

Full contents

Conventions	xxii
List of <i>The chemist's toolkits</i>	xxiii
List of tables	xxiv
List of Impacts	xxvi
Energy, temperature, and chemistry	1

FOCUS 1

The properties of gases	3
--------------------------------	----------

1A The perfect gas

1A.1 The perfect gas equation of state	6
1A.2 Using the perfect gas law	9
1A.3 Mixtures of gases: partial pressures	10
CHECKLIST OF KEY CONCEPTS	12

1B The kinetic model of gases

1B.1 The pressure of a gas according to the kinetic model	13
1B.2 The root-mean-square speed of gas molecules	16
1B.3 The Maxwell distribution of speeds	16
1B.4 Diffusion and effusion	18
1B.5 Molecular collisions	19
CHECKLIST OF KEY CONCEPTS	22

1C Real gases

1C.1 Molecular interactions	24
1C.2 The critical temperature	24
1C.3 The compression factor	26
1C.4 The virial equation of state	27
1C.5 The van der Waals equation of state	28
1C.6 The liquefaction of gases	30
CHECKLIST OF KEY CONCEPTS	32

Exercises, discussion questions, problems, and projects

33

5.3.3 The variation of potential with pH	33
5.3.4 The second law of standard potentials	37
5.3.5 Thermodynamic data from standard potentials	37
5.3.6 The direction of spontaneous change	37

FOCUS 2

The First Law of thermodynamics	37
--	-----------

2A Work

2A.1 Systems and surroundings	40
2A.2 Expansion work	41
2A.3 Reversible expansion	43
CHECKLIST OF KEY CONCEPTS	46

2B Heat

2B.1 Conventions	47
2B.2 Heat capacity	48
2B.3 Calorimetry	49
2B.4 Heat influx during expansion	51
CHECKLIST OF KEY CONCEPTS	51

2C Internal energy

2C.1 The internal energy	52
2C.2 The internal energy as a state function	53
2C.3 Changes in the internal energy	53
2C.4 The molecular basis of the internal energy	55
CHECKLIST OF KEY CONCEPTS	56

2D Enthalpy

2D.1 The definition of enthalpy	58
2D.2 Changes in enthalpy	58
2D.3 The temperature dependence of the enthalpy	59
CHECKLIST OF KEY CONCEPTS	61

2E Physical change

2E.1 The enthalpy of phase transition	62
2E.2 Ionization and electron attachment	66
CHECKLIST OF KEY CONCEPTS	68

2F Chemical change

2F.1 Bond dissociation	69
2F.2 Enthalpies of combustion	71
2F.3 The combination of reaction enthalpies	73
2F.4 Standard enthalpies of formation	74
2F.5 The variation of reaction enthalpy with temperature	76
CHECKLIST OF KEY CONCEPTS	78

Exercises, discussion questions, problems, and projects

79

FOCUS 3		
The Second Law of thermodynamics	87	
3A Entropy	88	
3A.1 The direction of spontaneous change	88	
3A.2 Entropy and the Second Law	89	
3A.3 Heat engines, refrigerators, and heat pumps	90	
CHECKLIST OF KEY CONCEPTS	92	
3B Entropy changes	93	
3B.1 The entropy change accompanying a change in volume	93	
3B.2 The entropy change accompanying a change in temperature	94	
3B.3 The entropy change accompanying a phase transition	96	
3B.4 Entropy changes in the surroundings	98	
CHECKLIST OF KEY CONCEPTS	99	
3C Absolute entropy	100	
3C.1 The Third Law of thermodynamics	100	
3C.2 The molecular interpretation of entropy	102	
3C.3 Residual entropy	104	
CHECKLIST OF KEY CONCEPTS	105	
3D The Gibbs energy	106	
3D.1 The standard reaction entropy	106	
3D.2 The spontaneity of chemical reactions	107	
3D.3 Focusing on the system	107	
3D.4 Properties of the Gibbs energy	108	
CHECKLIST OF KEY CONCEPTS	110	
Exercises, discussion questions, problems, and projects	111	
FOCUS 4		
Physical transformations	115	
4A The thermodynamics of transition	117	
4A.1 The condition of stability	117	
4A.2 The variation of Gibbs energy with pressure	118	
4A.3 The variation of Gibbs energy with temperature	120	
4A.4 The Gibbs–Helmholtz equation	122	
CHECKLIST OF KEY CONCEPTS	123	
4B Phase diagrams of pure substances	124	
4B.1 Phase boundaries	124	
4B.2 The location of phase boundaries	126	
4B.3 Characteristic points	130	
4B.4 The phase rule	131	
4B.5 Phase diagrams of typical materials	133	
CHECKLIST OF KEY CONCEPTS	135	
4C Partial molar quantities	136	
4C.1 Partial molar volume	136	
4C.2 The chemical potential	137	
4C.3 Spontaneous mixing	139	
CHECKLIST OF KEY CONCEPTS	141	
4D Solutions	142	
4D.1 Ideal solutions	142	
4D.2 The chemical potential of the solvent	144	
4D.3 Ideal–dilute solutions	145	
4D.4 The chemical potential of the solute	147	
4D.5 Real solutions: activities	149	
CHECKLIST OF KEY CONCEPTS	150	
4E Colligative properties	151	
4E.1 The modification of boiling and freezing points	151	
4E.2 Osmosis	154	
CHECKLIST OF KEY CONCEPTS	157	
4F Phase diagrams of mixtures	158	
4F.1 Mixtures of volatile liquids	158	
4F.2 Liquid–liquid phase diagrams	160	
4F.3 Liquid–solid phase diagrams	162	
4F.4 Zone refining	164	
4F.5 The Nernst distribution law	165	
CHECKLIST OF KEY CONCEPTS	166	
Exercises, discussion questions, problems, and projects	167	
FOCUS 5		
Chemical change	175	
5A The thermodynamics of reaction	177	
5A.1 The reaction Gibbs energy	177	
5A.2 The variation of $\Delta_r G$ with composition	179	
5A.3 Reactions at equilibrium	180	
5A.4 The standard reaction Gibbs energy	183	
CHECKLIST OF KEY CONCEPTS	184	
5B The equilibrium constant	185	
5B.1 The composition at equilibrium	185	
5B.2 The equilibrium constant in terms of concentration	187	

5B.3	The molecular interpretation of equilibrium constants	188	5J.3	The variation of potential with pH	235
CHECKLIST OF KEY CONCEPTS		189	5J.4	The electrochemical series	236
5C Response to conditions		190	5J.5	The combination of standard potentials	237
5C.1	The effect of temperature	190	5J.6	Thermodynamic data from standard potentials	237
5C.2	The effect of compression	192	CHECKLIST OF KEY CONCEPTS		238
5C.3	The presence of a catalyst	194	Exercises, discussion questions, problems, and projects		239
CHECKLIST OF KEY CONCEPTS		194	FOCUS 6		
5D Proton transfer equilibria		195	Chemical kinetics		249
5D.1	Brønsted–Lowry theory	195	6A Empirical chemical kinetics		251
5D.2	Protonation and deprotonation	196	6A.1	The definition of rate	251
CHECKLIST OF KEY CONCEPTS		201	6A.2	Experimental techniques	252
5E Polyprotic acids		202	CHECKLIST OF KEY CONCEPTS		255
5E.1	Successive deprotonation	202	6B Rate laws		256
5E.2	Speciation	202	6B.1	The rate constant	256
CHECKLIST OF KEY CONCEPTS		205	6B.2	Reaction order	258
5F Acid–base equilibria of salts in water		206	6B.3	The determination of the rate law	259
5F.1	The pH of salt solutions	206	CHECKLIST OF KEY CONCEPTS		261
5F.2	Acid–base titrations	208	6C Integrated rate laws		262
5F.3	Buffer action	211	6C.1	Zeroth-order reactions	262
CHECKLIST OF KEY CONCEPTS		212	6C.2	First-order reactions	262
5G Solubility equilibria		213	6C.3	Second-order reactions of the type A → products	264
5G.1	The solubility constant	213	6C.4	Second-order reactions of the type A + B → products	265
5G.2	The common-ion effect	214	6C.5	Half-lives	267
5G.3	The effect of added salts on solubility	215	CHECKLIST OF KEY CONCEPTS		268
CHECKLIST OF KEY CONCEPTS		216	6D The temperature dependence of reaction rates		269
5H Ions in solution		217	6D.1	The Arrhenius parameters	269
5H.1	Mean activity coefficients	218	6D.2	Collision theory of gas-phase reactions	272
5H.2	The Debye–Hückel theory	219	6D.3	Transition-state theory	274
5H.3	The migration of ions	220	CHECKLIST OF KEY CONCEPTS		276
CHECKLIST OF KEY CONCEPTS		223	6E The approach to equilibrium		277
5I Electrochemical cells		224	6E.1	Equilibria and rates	277
5I.1	Half-reactions and electrodes	225	6E.2	Relaxation	279
5I.2	Reactions at electrodes	227	CHECKLIST OF KEY CONCEPTS		280
5I.3	Varieties of cell	229	6F Reaction mechanisms		281
5I.4	The cell reaction	230	6F.1	Elementary reactions	281
5I.5	The cell potential	230	6F.2	The formulation of rate laws	282
CHECKLIST OF KEY CONCEPTS		232	6F.3	Consecutive reactions	283
5J Standard potentials		233	6F.4	Pre-equilibrium	284
5J.1	The contributions of individual electrodes	233			
5J.2	Equilibrium constants from standard potentials	234			

6F.5	The steady-state approximation	284	7D	Rotation	340	
6F.6	The rate-determining step	286	7D.1	Rotation in two dimensions	341	
6F.7	Kinetic control	286	7D.2	Rotation in three dimensions	343	
6F.8	Unimolecular reactions	287	CHECKLIST OF KEY CONCEPTS			346
CHECKLIST OF KEY CONCEPTS						
6G	Reactions in solution	289	7E	Vibration	347	
6G.1	Activation control and diffusion control	289	7E.1	The harmonic oscillator	347	
6G.2	Diffusion	290	7E.2	The quantum mechanical treatment	348	
CHECKLIST OF KEY CONCEPTS			CHECKLIST OF KEY CONCEPTS			350
6H	Homogeneous catalysis	295	Exercises, discussion questions, problems, and projects			351
6H.1	The Michaelis–Menten mechanism of enzyme catalysis	295	FOCUS 8			
6H.2	The analysis of rates of enzyme-catalysed reactions	297	Atomic structure			355
CHECKLIST OF KEY CONCEPTS						
6I	Heterogeneous catalysis	300	8A	Hydrogenic atoms	356	
6I.1	Physisorption and chemisorption	301	8A.1	The permitted energies of hydrogenic atoms	356	
6I.2	Adsorption isotherms	302	8A.2	Quantum numbers	359	
6I.3	Mechanisms of surface-catalysed reactions	305	8A.3	The s orbitals	362	
CHECKLIST OF KEY CONCEPTS			8A.4	The p and d orbitals	365	
Exercises, discussion questions, problems, and projects			CHECKLIST OF KEY CONCEPTS			367
FOCUS 7			8B	Many-electron atoms	368	
Quantum theory		315	8B.1	The orbital approximation	368	
7A	The emergence of quantum theory	316	8B.2	Electron spin	369	
7A.1	The evidence for discrete energies	317	8B.3	The Pauli principle	370	
7A.2	The evidence for radiation as particles	319	8B.4	Penetration and shielding	370	
7A.3	The evidence for particles as waves	320	8B.5	The building-up principle	372	
CHECKLIST OF KEY CONCEPTS			8B.6	The occupation of d orbitals	373	
7B	The dynamics of microscopic systems	323	8B.7	The configurations of cations and anions	373	
7B.1	The Schrödinger equation	323	8B.8	Self-consistent field orbitals	374	
7B.2	The Born interpretation	326	CHECKLIST OF KEY CONCEPTS			374
7B.3	The uncertainty principle	328	8C	Periodic trends of atomic properties	375	
CHECKLIST OF KEY CONCEPTS			8C.1	Atomic and ionic radii	375	
7C	Translation	331	8C.2	Ionization energy and electron affinity	377	
7C.1	Motion in one dimension	331	CHECKLIST OF KEY CONCEPTS			379
7C.2	Tunnelling	335	8D	Atomic spectroscopy	380	
7C.3	Motion in two dimensions	336	8D.1	The spectra of hydrogenic atoms	380	
CHECKLIST OF KEY CONCEPTS			8D.2	The energies of many-electron atoms	381	
Exercises, discussion questions, problems, and projects			8D.3	Spin–orbit coupling	383	
			8D.4	Selection rules for many-electron atoms	385	
			CHECKLIST OF KEY CONCEPTS			385
			Exercises, discussion questions, problems, and projects			386

FOCUS 9	
The chemical bond	389
<hr/>	
9A Valence bond theory	391
9A.1 Diatomic molecules	392
9A.2 Polyatomic molecules	394
9A.3 Promotion and hybridization	395
9A.4 Resonance	398
9A.5 The language of valence bond theory	399
CHECKLIST OF KEY CONCEPTS	400
<hr/>	
9B Molecular orbital theory: homonuclear diatomics	401
9B.1 The construction of molecular orbitals	401
9B.2 Bonding and antibonding orbitals	403
9B.3 Inversion symmetry	404
9B.4 The chemical bond in molecular orbital theory	404
9B.5 Many-electron homonuclear diatomics	406
9B.6 The configurations of Period 2 homonuclear diatomics	408
9B.7 The criteria for building molecular orbitals	409
CHECKLIST OF KEY CONCEPTS	410
<hr/>	
9C Molecular orbital theory: heteronuclear diatomics	411
9C.1 Polar bonds	411
9C.2 The formulation of molecular orbitals	412
9C.3 Molecular orbital diagrams	414
CHECKLIST OF KEY CONCEPTS	415
<hr/>	
9D Molecular orbital theory: polyatomic molecules	416
9D.1 The molecular orbitals of H_2O	416
9D.2 The Hückel method	417
9D.3 The molecular orbitals of benzene	420
9D.4 Computational chemistry	421
CHECKLIST OF KEY CONCEPTS	423
Exercises, discussion questions, problems, and projects	424
<hr/>	
FOCUS 10	
Molecular interactions	427
<hr/>	
10A Electric properties of molecules	428
10A.1 Electric dipole moments	428
10A.2 Dipole moments of polyatomic molecules	429
10A.3 Polarizabilities	431
CHECKLIST OF KEY CONCEPTS	432

10B Interactions between molecules	433
10B.1 Interactions between partial charges	433
10B.2 Charge–dipole interactions	434
10B.3 Dipole–dipole interactions	435
10B.4 Dipole–induced dipole interactions	437
10B.5 Dispersion interactions	437
10B.6 Hydrogen bonding	439
10B.7 The hydrophobic effect	440
10B.8 Modelling the total interaction	440
CHECKLIST OF KEY CONCEPTS	442
Exercises, discussion questions, problems, and projects	443
Part 1 Common integrals	
Part 2 Units	
FOCUS 11	
Molecular spectroscopy	447
<hr/>	
11A General features of molecular spectroscopy	449
11A.1 Spectrometers	450
11A.2 Absorption and emission	451
11A.3 Raman scattering	455
11A.4 Linewidths	455
CHECKLIST OF KEY CONCEPTS	457
<hr/>	
11B Rotational spectroscopy	458
11B.1 The rotational energy levels of molecules	458
11B.2 Forbidden and allowed rotational states	462
11B.3 Populations at thermal equilibrium	463
11B.4 Microwave spectroscopy	464
11B.5 Rotational Raman spectra	466
CHECKLIST OF KEY CONCEPTS	467
<hr/>	
11C Vibrational spectroscopy	468
11C.1 The vibrations of molecules	468
11C.2 Vibrational transitions	470
11C.3 Anharmonicity	471
11C.4 Vibrational Raman spectra of diatomic molecules	471
11C.5 The vibrations of polyatomic molecules	472
11C.6 Vibration–rotation spectra	474
11C.7 Vibrational Raman spectra of polyatomic molecules	475
CHECKLIST OF KEY CONCEPTS	476
<hr/>	
11D Electronic spectroscopy	477
11D.1 Ultraviolet and visible spectra	477
11D.2 Specific types of transitions	479

11D.3	Analysis of mixtures by electronic spectroscopy	480	FOCUS 13		
11D.4	Photoelectron spectroscopy	481	Magnetic resonance	523	
CHECKLIST OF KEY CONCEPTS		483			
11E	The decay of excited states	484			
11E.1	Fluorescence and phosphorescence	485	13A Nuclear magnetic resonance	524	
11E.2	Mechanism of decay of excited states	487	13A.1	Nuclei in magnetic fields	524
11E.3	Quenching	488	13A.2	The resonance condition	526
11E.4	Resonance energy transfer	490	13A.3	The technique	527
CHECKLIST OF KEY CONCEPTS		491	CHECKLIST OF KEY CONCEPTS	528	
Exercises, discussion questions, problems, and projects		492			
FOCUS 12			13B The information in NMR spectra	529	
Statistical thermodynamics		499	13B.1	The chemical shift	529
12A	The Boltzmann distribution	500	13B.2	The fine structure	532
12A.1	The population of states	500	13B.3	The origin of spin–spin splitting	534
12A.2	The general form of the Boltzmann distribution	501	13B.4	Spin relaxation	535
12A.3	The origins of the Boltzmann distribution	502	13B.5	Conformational conversion and chemical exchange	536
CHECKLIST OF KEY CONCEPTS		503	CHECKLIST OF KEY CONCEPTS	537	
12B	The partition function	504			
12B.1	The interpretation of the partition function	504	13C	Electron paramagnetic resonance	539
12B.2	The molecular partition function	506	13C.1	Electrons in magnetic fields	539
12B.3	The translational partition function	506	13C.2	The technique	540
12B.4	The rotational partition function	508	13C.3	The <i>g</i> -value	541
12B.5	The vibrational partition function	509	13C.4	Hyperfine structure	541
12B.6	The electronic partition function	510	CHECKLIST OF KEY CONCEPTS	543	
12B.7	The significance of the molecular partition function	510			
CHECKLIST OF KEY CONCEPTS		511			
12C	The origin of thermodynamic properties	512			
12C.1	The internal energy	512	14A	Biological and synthetic macromolecules	548
12C.2	The heat capacity	514	14A.1	Average molar masses	548
12C.3	The entropy	515	14A.2	Models of structure	549
12C.4	The Gibbs energy	516	14A.3	Random coils	550
12C.5	The equilibrium constant	517	14A.4	Polypeptides and polynucleotides	552
CHECKLIST OF KEY CONCEPTS		519	14A.5	The prediction of structure	553
Exercises, discussion questions, problems, and projects		520	14A.6	Mechanical properties of polymers	555
FOCUS 14			14A.7	Thermal properties of polymers	557
Macromolecules and aggregates		547	CHECKLIST OF KEY CONCEPTS	558	
14A	Biological and synthetic macromolecules	548			
14A.1	Average molar masses	548	14B	Mesophases and disperse systems	559
14A.2	Models of structure	549	14B.1	Liquid crystals	559
14A.3	Random coils	550	14B.2	Classification of disperse systems	560
14A.4	Polypeptides and polynucleotides	552	14B.3	Surface, structure, and stability	561
14A.5	The prediction of structure	553	14B.4	The electric double layer	563
14A.6	Mechanical properties of polymers	555	14B.5	Liquid surfaces and surfactants	565
14A.7	Thermal properties of polymers	557	CHECKLIST OF KEY CONCEPTS	567	
CHECKLIST OF KEY CONCEPTS		558			
Exercises, discussion questions, problems, and projects		568			

FOCUS 15		
Solids	571	
15A Crystal structure	572	
15A.1 The identification of crystal planes	573	
15A.2 The determination of structure	575	
15A.3 Bragg's law	577	
15A.4 Experimental techniques	577	
CHECKLIST OF KEY CONCEPTS	580	
15B Bonding in solids	581	
15B.1 Metallic solids	581	
15B.2 Ionic solids	584	
15B.3 The electronic structure of metallic and ionic solids	586	
15B.4 The energetics of bonding in ionic solids	587	
15B.5 Molecular solids	590	
15B.6 Covalent networks	591	
CHECKLIST OF KEY CONCEPTS	592	
15C The properties of solids	593	
15C.1 Electrical properties	593	
15C.2 Superconductivity	595	
15C.3 Optical properties	595	
15C.4 Solid-state lasers	596	
15C.5 Magnetic properties	597	
CHECKLIST OF KEY CONCEPTS	599	
Exercises, discussion questions, problems, and project	600	
Resource section	603	
Part 1 Common integrals	604	
Part 2 Units	605	
Part 3 Data	607	
Index	617	
4A The rules of differentiation	123	
4D Measures of concentration	148	
5B Quadratic equations	187	
5H The Coulomb potential	217	
5H Resistance and conductance	221	
5I Oxidation numbers	225	
6G Partial derivatives	292	
7A Electromagnetic waves	316	
7B Ordinary differential equations	324	
7B Operators	326	
7C Partial differential equations	338	
7D Angular momentum	340	
7D Vectors	345	
8D Addition and subtraction of vectors	382	
9A The Lewis theory of covalent bonding	391	
9A The VSEPR model	391	
9D Simultaneous equations	419	
13A Magnetic fields	525	