zeroth-order reactions	731	(c) The steric requirement	784
17B.2 First-order reactions	731	18A.2 The RRK model	785
17B.3 Second-order reactions	733	Checklist of concepts	786
Checklist of concepts	736	Checklist of equations	786
Checklist of equations	736	TOPIC 18B Diffusion-controlled reactions	787
TOPIC 17C Reactions approaching equilibrium	737	18B.1 Reactions in solution	787
17C.1 First-order reactions approaching equilibrium	737	(a) Classes of reaction	787
17C.2 Relaxation methods	738	(b) Diffusion and reaction	788
Checklist of concepts	740	18B.2 The material-balance equation	789
Checklist of equations	740	(a) The formulation of the equation	789
TOPIC 17D The Arrhenius equation	741	(b) Solutions of the equation	790
17D.1 The temperature dependence of reaction rates	741	Checklist of concepts	790
17D.2 The interpretation of the Arrhenius parameters	742	Checklist of equations	791
(a) A first look at the energy requirements of reactions	743	TOPIC 18C Transition-state theory	792
(b) The effect of a catalyst on the activation energy	744	18C.1 The Eyring equation	792
Checklist of concepts	745	(a) The formulation of the equation	792
Checklist of equations	745	(b) The rate of decay of the activated complex	793
TOPIC 17E Reaction mechanisms	746	(c) The concentration of the activated complex	793
17E.1 Elementary reactions	746	(d) The rate constant	794
17E.2 Consecutive elementary reactions	747	18C.2 Thermodynamic aspects	795
17E.3 The steady-state approximation	748	(a) Activation parameters	795
17E.4 The rate-determining step	749	(b) Reactions between ions	797
17E.5 Pre-equilibria	750	18C.3 The kinetic isotope effect	798
17E.6 Kinetic and thermodynamic control of reactions	752	Checklist of concepts	800
Checklist of concepts	752	Checklist of equations	800
Checklist of equations	752	TOPIC 18D The dynamics of molecular collisions	801
TOPIC 17F Examples of reaction mechanisms	753	18D.1 Molecular beams	801
17F.1 Unimolecular reactions	753	(a) Techniques	801
17F.2 Polymerization kinetics	754	(b) Experimental results	802
		18D.2 Reactive collisions	804
		(a) Probes of reactive collisions	804

(b) State-to-state reaction dynamics	804	(d) The Temkin and Freundlich isotherms	837
18D.3 Potential energy surfaces	805	19B.2 The rates of adsorption and desorption	837
18D.4 Some results from experiments and calculations	806	(a) The precursor state	837
(a) The direction of attack and separation	807	(b) Adsorption and desorption at the molecular level	838
(b) Attractive and repulsive surfaces	808	(c) Mobility on surfaces	839
(c) Quantum mechanical scattering theory	808	Checklist of concepts	840
Checklist of concepts	809	Checklist of equations	840
Checklist of equations	809	TOPIC 19C Heterogeneous catalysis	841
TOPIC 18E Electron transfer in homogeneous systems	810	19C.1 Mechanisms of heterogeneous catalysis	841
18E.1 The rate law	810	(a) Unimolecular reactions	841
18E.2 The role of electron tunnelling	811	(b) The Langmuir–Hinshelwood mechanism	842
18E.3 The rate constant	812	(c) The Eley–Rideal mechanism	843
18E.4 Experimental tests of the theory	813	19C.2 Catalytic activity at surfaces	843
Checklist of concepts	815	Checklist of concepts	844
Checklist of equations	815	Checklist of equations	844
FOCUS 19 Processes at solid surfaces	823	TOPIC 19D Processes at electrodes	845
TOPIC 19A An introduction to solid surfaces	824	19D.1 The electrode–solution interface	845
19A.1 Surface growth	824	19D.2 The current density at an electrode	846
19A.2 Physisorption and chemisorption	825	(a) The Butler–Volmer equation	846
19A.3 Experimental techniques	826	(b) Tafel plots	850
(a) Microscopy	827	19D.3 Voltammetry	850
(b) Ionization techniques	828	19D.4 Electrolysis	852
(c) Diffraction techniques	829	19D.5 Working galvanic cells	853
(d) Determination of the extent and rates of adsorption and desorption	830	Checklist of concepts	854
Checklist of concepts	831	Checklist of equations	854
Checklist of equations	831	Resource section	861
TOPIC 19B Adsorption and desorption	832	1 Common integrals	862
19B.1 Adsorption isotherms	832	2 Units	864
(a) The Langmuir isotherm	832	3 Data	865
(b) The isosteric enthalpy of adsorption	834	4 Character tables	895
(c) The BET isotherm	835	Index	899