



Summary of contents

Guided tour

xxxiv

Preface to the fifth edition

xxxvii

Acknowledgements

xxxix

1 Basic concepts: atoms	1
2 Basic concepts: molecules	32
3 Introduction to molecular symmetry	62
4 Experimental techniques	90
5 Bonding in polyatomic molecules	144
6 Structures and energetics of metallic and ionic solids	177
7 Acids, bases and ions in aqueous solution	218
8 Reduction and oxidation	255
9 Non-aqueous media	283
10 Hydrogen	314
11 Group 1: the alkali metals	341
12 The group 2 metals	364
13 The group 13 elements	387
14 The group 14 elements	443
15 The group 15 elements	502
16 The group 16 elements	564
17 The group 17 elements	611
18 The group 18 elements	645
19 <i>d</i> -Block metal chemistry: general considerations	661
20 <i>d</i> -Block metal chemistry: coordination complexes	687
21 <i>d</i> -Block metal chemistry: the first row metals	738
22 <i>d</i> -Block metal chemistry: the heavier metals	803
23 Organometallic compounds of <i>s</i> - and <i>p</i> -block elements	875
24 Organometallic compounds of <i>d</i> -block elements	915

25	Catalysis and some industrial processes	971
26	d-Block metal complexes: reaction mechanisms	1007
27	The f-block metals: lanthanoids and actinoids	1033
28	Inorganic materials and nanotechnology	1065
29	The trace metals of life	1098

First published 2001 (print)

Second edition published 2005 (print)

Third edition published 2008 (print)

Fourth edition published 2012 (print)

Fifth edition published 2018 (print) (online)

© Pearson Education Limited 2000
© Pearson Education Limited 2005 (print)
© Pearson Education Limited 2008 (print)
© Pearson Education Limited 2012 (print)
© Pearson Education Limited 2018 (print) (online)

The rights of Catherine E. Housecroft and Alan G. Sharpen to be identified as authors of this work have been asserted by them in accordance with the Copyright, Designs, and Patents Act 1988.

The print publication is protected by copyright. Prior to any prohibited reproduction, storage in a retrieval system, distribution or transmission in any form or by any means, electronic, mechanical, recording or otherwise, permission should be obtained from the publisher or, where applicable, a licence permitting restricted copying in the United Kingdom should be obtained from the Copyright Licensing Agency, Ltd, Barnard's Inn, 86 Fetter Lane, London EC4P 4EE.

The ePublication is protected by copyright and must not be copied, reproduced, transferred, distributed, leased, hired, loaned, publicly performed or used in any way except as specifically permitted in writing by the publishers, as allowed under the terms and conditions under which it was purchased, or as explicitly permitted by applicable copyright law. Any unauthorised distribution or use of this text may be a direct infringement of the author's and the publisher's rights and may result in legal action being taken against you.

All trademarks used herein are the property of their respective owners. The use of any trademark in this text does not vest in the author or publisher any rights in such trademarks, nor does the use of such trademarks imply any affiliation with or endorsement of this book by such owners.

Pearson Education is not responsible for the content of any external websites. ISBN 978-1-292-13414-7 (print)
ISBN 978-1-292-13416-1 (PDF)
ISBN 978-1-292-30496-3 (ePub)

E&E: Library Cataloguing-in-Publication Data

A record for the print edition is available from the British Library.

500: 1st ed. Cataloguing-in-Publication Data

Author: Housecroft, Catherine E., 1955- author.

Title: Inorganic chemistry / Catherine E. Housecroft and Alan G. Sharpen.

Other titles: Fifth edition. | Harlow, England : Pearson, 2018.

Format: 1 online resource (xviii, 1200 pages) : illustrations ; ISBN 9781292134147 (print) | ISBN 9781292134161 (PDF) | ISBN 9781292304963 (ePub).

Subject: Inorganic chemistry. | Inorganic chemistry--Textbooks.

Classification: Dewey: 547.151.3 H683 2018 | DDC 546 -- dc23

Availability: Available at https://academic.pearsonpoint.com/2/and/or https://www.pearson.com/uk/subjects/science/chemistry/inorganic-chemistry.html

Notes: Includes bibliographical references and index.

Summary: This fifth edition of Inorganic Chemistry provides a comprehensive introduction to the subject.

Contents: Part I: The elements and periodicity; Part II: Bonding and structures; Part III: Reactivity; Part IV: Materials and applications.

Supplementary material: Includes access to the Pearson eText version of the book.

Accessories: Includes access to the Pearson eText version of the book.

Print edition: ISBN 9781292134147 | ISBN 9781292304963

Printed in Shandong, China | © Pearson Education, Inc., 2018

NOTE THAT ANY PURCHASE OF THIS EDITION WILL NOT INCLUDE ACCESS TO THE PEARSON E-TEXT VERSION.

Appendices

Answers to non-descriptive problems	1141
--	-------------

Index

Index (online)	1191
-----------------------	-------------

IUPAC: Brief Guide to the Nomenclature of Inorganic Chemistry

1248



Contents

3 Introduction to molecular symmetry	62
3.1 Introduction	62
3.2 Symmetry operations	62
Rotation about an n -fold axis of symmetry	63
Guided tour	xxxiv
Preface to the fifth edition	xxxvii
Acknowledgements	xxxix
1 Basic concepts: atoms	1
1.1 Introduction	1
Inorganic chemistry: it is not an isolated branch of chemistry	1
The aims of Chapters 1 and 2	1
1.2 Fundamental particles of an atom	1
1.3 Atomic number, mass number and isotopes	2
Nuclides, atomic number and mass number	2
Relative atomic mass	2
Isotopes	2
1.4 Successes in early quantum theory	4
Some important successes of classical quantum theory	4
Bohr's theory of the atomic spectrum of hydrogen	5
1.5 An introduction to wave mechanics	7
The wave-nature of electrons	7
The uncertainty principle	7
The Schrödinger wave equation	7
1.6 Atomic orbitals	9
The quantum numbers n , l and m_l	9
The radial part of the wavefunction, $R(r)$	10
The radial distribution function, $4\pi r^2 R(r)^2$	12
The angular part of the wavefunction, $A(\theta, \phi)$	12
Orbital energies in a hydrogen-like species	15

Size of orbitals	16
The spin quantum number and the magnetic spin quantum number	16
The ground state of the hydrogen atom	18
1.7 Many-electron atoms	18
The helium atom: two electrons	18
Ground state electronic configurations: experimental data	18
Penetration and shielding	20
1.8 The periodic table	22
1.9 The <i>aufbau</i> principle	22
Ground state electronic configurations	22
Valence and core electrons	24
Diagrammatic representations of electronic configurations	24
1.10 Ionization energies and electron affinities	25
Ionization energies	25
Electron affinities	27
2 Basic concepts: molecules	32
2.1 Bonding models: an introduction	32
A historical overview	32
Lewis structures	32
2.2 Homonuclear diatomic molecules: valence bond (VB) theory	33
Uses of the term <i>homonuclear</i>	33
Covalent bond distance, covalent radius and van der Waals radius	33
The valence bond (VB) model of bonding in H ₂	34
The valence bond (VB) model applied to F ₂ , O ₂ and N ₂	35
2.3 Homonuclear diatomic molecules: molecular orbital (MO) theory	35
An overview of the MO model	35
Molecular orbital theory applied to the bonding in H ₂	36
The bonding in He ₂ , Li ₂ and Be ₂	38
The bonding in F ₂ and O ₂	39
What happens if the <i>s–p</i> separation is small?	41
2.4 The octet rule and isoelectronic species	42
The octet rule: first row <i>p</i> -block elements	42
Isoelectronic species	43
The octet rule: heavier <i>p</i> -block elements	44
2.5 Electronegativity values	44
Pauling electronegativity values, χ^P	44
Mulliken electronegativity values, χ^M	45
Allred–Rochow electronegativity values, χ^{AR}	46
Electronegativity: final remarks	46
2.6 Dipole moments	47
Polar diatomic molecules	47
Molecular dipole moments	48
2.7 MO theory: heteronuclear diatomic molecules	49
Which orbital interactions should be considered?	49

Hydrogen fluoride	50
Carbon monoxide	52
2.8 Molecular shape and the VSEPR model	52
Valence-shell electron-pair repulsion model	52
Structures derived from a trigonal bipyramidal	55
Limitations of the VSEPR model	56
2.9 Molecular shape: stereoisomerism	56
Square planar species	56
Octahedral species	57
Trigonal bipyramidal species	57
High coordination numbers	57
Double bonds	58
Hückel MO theory	58
Molecular mechanics (MM)	58
3 Introduction to molecular symmetry	62
3.1 Introduction	62
3.2 Symmetry operations and symmetry elements	62
Rotation about an n -fold axis of symmetry	63
Reflection through a plane of symmetry (mirror plane)	63
Reflection through a centre of symmetry (inversion centre)	65
Rotation about an axis, followed by reflection through a plane perpendicular to this axis	66
Identity operator	66
3.3 Successive operations	68
3.4 Point groups	69
C_1 point group	69
$C_{\infty v}$ point group	70
$D_{\infty h}$ point group	70
T_d , O_h or I_h point groups	70
Determining the point group of a molecule or molecular ion	70
3.5 Character tables: an introduction	73
3.6 Why do we need to recognize symmetry elements?	74
3.7 Vibrational spectroscopy	74
How many vibrational modes are there for a given molecular species?	74
Selection rules for an infrared or Raman active mode of vibration	75
Linear ($D_{\infty h}$ or $C_{\infty v}$) and bent (C_{2v}) triatomic molecules	76
Bent molecules XY_2 : using the C_{2v} character table	77
XY_3 molecules with D_{3h} symmetry	78
XY_3 molecules with C_{3v} symmetry	80
XY_4 molecules with T_d or D_{4h} symmetry	81
XY_6 molecules with O_h symmetry	81
Metal carbonyl complexes, $M(CO)_n$	82
Metal carbonyl complexes $M(CO)_6X_n$	82
Observing IR spectroscopic absorptions	84
3.8 Chiral molecules	85
SP_3 tetrahedral molecules	165
Three-centre two-electron interactions	167
A more advanced problem: B_2H_6	169

4 Experimental techniques	90
4.1 Introduction	90
4.2 Separation and purification techniques	90
Gas chromatography (GC)	90
Liquid chromatography (LC)	91
High-performance liquid chromatography (HPLC)	92
Recrystallization	93
4.3 Elemental analysis	93
CHN analysis by combustion	93
Atomic absorption spectroscopy (AAS)	94
4.4 Compositional analysis: thermogravimetry (TG)	96
4.5 Mass spectrometry	97
Electron ionization (EI)	97
Fast atom bombardment (FAB)	98
Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF)	99
Electrospray ionization (ESI)	101
4.6 Infrared and Raman spectroscopies	102
Energies and wavenumbers of molecular vibrations	102
The Fourier transform infrared (FT-IR) spectrometer and sample preparation	103
Diagnostic absorptions	103
Deuterium/hydrogen exchange	104
Raman spectroscopy	106
4.7 Electronic spectroscopy	108
UV-VIS absorption spectroscopy	108
Types of absorption	108
Absorbance and the Beer–Lambert Law	109
Emission spectroscopy	110
4.8 Nuclear magnetic resonance (NMR) spectroscopy	110
NMR active nuclei and isotope abundance	111
Which nuclei are suitable for NMR spectroscopic studies?	111
Resonance frequencies and chemical shifts	112
Chemical shift ranges	112
Solvents for solution studies	112
Integration of signals and signal broadening	114
Homonuclear spin–spin coupling: ^1H – ^1H	114
Heteronuclear spin–spin coupling: ^{13}C – ^1H	115
Case studies	115
Stereochemically non-rigid species	117
Exchange processes in solution	120
4.9 Electron paramagnetic resonance (EPR) spectroscopy	121
What is EPR spectroscopy?	121
The Zeeman electronic effect	121
EPR spectra	122
4.10 Mössbauer spectroscopy	124
The technique of Mössbauer spectroscopy	124
What can isomer shift data tell us?	125

4.11	Structure determination: diffraction methods	126
	X-ray diffraction (XRD)	126
	Single crystal X-ray diffraction	127
	Powder X-ray diffraction	129
	Single crystal neutron diffraction	129
6.14	Electron diffraction	130
	Low-energy electron diffraction (LEED)	130
	Structural databases	130
4.12	Photoelectron spectroscopy (PES, UPS, XPS, ESCA)	130
4.13	Computational methods	131
	Hartree–Fock theory	132
6.17	Density functional theory	132
	Hückel MO theory	132
	Molecular mechanics (MM)	132
	Estimation of standard enthalpies of formation by proportionation	139
6.5	Bonding in polyatomic molecules	144
5.1	Introduction	144
5.2	Valence bond theory: hybridization of atomic orbitals	144
	What is orbital hybridization?	144
	<i>sp</i> Hybridization: a scheme for linear species	145
	<i>sp</i> ² Hybridization: a scheme for trigonal planar species	146
	<i>sp</i> ³ Hybridization: a scheme for tetrahedral and related species	147
	Other hybridization schemes	148
5.3	Valence bond theory: multiple bonding in polyatomic molecules	149
7.1	C₂H₄	149
7.2	Properties of water	149
	BF ₃	150
5.4	Natural bond orbitals	151
5.5	Molecular orbital theory: the ligand group orbital approach and application to triatomic molecules	151
7.3	Molecular orbital diagrams: moving from a diatomic to polyatomic species	151
	MO approach to bonding in linear XH ₂ : symmetry matching by inspection	152
	MO approach to bonding in linear XH ₂ : working from molecular symmetry	153
7.4	A bent triatomic: H₂O	153
5.6	Molecular orbital theory applied to the polyatomic molecules BH₃, NH₃ and CH₄	156
	BH ₃	156
	NH ₃	157
7.5	CH₄	159
	A comparison of the MO and VB bonding models	160
5.7	Molecular orbital theory: bonding analyses soon become complicated	161
5.8	Molecular orbital theory: learning to use the theory objectively	164
	π-Bonding in CO ₂	164
	[NO ₃] ⁻	165
	SF ₆	165
	Three-centre two-electron interactions	167
	A more advanced problem: B ₂ H ₆	169

6 Structures and energetics of metallic and ionic solids

177

6.1	Introduction	177
6.2	Packing of spheres	177
	Cubic and hexagonal close-packing	177
	The unit cell: hexagonal and cubic close-packing	178
	Interstitial holes: hexagonal and cubic close-packing	179
	Non-close-packing: simple cubic and body-centred cubic arrays	180
6.3	The packing-of-spheres model applied to the structures of elements	180
	Group 18 elements in the solid state	180
	H_2 and F_2 in the solid state	181
	Metallic elements in the solid state	181
6.4	Polymorphism in metals	182
	Polymorphism: phase changes in the solid state	182
	Phase diagrams	183
6.5	Metallic radii	183
6.6	Melting points and standard enthalpies of atomization of metals	184
6.7	Alloys and intermetallic compounds	184
	Substitutional alloys	185
	Interstitial alloys	185
	Intermetallic compounds	188
6.8	Bonding in metals and semiconductors	188
	Electrical conductivity and resistivity	188
	Band theory of metals and insulators	189
	The Fermi level	190
6.9	Semiconductors	190
	Intrinsic semiconductors	191
	Extrinsic (n- and p-type) semiconductors	191
6.10	Sizes of ions	191
	Ionic radii	193
	Periodic trends in ionic radii	193
6.11	Ionic lattices	195
	The rock salt ($NaCl$) structure type	196
	The caesium chloride ($CsCl$) structure type	197
	The fluorite (CaF_2) structure type	198
	The antifluorite structure type	198
	The zinc blende (ZnS) structure type: a diamond-type network	198
	The β -cristobalite (SiO_2) structure type	199
	The wurtzite (ZnS) structure type	199
	The rutile (TiO_2) structure type	199
	CdI_2 and $CdCl_2$: layer structures	200
	The perovskite ($CaTiO_3$) structure type: a double oxide	200
6.12	Crystal structures of semiconductors	201
6.13	Lattice energy: estimates from an electrostatic model	201
	Coulombic attraction within an isolated ion-pair	201
	Coulombic interactions in an ionic lattice	202

8.7	Born forces	202
8.8	The Born–Landé equation	203
8.9	Madelung constants	203
8.10	Refinements to the Born–Landé equation	204
8.11	Overview	204
8.12	6.14 Lattice energy: the Born–Haber cycle	204
8.13	6.15 Lattice energy: ‘calculated’ versus ‘experimental’ values	206
8.14	6.16 Estimating lattice energies of new materials	206
8.15	The Kapustinskii equation	206
8.16	The volume-based thermodynamic (VBT) approach	206
8.17	6.17 Applications of lattice energies	208
8.18	Estimation of electron affinities	208
8.19	Fluoride affinities	208
8.20	Estimation of standard enthalpies of formation and disproportionation	209
8.21	6.18 Defects in solid state lattices	210
8.22	Schottky defect	210
8.23	Frenkel defect	211
8.24	Experimental observation of Schottky and Frenkel defects	211
8.25	Non-stoichiometric compounds	211
8.26	Colour centres (F-centres)	212
8.27	Thermodynamic effects of crystal defects	212
8.28	9.6 Liquid ammonia	208
7	7 Acids, bases and ions in aqueous solution	218
7.1	Introduction	218
7.2	Properties of water	218
7.3	Structure and hydrogen bonding	218
7.4	The self-ionization of water	220
7.5	Water as a Brønsted acid or base	220
7.6	Definitions and units in aqueous solution	221
7.7	Molarity and molality	221
7.8	Standard state	221
7.9	Activity	222
7.10	7.4 Some Brønsted acids and bases	222
7.11	Carboxylic acids: examples of mono-, di- and polybasic acids	222
7.12	Inorganic acids	224
7.13	Inorganic bases: hydroxides	225
7.14	Inorganic bases: nitrogen bases	225
7.15	7.5 The energetics of acid dissociation in aqueous solution	226
7.16	Hydrogen halides	226
7.17	H ₂ S, H ₂ Se and H ₂ Te	227
7.18	7.6 Trends within a series of oxoacids EO_n(OH)_m	227
7.19	7.7 Aquated cations: formation and acidic properties	228
7.20	Water as a Lewis base	228
7.21	Aquated cations as Brønsted acids	230

7.8	Amphoteric oxides and hydroxides	231
6.1	Amphoteric behaviour	231
	Periodic trends in amphoteric properties	231
7.9	Solubilities of ionic salts	232
	Solubility and saturated solutions	232
	Sparingly soluble salts and solubility products	232
	The energetics of the dissolution of an ionic salt: $\Delta_{\text{sol}}G^\circ$	233
	The energetics of the dissolution of an ionic salt: hydration of ions	234
6.3	Solubilities: some concluding remarks	236
7.10	Common-ion effect	236
7.11	Coordination complexes: an introduction	237
6.4	Definitions and terminology	237
	Investigating coordination complex formation	238
7.12	Stability constants of coordination complexes	239
6.5	Determination of stability constants	241
	Trends in stepwise stability constants	241
	Thermodynamic considerations of complex formation: an introduction	242
7.13	Factors affecting the stabilities of complexes containing only monodentate ligands	246
	Ionic size and charge	246
	Hard and soft metal centres and ligands	246
	Bonding in metals and semiconductors	188
8	Reduction and oxidation	255
8.1	Introduction	255
6.9	Oxidation and reduction	255
	Oxidation states	256
	Stock nomenclature	256
8.2	Standard reduction potentials, E°, and relationships between E°, ΔG° and K	257
	Half-cells and galvanic cells	257
	Defining and using standard reduction potentials, E°	258
	Dependence of reduction potentials on cell conditions	261
8.3	The effect of complex formation or precipitation on M^{z+}/M reduction potentials	265
	Half-cells involving silver halides	266
	Modifying the relative stabilities of different oxidation states of a metal	267
8.4	Disproportionation reactions	269
	Disproportionation	269
	Stabilizing species against disproportionation	270
8.5	Potential diagrams	270
8.6	Frost–Ebsworth diagrams	272
	Frost–Ebsworth diagrams and their relationship to potential diagrams	272
	Interpretation of Frost–Ebsworth diagrams	273

8.7	The relationships between standard reduction potentials and some other quantities	275
	Factors influencing the magnitudes of standard reduction potentials	275
	Values of $\Delta_f G^\circ$ for aqueous ions	276
8.8	Applications of redox reactions to the extraction of elements from their ores	277
	Ellingham diagrams	277
9	Non-aqueous media	283
9.1	Introduction	283
9.2	Relative permittivity	284
9.3	Energetics of ionic salt transfer from water to an organic solvent	285
9.4	Acid-base behaviour in non-aqueous solvents	286
	Strengths of acids and bases	286
	Levelling and differentiating effects	286
	'Acids' in acidic solvents	286
	Acids and bases: a solvent-oriented definition	287
	Proton-containing and aprotic solvents	287
9.5	Liquid sulfur dioxide	287
9.6	Liquid ammonia	288
	Physical properties	288
	Self-ionization	288
	Reactions in liquid NH_3	288
	Solutions of <i>s</i> -block metals in liquid NH_3	290
	Redox reactions in liquid NH_3	291
9.7	Liquid hydrogen fluoride	291
	Physical properties	291
	Acid-base behaviour in liquid HF	291
	Electrolysis in liquid HF	293
9.8	Sulfuric acid and fluorosulfonic acid	293
	Physical properties of sulfuric acid	293
	Acid-base behaviour in liquid H_2SO_4	293
	Physical properties of fluorosulfonic acid	294
9.9	Superacids	294
9.10	Bromine trifluoride	296
	Physical properties	296
	Behaviour of fluoride salts and molecular fluorides in BrF_3	296
	Reactions in BrF_3	297
9.11	Dinitrogen tetroxide	297
	Physical properties	297
	Reactions in N_2O_4	297
9.12	Ionic liquids	299
	Molten salt solvent systems	299
	Ionic liquids at ambient temperatures	300

9.13e Supercritical fluids	307
Properties of supercritical fluids and their uses as solvents	307
Supercritical fluids as media for inorganic chemistry	309
10 Hydrogen	314
10.1 Hydrogen: the simplest atom	314
10.2 The H⁺ and H⁻ ions	314
The hydrogen ion (proton)	314
The hydride ion	315
10.3 Isotopes of hydrogen	315
Protium and deuterium	315
Kinetic isotope effects	316
Deuterated compounds	316
Tritium	318
10.4 Dihydrogen	318
Occurrence	318
Physical properties	318
Synthesis and uses	318
Reactivity	322
10.5 Polar and non-polar E-H bonds	323
10.6 Hydrogen bonding	324
The hydrogen bond	324
Trends in boiling points, melting points and enthalpies of vaporization for <i>p</i> -block binary hydrides	327
Infrared spectroscopy	328
Solid state structures	329
Hydrogen bonding in biological systems	331
10.7 Binary hydrides: classification and general properties	332
Classification	332
Metallic hydrides	334
Saline hydrides	334
Molecular hydrides and complexes derived from them	335
Covalent hydrides with extended structures	336
11 Group 1: the alkali metals	341
11.1 Introduction	341
11.2 Occurrence, extraction and uses	341
Occurrence	341
Extraction	342
Major uses of the alkali metals and their compounds	343
11.3 Physical properties	344
General properties	344
Atomic spectra and flame tests	344
Radioactive isotopes	346
NMR active nuclei	348

11.4	The metals	348
	Appearance	348
	Reactivity	348
11.5	Halides	350
	Oxidation state and bonding considerations	350
11.6	Oxides and hydroxides	351
	Oxides, peroxides, superoxides, suboxides and ozonides	351
	Hydroxides	353
11.7	Salts of oxoacids: carbonates and hydrogencarbonates	353
11.8	Aqueous solution chemistry and macrocyclic complexes	354
	Hydrated ions	354
	Complex ions	355
11.9	Non-aqueous coordination chemistry	359
12	The group 2 metals	364
12.1	Introduction	364
12.2	Occurrence, extraction and uses	364
	Occurrence	364
	Extraction	365
	Major uses of the group 2 metals and their compounds	365
12.3	Physical properties	367
	General properties	367
12.4	The metals	369
	Appearance	369
	Reactivity	369
12.5	Halides	370
	Beryllium halides	370
	Halides of Mg, Ca, Sr and Ba	372
12.6	Oxides and hydroxides	374
	Oxides and peroxides	374
	Hydroxides	377
12.7	Salts of oxoacids	378
12.8	Complex ions in aqueous solution	378
	Aqua species of beryllium	378
	Aqua species of Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}	379
	Complexes with ligands other than water	380
12.9	Complexes with amido or alkoxy ligands	381
12.10	Diagonal relationships between Li and Mg, and between Be and Al	382
	Lithium and magnesium	382
	Beryllium and aluminium	383

13 The group 13 elements	387
13.1 Introduction	387
13.2 Occurrence, extraction and uses	387
Occurrence	387
Extraction	387
Major uses of the group 13 elements and their compounds	389
13.3 Physical properties	391
Electronic configurations and oxidation states	391
NMR active nuclei	395
13.4 The elements	395
Appearance	395
Structures of the elements	395
Reactivity	395
13.5 Simple hydrides	396
Neutral hydrides	396
The $[\text{MH}_4]^-$ ions	402
13.6 Halides and complex halides	403
Boron halides: BX_3 and B_2X_4	403
Al(III), Ga(III), In(III) and Tl(III) halides and their complexes	406
Lower oxidation state Al, Ga, In and Tl halides	409
13.7 Oxides, oxoacids, oxoanions and hydroxides	411
Boron oxides, oxoacids and oxoanions	411
Aluminium oxides, oxoacids, oxoanions and hydroxides	414
Oxides of Ga, In and Tl	416
13.8 Compounds containing nitrogen	416
Nitrides	416
Ternary boron nitrides	416
Molecular species containing B–N or B–P bonds	419
Molecular species containing group 13 metal–nitrogen bonds	422
13.9 Aluminium to thallium: salts of oxoacids, aqueous solution chemistry and complexes	423
Aluminium sulfate and alums	423
Aqua ions	423
Redox reactions in aqueous solution	424
Coordination complexes of the M^{3+} ions	425
13.10 Metal borides	426
13.11 Electron-deficient borane and carbaborane clusters: an introduction	426
14 The group 14 elements	443
14.1 Introduction	443
14.2 Occurrence, extraction and uses	443
Occurrence	443
Extraction and manufacture	444
Uses	444

14.3 Physical properties	448
Ionization energies and cation formation	448
Some energetic and bonding considerations	450
NMR active nuclei	452
Mössbauer spectroscopy	452
14.4 Allotropes of carbon	452
Graphite and diamond: structure and properties	452
Graphite: intercalation compounds	454
Fullerenes: synthesis and structure	455
Fullerenes: reactivity	456
Carbon nanotubes	461
14.5 Structural and chemical properties of silicon, germanium, tin and lead	461
Structures	461
Chemical properties	461
14.6 Hydrides	462
Binary hydrides	463
Halohydrides of silicon and germanium	465
14.7 Carbides, silicides, germides, stannides and plumbides	466
Carbides	466
Silicides	467
Zintl ions containing Si, Ge, Sn and Pb	467
14.8 Halides and complex halides	471
Carbon halides	471
Silicon halides	473
Halides of germanium, tin and lead	474
14.9 Oxides, oxoacids and hydroxides	477
Oxides and oxoacids of carbon	477
Silica, silicates and aluminosilicates	480
Oxides, hydroxides and oxoacids of germanium, tin and lead	488
14.10 Siloxanes and polysiloxanes (silicones)	490
14.11 Sulfides	491
14.12 Cyanogen, silicon nitride and tin nitride	494
Cyanogen and its derivatives	494
Silicon nitride	496
Tin(IV) nitride	496
14.13 Aqueous solution chemistry and salts of oxoacids of germanium, tin and lead	496
15 The group 15 elements	502
15.1 Introduction	502
15.2 Occurrence, extraction and uses	503
Occurrence	503
Extraction	504
Uses	505

15.3	Physical properties	507
13.1	Bonding considerations	508
13.2	NMR active nuclei	509
13.3	Radioactive isotopes	510
15.4	The elements	510
13.4	Nitrogen	510
13.5	Phosphorus	510
13.6	Arsenic, antimony and bismuth	512
15.5	Hydrides	513
13.7	Trihydrides, EH_3 ($E = N, P, As, Sb$ and Bi)	513
13.8	Hydrides E_2H_4 ($E = N, P, As$)	517
13.9	Chloramine and hydroxylamine	518
13.10	Hydrogen azide and azide salts	520
15.6	Nitrides, phosphides, arsenides, antimonides and bismuthides	521
13.11	Nitrides	521
13.12	Phosphides	523
13.13	Arsenides, antimonides and bismuthides	524
15.7	Halides, oxohalides and complex halides	525
13.14	Nitrogen halides	525
13.15	Oxofluorides and oxochlorides of nitrogen	527
13.16	Phosphorus halides	528
13.17	Phosphoryl trichloride, $POCl_3$	531
13.18	Arsenic and antimony halides	531
13.19	Bismuth halides	533
15.8	Oxides of nitrogen	534
13.20	Dinitrogen monoxide, N_2O	534
13.21	Nitrogen monoxide, NO	535
13.22	Dinitrogen trioxide, N_2O_3	537
13.23	Dinitrogen tetraoxide, N_2O_4 , and nitrogen dioxide, NO_2	537
13.24	Dinitrogen pentaoxide, N_2O_5	539
15.9	Oxoacids of nitrogen	539
13.25	Isomers of $H_2N_2O_2$	539
13.26	Nitrous acid, HNO_2	540
13.27	Nitric acid, HNO_3 , and its derivatives	540
15.10	Oxides of phosphorus, arsenic, antimony and bismuth	544
13.28	Oxides of phosphorus	544
13.29	Oxides of arsenic, antimony and bismuth	545
15.11	Oxoacids of phosphorus	545
13.30	Phosphinic acid, H_3PO_2	547
13.31	Phosphonic acid, H_3PO_3	547
13.32	Hypodiphosphoric acid, $H_4P_2O_6$	547
13.33	Phosphoric acid, H_3PO_4 , and its derivatives	548
13.34	Chiral phosphate anions	550
15.12	Oxoacids of arsenic, antimony and bismuth	550
15.13	Phosphazenes	553

15.14	Sulfides and selenides	556
	Sulfides and selenides of phosphorus	556
	Arsenic, antimony and bismuth sulfides	557
15.15	Aqueous solution chemistry and complexes	558
	Other compounds of xenon	558
16	The group 16 elements	564
16.1	Introduction	564
16.2	Occurrence, extraction and uses	565
	Occurrence	565
	Extraction	565
	Uses	565
16.3	Physical properties and bonding considerations	567
	NMR active nuclei and isotopes as tracers	569
16.4	The elements	570
	Dioxygen	570
	Ozone	571
	Sulfur: allotropes	573
	Sulfur: reactivity	574
	Selenium and tellurium	575
16.5	Hydrides	576
	Water, H ₂ O	576
	Hydrogen peroxide, H ₂ O ₂	577
	Hydrides H ₂ E (E = S, Se, Te)	580
	Polysulfanes	581
16.6	Metal sulfides, polysulfides, polyselenides and polytellurides	581
	Sulfides	581
	Polysulfides	581
	Polyselelenides and polytellurides	582
16.7	Halides, oxohalides and complex halides	584
	Oxygen fluorides	584
	Sulfur fluorides and oxofluorides	585
	Sulfur chlorides and oxochlorides	588
	Halides of selenium and tellurium	589
16.8	Oxides	591
	Oxides of sulfur	591
	Oxides of selenium and tellurium	596
16.9	Oxoacids and their salts	597
	Dithionous acid, H ₂ S ₂ O ₄	597
	Sulfurous and disulfurous acids, H ₂ SO ₃ and H ₂ S ₂ O ₅	599
	Dithionic acid, H ₂ S ₂ O ₆	600
	Sulfuric acid, H ₂ SO ₄	600
	Fluoro- and chlorosulfonic acids, HSO ₃ F and HSO ₃ Cl	602
	Polyoxoacids with S–O–S units	602
	Peroxysulfuric acids, H ₂ S ₂ O ₈ and H ₂ SO ₅	602
	Thiosulfuric acid, H ₂ S ₂ O ₃ , and polythionates	602
	Oxoacids of selenium and tellurium	603

16.10	Compounds of sulfur and selenium with nitrogen Sulfur–nitrogen compounds Tetraselenium tetranitride	604 604 606
16.11	Aqueous solution chemistry of sulfur, selenium and tellurium	606
15.4	The elements	510
17	The group 17 elements	611
17.1	Introduction	611
15.5	Fluorine, chlorine, bromine and iodine Astatine and tennessine	611 612
17.2	Occurrence, extraction and uses Occurrence Extraction Uses	612 612 612 613
17.3	Physical properties and bonding considerations NMR active nuclei and isotopes as tracers	615 618
17.4	The elements Difluorine Dichlorine, dibromine and diiodine Charge transfer complexes Clathrates	620 620 620 621 623
17.5	Hydrogen halides	623
17.6	Metal halides: structures and energetics	624
17.7	Interhalogen compounds and polyhalogen ions Interhalogen compounds Bonding in $[XY_2]^-$ ions Polyhalogen cations Polyhalide anions	626 626 630 630 631
17.8	Oxides and oxofluorides of chlorine, bromine and iodine Oxides Oxofluorides	631 632 633
17.9	Oxoacids and their salts	634
15.10	Hypofluorous acid, HOF Oxoacids of chlorine, bromine and iodine	634 634
17.10	Aqueous solution chemistry	638
15.11	Oxoacids of phosphorus and sulfur Oxides of selenium and tellurium	545
18	The group 18 elements	645
18.1	Introduction	645
18.2	Occurrence, extraction and uses Occurrence Extraction Uses	646 646 647 647
18.3	Physical properties NMR active nuclei	648 648

18.4	Compounds of xenon	650
21.1	Fluorides	650
21.2	Chlorides	654
	Oxides	654
	Oxofluorides and oxochlorides	654
	Other compounds of xenon	655
18.5	Compounds of argon, krypton and radon	657
19	d-Block metal chemistry: general considerations	661
19.1	Topic overview	661
19.2	Ground state electronic configurations	661
	<i>d</i> -Block metals versus transition elements	661
	Electronic configurations	662
19.3	Physical properties	662
19.4	The reactivity of the metals	664
19.5	Characteristic properties: a general perspective	664
	Colour	664
21.7	Paramagnetism	665
	Complex formation	665
	Variable oxidation states	665
19.6	Electroneutrality principle	666
19.7	Coordination numbers and geometries	667
	The Kepert model	668
	Coordination numbers in the solid state	669
	Coordination number 2	669
	Coordination number 3	669
	Coordination number 4	669
	Coordination number 5	671
	Coordination number 6	672
	Coordination number 7	673
	Coordination number 8	674
	Coordination number 9	675
	Coordination numbers of 10 and above	676
19.8	Isomerism in <i>d</i> -block metal complexes	676
	Structural isomerism: ionization isomers	676
	Structural isomerism: hydration isomers	677
	Structural isomerism: coordination isomerism	677
	Structural isomerism: linkage isomerism	677
	Stereoisomerism: diastereoisomers	678
	Stereoisomerism: enantiomers	679
20	<i>d</i>-Block metal chemistry: coordination complexes	687
20.1	Introduction	687
	High- and low-spin states	687

20.2	Bonding in <i>d</i> -block metal complexes: valence bond theory	688
	Hybridization schemes	688
20.3	Crystal field theory	689
	The octahedral crystal field	689
	Crystal field stabilization energy: high- and low-spin octahedral complexes	691
	Jahn–Teller distortions	693
	The tetrahedral crystal field	693
	The square planar crystal field	695
	Other crystal fields	696
	Crystal field theory: uses and limitations	696
20.4	Molecular orbital theory: octahedral complexes	697
	Complexes with <i>no</i> metal–ligand π -bonding	697
	Complexes with metal–ligand π -bonding	698
20.5	Ligand field theory	703
20.6	Describing electrons in multi-electron systems	703
	Quantum numbers L and M_L for multi-electron species	703
	Quantum numbers S and M_S for multi-electron species	704
	Microstates and term symbols	704
	The quantum numbers J and M_J	705
	Ground states of elements with $Z = 1–10$	706
	The d^2 configuration	708
20.7	Electronic spectra: absorption	709
	Spectral features	709
	Charge transfer absorptions	710
	Selection rules	711
	Electronic absorption spectra of octahedral and tetrahedral complexes	712
	Interpretation of electronic absorption spectra: use of Racah parameters	715
	Interpretation of electronic absorption spectra: Tanabe–Sugano diagrams	718
20.8	Electronic spectra: emission	719
20.9	Evidence for metal–ligand covalent bonding	720
	The nephelauxetic effect	720
	EPR spectroscopy	721
20.10	Magnetic properties	721
	Magnetic susceptibility and the spin-only formula	721
	Spin and orbital contributions to the magnetic moment	723
	The effects of temperature on μ_{eff}	725
	Spin crossover	726
	Ferromagnetism, antiferromagnetism and ferrimagnetism	726
20.11	Thermodynamic aspects: ligand field stabilization energies (LFSE)	728
	Trends in LFSE	728
	Lattice energies and hydration energies of M^{n+} ions	729
	Octahedral versus tetrahedral coordination: spinels	730
20.12	Thermodynamic aspects: the Irving–Williams series	730
20.13	Thermodynamic aspects: oxidation states in aqueous solution	731

21 d-Block metal chemistry: the first row metals	738
Technetium(IV) and rhenium(V)	738
22.1 Introduction	738
22.2 Occurrence, extraction and uses	738
22.3 Physical properties: an overview	743
22.4 Group 3: scandium	743
The metal	743
Scandium(III)	743
22.5 Group 4: titanium	744
The metal	744
Titanium(IV)	745
Titanium(III)	748
Low oxidation states	748
22.6 Group 5: vanadium	749
The metal	749
Vanadium(V)	749
Vanadium(IV)	750
Vanadium(III)	752
Vanadium(II)	753
22.7 Group 6: chromium	754
The metal	754
Chromium(VI)	754
Chromium(V) and chromium(IV)	756
Chromium(III)	756
Chromium(II)	758
Chromium–chromium multiple bonds	759
22.8 Group 7: manganese	761
The metal	761
Manganese(VII)	762
Manganese(VI)	763
Manganese(V)	763
Manganese(IV)	764
Manganese(III)	766
Manganese(II)	767
Manganese(I)	768
22.9 Group 8: iron	769
The metal	769
Iron(VI), iron(V) and iron(IV)	769
Iron(III)	771
Iron(II)	775
Iron in low oxidation states	777
22.10 Group 9: cobalt	777
The metal	777
Cobalt(IV)	778
Cobalt(III)	778
Cobalt(II)	781
22.11 Group 10: nickel, palladium and platinum	884
Nickel(IV)	884
Nickel(III)	884
Nickel(II)	884
Nickel(0)	884
Copper(IV)	887
Copper(III)	887
Copper(II)	887
Copper(0)	887
22.12 Group 11: copper, zinc and tin	887
Copper(IV)	887
Copper(III)	887
Copper(II)	887
Copper(0)	887
Zinc(IV)	887
Zinc(III)	887
Zinc(II)	887
Zinc(0)	887
Tin(IV)	887
Tin(III)	887
Tin(II)	887
Tin(0)	887
22.13 Group 12: zinc, cadmium and mercury	887
Zinc(IV)	887
Zinc(III)	887
Zinc(II)	887
Zinc(0)	887
Cadmium(IV)	887
Cadmium(III)	887
Cadmium(II)	887
Cadmium(0)	887
Mercury(IV)	887
Mercury(III)	887
Mercury(II)	887
Mercury(0)	887
22.14 Group 13: aluminium, gallium, indium and thallium	887
Aluminium(IV)	887
Aluminium(III)	887
Aluminium(II)	887
Aluminium(0)	887
Gallium(IV)	887
Gallium(III)	887
Gallium(II)	887
Gallium(0)	887
Indium(IV)	887
Indium(III)	887
Indium(II)	887
Indium(0)	887
Thallium(IV)	887
Thallium(III)	887
Thallium(II)	887
Thallium(0)	887
22.15 Group 14: silicon, germanium, tin and lead	887
Silicon(IV)	887
Silicon(III)	887
Silicon(II)	887
Silicon(0)	887
Germanium(IV)	887
Germanium(III)	887
Germanium(II)	887
Germanium(0)	887
Tin(IV)	887
Tin(III)	887
Tin(II)	887
Tin(0)	887
Lead(IV)	887
Lead(III)	887
Lead(II)	887
Lead(0)	887
22.16 Group 15: nitrogen, phosphorus, arsenic, antimony and bismuth	887
Nitrogen(IV)	887
Nitrogen(III)	887
Nitrogen(II)	887
Nitrogen(0)	887
Phosphorus(IV)	887
Phosphorus(III)	887
Phosphorus(II)	887
Phosphorus(0)	887
Arsenic(IV)	887
Arsenic(III)	887
Arsenic(II)	887
Arsenic(0)	887
Antimony(IV)	887
Antimony(III)	887
Antimony(II)	887
Antimony(0)	887
Bismuth(IV)	887
Bismuth(III)	887
Bismuth(II)	887
Bismuth(0)	887
22.17 Group 16: oxygen, sulphur, selenium, tellurium and polonium	887
Oxygen(IV)	887
Oxygen(III)	887
Oxygen(II)	887
Oxygen(0)	887
Sulphur(IV)	887
Sulphur(III)	887
Sulphur(II)	887
Sulphur(0)	887
Selenium(IV)	887
Selenium(III)	887
Selenium(II)	887
Selenium(0)	887
Tellurium(IV)	887
Tellurium(III)	887
Tellurium(II)	887
Tellurium(0)	887
Polonium(IV)	887
Polonium(III)	887
Polonium(II)	887
Polonium(0)	887
22.18 Group 17: fluorine, chlorine, bromine, iodine and astatine	887
Fluorine(IV)	887
Fluorine(III)	887
Fluorine(II)	887
Fluorine(0)	887
Chlorine(IV)	887
Chlorine(III)	887
Chlorine(II)	887
Chlorine(0)	887
Bromine(IV)	887
Bromine(III)	887
Bromine(II)	887
Bromine(0)	887
Iodine(IV)	887
Iodine(III)	887
Iodine(II)	887
Iodine(0)	887
Astatine(IV)	887
Astatine(III)	887
Astatine(II)	887
Astatine(0)	887
22.19 Group 18: helium, neon, argon, krypton, xenon and radon	887
Helium(IV)	887
Helium(III)	887
Helium(II)	887
Helium(0)	887
Neon(IV)	887
Neon(III)	887
Neon(II)	887
Neon(0)	887
Argon(IV)	887
Argon(III)	887
Argon(II)	887
Argon(0)	887
Krypton(IV)	887
Krypton(III)	887
Krypton(II)	887
Krypton(0)	887
Xenon(IV)	887
Xenon(III)	887
Xenon(II)	887
Xenon(0)	887
Radon(IV)	887
Radon(III)	887
Radon(II)	887
Radon(0)	887

21.11 Group 10: nickel	785
The metal on schemes	785
20.3 Nickel(IV) and nickel(III)	785
Nickel(II)	786
Nickel(I)	788
21.12 Group 11: copper	788
The metal	788
20.3 Crystal field theory	788
Nickel(IV) and nickel(III)	789
Copper(II) fields	790
Copper(I) theory: uses and limitations	793
21.13 Group 12: zinc	796
The metal	796
20.5 Zinc(IV) and zinc(III)	796
Zinc(II)	796
Zinc(I)	797
20.5 Lattice field theory	797
22 d-Block metal chemistry: the heavier metals	803
22.1 Introduction	803
22.2 Occurrence, extraction and uses	803
22.3 Physical properties	806
Effects of the lanthanoid contraction	809
Coordination numbers	809
NMR active nuclei	809
22.4 Group 3: yttrium	810
The metal	810
Yttrium(III)	810
22.5 Group 4: zirconium and hafnium	810
The metals	810
Zirconium(IV) and hafnium(IV)	810
Lower oxidation states of zirconium and hafnium	812
Zirconium clusters	812
22.6 Group 5: niobium and tantalum	812
The metals	812
Niobium(V) and tantalum(V)	813
Niobium(IV) and tantalum(IV)	815
Lower oxidation state halides	816
22.7 Group 6: molybdenum and tungsten	817
The metals	817
Molybdenum(VI) and tungsten(VI)	818
Molybdenum(V) and tungsten(V)	823
Molybdenum(IV) and tungsten(IV)	823
Molybdenum(III) and tungsten(III)	825
Molybdenum(II) and tungsten(II)	826
22.8 Group 7: technetium and rhenium	829
The metals	829
High oxidation states of technetium and rhenium: M(VII), M(VI) and M(V)	829
Technetium(IV) and rhenium(IV)	832

Techneum(III) and rhenium(III)	834
Techneum(I) and rhenium(I)	835
22.9 Group 8: ruthenium and osmium	836
The metals	836
High oxidation states of ruthenium and osmium: M(VIII), M(VII) and M(VI)	836
Ruthenium(V), (IV) and osmium(V), (IV)	839
Ruthenium(III) and osmium(III)	841
Ruthenium(II) and osmium(II)	843
Mixed-valence ruthenium complexes	846
22.10 Group 9: rhodium and iridium	847
The metals	847
High oxidation states of rhodium and iridium: M(VI) and M(V)	847
Rhodium(IV) and iridium(IV)	847
Rhodium(III) and iridium(III)	848
Rhodium(II) and iridium(II)	851
Rhodium(I) and iridium(I)	851
22.11 Group 10: palladium and platinum	852
The metals	852
The highest oxidation states: M(VI) and M(V)	852
Palladium(IV) and platinum(IV)	853
Palladium(III), platinum(III) and mixed-valence complexes	854
Palladium(II) and platinum(II)	855
Platinum(-II)	858
22.12 Group 11: silver and gold	860
The metals	860
Gold(V) and silver(V)	860
Gold(III) and silver(III)	860
Gold(II) and silver(II)	861
Gold(I) and silver(I)	863
Gold(-I) and silver(-I)	866
22.13 Group 12: cadmium and mercury	866
The metals	866
Cadmium(II)	867
Mercury(II)	867
Mercury(I)	868
Polymer-supported catalysts	868
23 Organometallic compounds of s- and p-block elements	875
23.1 Introduction	875
23.2 Group 1: alkali metal organometallics	875
23.3 Group 2 organometallics	879
Beryllium	879
Magnesium	880
Calcium, strontium and barium	882
23.4 Group 13: catalysts for organic transformations; uses of ZSM-5	884
Boron	884
Aluminium	884
Gallium, indium and thallium	887

23.5 Group 14	892
Silicon	893
Germanium	895
Tin	897
Lead	901
Coparallel and tilted C ₅ -rings in group 14 metallocenes	903
23.6 Group 15	904
Bonding aspects and E=E bond formation	904
Arsenic, antimony and bismuth	905
23.7 Group 16	909
Selenium and tellurium	909
24 Organometallic compounds of d-block elements	915
24.1 Introduction	915
24.2 Common types of ligand: bonding and spectroscopy	915
σ-Bonded alkyl, aryl and related ligands	915
Carbonyl ligands	916
Hydride ligands	918
Phosphane and related ligands	918
π-Bonded organic ligands	920
Nitrogen monoxide	922
Dinitrogen	923
Dihydrogen	924
24.3 The 18-electron rule	925
24.4 Covalent bond classification (CBC)	926
24.5 Metal carbonyls: synthesis, physical properties and structure	928
Synthesis and physical properties	929
Structures	932
24.6 The isolobal principle and application of Wade's rules	934
24.7 Total valence electron counts in d-block organometallic clusters	937
Single cage structures	937
Condensed cages	939
Limitations of total valence counting schemes	939
24.8 Types of organometallic reactions	940
Substitution of CO ligands	940
Oxidative addition	940
Alkyl and hydrogen migrations	941
β-Hydrogen elimination	942
α-Hydrogen abstraction	943
Summary	943
24.9 Metal carbonyls: selected reactions	944
24.10 Metal carbonyl hydrides and halides	945
24.11 Alkyl, aryl, alkene and alkyne complexes	947
σ-Bonded alkyl and aryl ligands	947

Alkene ligands	947
Alkyne ligands	950
24.12 Allyl and buta-1,3-diene complexes	951
Allyl and related ligands	951
Buta-1,3-diene and related ligands	953
24.13 Carbene and carbyne complexes	953
24.14 Complexes containing η^5-cyclopentadienyl ligands	955
Ferrocene and other metallocenes	956
($\eta^5\text{-Cp}$) ₂ Fe ₂ (CO) ₄ and derivatives	958
24.15 Complexes containing η^6- and η^7-ligands	962
η^6 -Arene ligands	962
Cycloheptatriene and derived ligands	963
24.16 Complexes containing the η^4-cyclobutadiene ligand	964
25 Catalysis and some industrial processes	971
25.1 Introduction and definitions	971
25.2 Catalysis: introductory concepts	971
Energy profiles for a reaction: catalysed versus non-catalysed	971
Catalytic cycles	972
Choosing a catalyst	974
25.3 Homogeneous catalysis: alkene (olefin) and alkyne metathesis	974
25.4 Homogeneous catalytic reduction of N₂ to NH₃	977
25.5 Homogeneous catalysis: industrial applications	978
Alkene hydrogenation	978
Monsanto and Cativa acetic acid syntheses	982
Tennessee–Eastman acetic anhydride process	983
Hydroformylation (Oxo-process)	984
Alkene oligomerization	986
25.6 Homogeneous catalyst development	986
Polymer-supported catalysts	986
Biphasic catalysis	987
25.7 Heterogeneous catalysis: surfaces and interactions with adsorbates	989
25.8 Heterogeneous catalysis: commercial applications	991
Alkene polymerization: Ziegler–Natta catalysis and metallocene catalysts	991
Fischer–Tropsch carbon chain growth	993
Haber–Bosch process	994
Production of SO ₃ in the Contact process	995
Catalytic converters	996
Zeolites as catalysts for organic transformations: uses of ZSM-5	997
25.9 Heterogeneous catalysis: organometallic cluster models	998

26 d-Block metal complexes: reaction mechanisms	1007
26.1 Introduction	1007
26.2 Ligand substitutions: some general points	1007
Kinetically inert and labile complexes	1007
Stoichiometric equations say nothing about mechanism	1008
Types of substitution mechanism	1009
Activation parameters	1009
26.3 Substitution in square planar complexes	1010
Rate equations, mechanism and the <i>trans</i> -effect	1010
Ligand nucleophilicity	1013
26.4 Substitution and racemization in octahedral complexes	1015
Water exchange	1015
The Eigen–Wilkins mechanism	1017
Stereochemistry of substitution	1018
Base-catalysed hydrolysis	1020
Isomerization and racemization of octahedral complexes	1021
26.5 Electron-transfer processes	1022
Inner-sphere mechanism	1022
Outer-sphere mechanism	1025
27 The f-block metals: lanthanoids and actinoids	1033
27.1 Introduction	1033
27.2 f-Orbitals and oxidation states	1035
27.3 Atom and ion sizes	1036
The lanthanoid contraction	1036
Coordination numbers	1036
27.4 Spectroscopic and magnetic properties	1037
Electronic spectra and magnetic moments: lanthanoids	1037
Luminescence of lanthanoid complexes	1040
Electronic spectra and magnetic moments: actinoids	1041
27.5 Sources of the lanthanoids and actinoids	1041
Occurrence and separation of the lanthanoids	1041
The actinoids	1041
27.6 Lanthanoid metals	1043
27.7 Inorganic compounds and coordination complexes of the lanthanoids	1045
Halides	1045
Hydroxides and oxides	1046
Complexes of Ln(III)	1046
27.8 Organometallic complexes of the lanthanoids	1048
σ -Bonded complexes	1048
Cyclopentadienyl complexes	1051
Bis(arene) derivatives	1053
Complexes containing the η^8 -cyclooctatetraenyl ligand	1053

27.9	The actinoid metals	1053
27.10	Inorganic compounds and coordination complexes of thorium, uranium and plutonium	1054
	Thorium	1054
	Uranium	1055
	Plutonium	1057
27.11	Organometallic complexes of thorium and uranium	1058
	σ -Bonded complexes	1058
	Cyclopentadienyl derivatives	1058
	Complexes containing the η^8 -cyclooctatetraenyl ligand	1059
28	Inorganic materials and nanotechnology	1065
28.1	Introduction	1065
28.2	Electrical conductivity in ionic solids	1065
	Sodium and lithium ion conductors	1066
	d-Block metal(II) oxides	1068
28.3	Transparent conducting oxides and their applications in devices	1068
	Sn-doped In_2O_3 (ITO) and F-doped SnO_2 (FTO)	1068
	Dye-sensitized solar cells (DSCs)	1069
	Solid state lighting: OLEDs	1070
	Solid state lighting: LECs	1071
28.4	Superconductivity	1072
	Superconductors: early examples and basic theory	1072
	High-temperature superconductors	1073
	Iron-based superconductors	1075
	Chevrel phases	1076
	Superconducting properties of MgB_2	1077
	Applications of superconductors	1077
28.5	Ceramic materials: colour pigments	1078
	White pigments (opacifiers)	1078
	Adding colour	1079
28.6	Chemical vapour deposition (CVD)	1079
	High-purity silicon for semiconductors	1080
	α -Boron nitride	1080
	Silicon nitride and carbide	1080
	III–V Semiconductors	1081
	Metal deposition	1083
	Ceramic coatings	1083
	Perovskites and cuprate superconductors	1083
28.7	Inorganic fibres	1085
	Boron fibres	1085
	Carbon fibres	1086
	Silicon carbide fibres	1087
	Alumina fibres	1088
28.8	Graphene	1088
28.9	Carbon nanotubes	1091

29 The trace metals of life	1098
29.1 Introduction	1098
Amino acids, peptides and proteins: some terminology	1100
29.2 Metal storage and transport: Fe, Cu, Zn and V	1101
Iron storage and transport	1101
Metallothioneins: transporting some toxic metals	1108
29.3 Dealing with O ₂	1109
Haemoglobin and myoglobin	1109
Haemocyanin	1112
Haemerythrin	1114
Cytochromes P-450	1116
29.4 Biological redox processes	1117
Blue copper proteins	1117
The mitochondrial electron-transfer chain	1118
Iron-sulfur proteins	1120
Cytochromes	1127
29.5 The Zn ²⁺ ion: Nature's Lewis acid	1130
Carbonic anhydrase II	1130
Carboxypeptidase A	1132
Carboxypeptidase G2	1133
Cobalt-for-zinc ion substitution	1133
Appendices	1141
1 Greek letters with pronunciations	1142
2 Abbreviations and symbols for quantities and units	1143
3 Selected character tables	1149
4 The electromagnetic spectrum	1153
5 Naturally occurring isotopes and their abundances	1155
6 Van der Waals, metallic, covalent and ionic radii	1158
7 Pauling electronegativity values (χ^P) for selected elements of the periodic table	1160
8 Ground state electronic configurations of the elements and ionization energies	1161
9 Electron affinities	1164
10 Standard enthalpies of atomization ($\Delta_a H^\circ$) of the elements at 298 K	1165
11 Selected standard reduction potentials (298 K)	1166
12 Selected bond enthalpy terms	1169
Answers to non-descriptive problems	1170
Index	1191
IUPAC: Brief Guide to the Nomenclature of Inorganic Chemistry	1248