

Chemistry of the Elements

Second Edition

N. N. GREENWOOD and A. EARNSHAW

*School of Chemistry
University of Leeds, U.K.*



ELSEVIER
BUTTERWORTH
HEINEMANN

AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD
PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Contents

Preface to the second edition	xix	
Preface to the first edition	xxi	
Chapter 1	Origin of the Elements. Isotopes and Atomic Weights	1
1.1	Introduction	1
1.2	Origin of the Universe	1
1.3	Abundances of the Elements in the Universe	3
1.4	Stellar Evolution and the Spectral Classes of Stars	5
1.5	Synthesis of the Elements	9
1.5.1	Hydrogen burning	9
1.5.2	Helium burning and carbon burning	10
1.5.3	The α -process	11
1.5.4	The e-process (equilibrium process)	12
1.5.5	The s- and r-processes (slow and rapid neutron absorption)	12
1.5.6	The p-process (proton capture)	13
1.5.7	The x-process	13
1.6	Atomic Weights	15
1.6.1	Uncertainty in atomic weights	16
1.6.2	The problem of radioactive elements	18
Chapter 2	Chemical Periodicity and the Periodic Table	20
2.1	Introduction	20
2.2	The Electronic Structure of Atoms	21
2.3	Periodic Trends in Properties	23
2.3.1	Trends in atomic and physical properties	23
2.3.2	Trends in chemical properties	27
2.4	Prediction of New Elements and Compounds	29
Chapter 3	Hydrogen	32
3.1	Introduction	32
3.2	Atomic and Physical Properties of Hydrogen	34
3.2.1	Isotopes of hydrogen	34
3.2.2	<i>Ortho</i> - and <i>para</i> -hydrogen	35
3.2.3	Ionized forms of hydrogen	36
3.3	Preparation, Production and Uses	38
3.3.1	Hydrogen	38
3.3.2	Deuterium	39
3.3.3	Tritium	41
3.4	Chemical Properties and Trends	43
3.4.1	The coordination chemistry of hydrogen	44

3.5	Protonic Acids and Bases	48
3.6	The Hydrogen Bond	52
3.6.1	Influence on properties	53
3.6.2	Influence on structure	59
3.6.3	Strength of hydrogen bonds and theoretical description	61
3.7	Hydrides of the Elements	64
Chapter 4	Lithium, Sodium, Potassium, Rubidium, Caesium and Francium	68
4.1	Introduction	68
4.2	The Elements	68
4.2.1	Discovery and isolation	68
4.2.2	Terrestrial abundance and distribution	69
4.2.3	Production and uses of the metals	71
4.2.4	Properties of the alkali metals	74
4.2.5	Chemical reactivity and trends	76
4.2.6	Solutions in liquid ammonia and other solvents	77
4.3	Compounds	79
4.3.1	Introduction: the ionic-bond model	79
4.3.2	Halides and hydrides	82
4.3.3	Oxides, peroxides, superoxides and suboxides	84
4.3.4	Hydroxides	86
4.3.5	Oxoacid salts and other compounds	87
4.3.6	Coordination chemistry	90
4.3.7	Imides, amides and related compounds	99
4.3.8	Organometallic compounds	102
Chapter 5	Beryllium, Magnesium, Calcium, Strontium, Barium and Radium	107
5.1	Introduction	107
5.2	The Elements	108
5.2.1	Terrestrial abundance and distribution	108
5.2.2	Production and uses of the metals	110
5.2.3	Properties of the elements	111
5.2.4	Chemical reactivity and trends	112
5.3	Compounds	113
5.3.1	Introduction	113
5.3.2	Hydrides and halides	115
5.3.3	Oxides and hydroxides	119
5.3.4	Oxoacid salts and coordination complexes	122
5.3.5	Organometallic compounds	127
	Beryllium	127
	Magnesium	131
	Calcium, strontium and barium	136
Chapter 6	Boron	139
6.1	Introduction	139
6.2	Boron	140
6.2.1	Isolation and purification of the element	140
6.2.2	Structure of crystalline boron	141
6.2.3	Atomic and physical properties of boron	144
6.2.4	Chemical properties	144
6.3	Borides	145
6.3.1	Introduction	145
6.3.2	Preparation and stoichiometry	146
6.3.3	Structures of borides	147

Contents

vii

6.4	Boranes (Boron Hydrides)	151
6.4.1	Introduction	151
6.4.2	Bonding and topology	157
6.4.3	Preparation and properties of boranes	162
6.4.4	The chemistry of small boranes and their anions (B ₁ -B ₄)	164
6.4.5	Intermediate-sized boranes and their anions (B ₅ -B ₉)	170
6.4.6	Chemistry of <i>nido</i> -decaborane, B ₁₀ H ₁₄	173
6.4.7	Chemistry of <i>closo</i> -B _n H _n ²⁻	178
6.5	Carboranes	181
6.6	Metallocarboranes	189
6.7	Boron Halides	195
6.7.1	Boron trihalides	195
6.7.2	Lower halides of boron	200
6.8	Boron-Oxygen Compounds	203
6.8.1	Boron oxides and oxoacids	203
6.8.2	Borates	205
6.8.3	Organic compounds containing boron-oxygen bonds	207
6.9	Boron-Nitrogen Compounds	207
6.10	Other Compounds of Boron	211
6.10.1	Compounds with bonds to P, As or Sb	211
6.10.2	Compounds with bonds to S, Se and Te	213

Chapter 7 Aluminium, Gallium, Indium and Thallium 216

7.1	Introduction	216
7.2	The Elements	217
7.2.1	Terrestrial abundance and distribution	217
7.2.2	Preparation and uses of the metals	219
7.2.3	Properties of the elements	222
7.2.4	Chemical reactivity and trends	224
7.3	Compounds	227
7.3.1	Hydrides and related complexes	227
7.3.2	Halides and halide complexes	233
	Aluminium trihalides	233
	Trihalides of gallium, indium and thallium	237
	Lower halides of gallium, indium and thallium	240
7.3.3	Oxides and hydroxides	242
7.3.4	Ternary and more complex oxide phases	247
	Spinel and related compounds	247
	Sodium- β -alumina and related phases	249
	Tricalcium aluminate, Ca ₃ Al ₂ O ₆	251
7.3.5	Other inorganic compounds	252
	Chalcogenides	252
	Compounds with bonds to N, P, As, Sb or Bi	255
	Some unusual stereochemistries	256
7.3.6	Organometallic compounds	257
	Organoaluminium compounds	258
	Organometallic compounds of Ga, In and Tl	262
	Al-N heterocycles and clusters	265

Chapter 8 Carbon 268

8.1	Introduction	268
8.2	Carbon	269
8.2.1	Terrestrial abundance and distribution	269
8.2.2	Allotropic forms	274
8.2.3	Atomic and physical properties	276
8.2.4	Fullerenes	278
	Structure of the fullerenes	280
	Other molecular allotropes of carbon	282
	Chemistry of the fullerenes	282
	Reduction of fullerenes to fullerides	285

	Addition reactions	286
	Heteroatom fullerene-type clusters	287
	Encapsulation of metal atoms by fullerene clusters	288
8.2.5	Chemical properties of carbon	289
8.3	Graphite Intercalation Compounds	293
8.4	Carbides	296
	Metallocarbohedrenes (met-cars)	300
8.5	Hydrides, Halides and Oxohalides	301
8.6	Oxides and Carbonates	305
8.7	Chalcogenides and Related Compounds	313
8.8	Cyanides and Other Carbon-Nitrogen Compounds	319
8.9	Organometallic Compounds	326
Chapter 9	Silicon	328
9.1	Introduction	328
9.2	Silicon	329
	9.2.1 Occurrence and distribution	329
	9.2.2 Isolation, production and industrial uses	330
	9.2.3 Atomic and physical properties	330
	9.2.4 Chemical properties	331
9.3	Compounds	335
	9.3.1 Silicides	335
	9.3.2 Silicon hydrides (silanes)	337
	9.3.3 Silicon halides and related complexes	340
	9.3.4 Silica and silicic acids	342
	9.3.5 Silicate minerals	347
	Silicates with discrete units	347
	Silicates with chain or ribbon structures	349
	Silicates with layer structures	349
	Silicates with framework structures	354
	9.3.6 Other inorganic compounds of silicon	359
	9.3.7 Organosilicon compounds and silicones	361
Chapter 10	Germanium, Tin and Lead	367
10.1	Introduction	367
10.2	The Elements	368
	10.2.1 Terrestrial abundance and distribution	368
	10.2.2 Production and uses of the elements	369
	10.2.3 Properties of the elements	371
	10.2.4 Chemical reactivity and group trends	373
10.3	Compounds	374
	10.3.1 Hydrides and hydrohalides	374
	10.3.2 Halides and related complexes	375
	Germanium halides	376
	Tin halides	377
	Lead halides	381
	10.3.3 Oxides and hydroxides	382
	10.3.4 Derivatives of oxoacids	387
	10.3.5 Other inorganic compounds	389
	10.3.6 Metal-metal bonds and clusters	391
	10.3.7 Organometallic compounds	396
	Germanium	396
	Tin	399
	Lead	404
Chapter 11	Nitrogen	406
11.1	Introduction	406

Contents

ix

11.2	The Element	407
11.2.1	Abundance and distribution	407
11.2.2	Production and uses of nitrogen	409
11.2.3	Atomic and physical properties	411
11.2.4	Chemical reactivity	412
11.3	Compounds	416
11.3.1	Nitrides, azides and nitrido complexes	417
11.3.2	Ammonia and ammonium salts	420
	Liquid ammonia as a solvent	424
11.3.3	Other hydrides of nitrogen	426
	Hydrazine	427
	Hydroxylamine	431
	Hydrogen azide	432
11.3.4	Thermodynamic relations between N-containing species	434
11.3.5	Nitrogen halides and related compounds	438
11.3.6	Oxides of nitrogen	443
	Nitrous oxide, N_2O	443
	Nitric oxide, NO	445
	Dinitrogen trioxide, N_2O_3	454
	Nitrogen dioxide, NO_2 , and dinitrogen tetroxide, N_2O_4	455
	Dinitrogen pentoxide, N_2O_5 , and nitrogen trioxide, NO_3	458
11.3.7	Oxoacids, oxoanions and oxoacid salts of nitrogen	459
	Hyponitrous acid and hyponitrites	459
	Nitrous acid and nitrites	461
	Nitric acid and nitrates	465
	Orthonitrates, M_3NO_4	471

Chapter 12 Phosphorus

473

12.1	Introduction	473
12.2	The Element	475
12.2.1	Abundance and distribution	475
12.2.2	Production and uses of elemental phosphorus	479
12.2.3	Allotropes of phosphorus	479
12.2.4	Atomic and physical properties	482
12.2.5	Chemical reactivity and stereochemistry	483
12.3	Compounds	489
12.3.1	Phosphides	489
12.3.2	Phosphine and related compounds	492
12.3.3	Phosphorus halides	495
	Phosphorus trihalides	495
	Diphosphorus tetrahalides and other lower halides of phosphorus	497
	Phosphorus pentahalides	498
	Pseudohalides of phosphorus(III)	501
12.3.4	Oxohalides and thiohalides of phosphorus	501
12.3.5	Phosphorus oxides, sulfides, selenides and related compounds	503
	Oxides	503
	Sulfides	506
	Oxosulfides	510
12.3.6	Oxoacids of phosphorus and their salts	510
	Hypophosphorous acid and hypophosphites [$H_2PO(OH)$ and $H_2PO_2^-$]	513
	Phosphorous acid and phosphites [$HPO(OH)_2$ and HPO_3^{2-}]	514
	Hypophosphoric acid ($H_4P_2O_6$) and hypophosphates	515
	Other lower oxoacids of phosphorus	516
	The phosphoric acids	516
	Orthophosphates	523
	Chain polyphosphates	526
	<i>Cyclo</i> -polyphosphoric acids and <i>cyclo</i> -polyphosphates	529
12.3.7	Phosphorus-nitrogen compounds	531
	Cyclophosphazanes	533
	Phosphazenes	534

	Polyphosphazenes	536
	Applications	542
12.3.8	Organophosphorus compounds	542

Chapter 13 Arsenic, Antimony and Bismuth 547

13.1	Introduction	547
13.2	The Elements	548
	13.2.1 Abundance, distribution and extraction	548
	13.2.2 Atomic and physical properties	550
	13.2.3 Chemical reactivity and group trends	552
13.3	Compounds of Arsenic, Antimony and Bismuth	554
	13.3.1 Intermetallic compounds and alloys	554
	13.3.2 Hydrides of arsenic, antimony and bismuth	557
	13.3.3 Halides and related complexes	558
	Trihalides, MX_3	558
	Pentahalides, MX_5	561
	Mixed halides and lower halides	563
	Halide complexes of M^{III} and M^V	564
	Oxide halides	570
	13.3.4 Oxides and oxo compounds	572
	Oxo compounds of M^{III}	573
	Mixed-valence oxides	576
	Oxo compounds of M^V	576
	13.3.5 Sulfides and related compounds	578
	13.3.6 Metal-metal bonds and clusters	583
	13.3.7 Other inorganic compounds	591
	13.3.8 Organometallic compounds	592
	Organoarsenic(III) compounds	593
	Organoarsenic(V) compounds	594
	Physiological activity of arsenicals	596
	Organoantimony and organobismuth compounds	596

Chapter 14 Oxygen 600

14.1	The Element	600
	14.1.1 Introduction	600
	14.1.2 Occurrence	602
	14.1.3 Preparation	603
	14.1.4 Atomic and physical properties	604
	14.1.5 Other forms of oxygen	607
	Ozone	607
	Atomic oxygen	611
	14.1.6 Chemical properties of dioxygen, O_2	612
14.2	Compounds of Oxygen	615
	14.2.1 Coordination chemistry: dioxygen as a ligand	615
	14.2.2 Water	620
	Introduction	620
	Distribution and availability	621
	Physical properties and structure	623
	Water of crystallization, aquo complexes and solid hydrates	625
	Chemical properties	627
	Polywater	627
	14.2.3 Hydrogen peroxide	632
	Physical properties	633
	Chemical properties	633
	14.2.4 Oxygen fluorides	634
	14.2.5 Oxides	638
	Various methods of classification	640
	Nonstoichiometry	640

Chapter 15	Sulfur	645
15.1	The Element	645
15.1.1	Introduction	645
15.1.2	Abundance and distribution	647
15.1.3	Production and uses of elemental sulfur	649
15.1.4	Allotropes of sulfur	652
15.1.5	Atomic and physical properties	661
15.1.6	Chemical reactivity	662
	Polyatomic sulfur cations	664
	Sulfur as a ligand	665
	Other ligands containing sulfur as donor atom	673
15.2	Compounds of Sulfur	676
15.2.1	Sulfides of the metallic elements	676
	General considerations	676
	Structural chemistry of metal sulfides	679
	Anionic polysulfides	681
15.2.2	Hydrides of sulfur (sulfanes)	682
15.2.3	Halides of sulfur	683
	Sulfur fluorides	683
	Chlorides, bromides and iodides of sulfur	689
15.2.4	Oxohalides of sulfur	693
15.2.5	Oxides of sulfur	695
	Lower oxides	695
	Sulfur dioxide, SO ₂	698
	Sulfur dioxide as a ligand	701
	Sulfur trioxide	703
	Higher oxides	704
15.2.6	Oxoacids of sulfur	706
	Sulfuric acid, H ₂ SO ₄	710
	Peroxo-sulfuric acids, H ₂ SO ₅ and H ₂ S ₂ O ₈	712
	Thiosulfuric acid, H ₂ S ₂ O ₃	714
	Dithionic acid, H ₂ S ₂ O ₆	715
	Polythionic acids, H ₂ S _n O ₆	716
	Sulfurous acid, H ₂ SO ₃	717
	Disulfurous acid, H ₂ S ₂ O ₅	720
	Dithionous acid, H ₂ S ₂ O ₄	720
15.2.7	Sulfur–nitrogen compounds	721
	Binary sulfur nitrides	722
	Sulfur–nitrogen cations and anions	730
	Sulfur imides, S _{8–n} (NH) _n	735
	Other cyclic sulfur–nitrogen compounds	736
	Sulfur–nitrogen–halogen compounds	736
	Sulfur–nitrogen–oxygen compounds	736
Chapter 16	Selenium, Tellurium and Polonium	747
16.1	The Elements	747
16.1.1	Introduction: history, abundance, distribution	747
16.1.2	Production and uses of the elements	748
16.1.3	Allotropy	751
16.1.4	Atomic and physical properties	753
16.1.5	Chemical reactivity and trends	754
16.1.6	Polyatomic cations, M _x ⁿ⁺	759
16.1.7	Polyatomic anions, M _x ^{2–}	762
16.2	Compounds of Selenium, Tellurium and Polonium	765
16.2.1	Selenides, tellurides and polonides	765
16.2.2	Hydrides	766
16.2.3	Halides	767
	Lower halides	768
	Tetrahalides	772

	Hexahalides	775
	Halide complexes	776
16.2.4	Oxohalides and pseudohalides	777
16.2.5	Oxides	779
16.2.6	Hydroxides and oxoacids	781
16.2.7	Other inorganic compounds	783
16.2.8	Organo-compounds	786

Chapter 17 The Halogens: Fluorine, Chlorine, Bromine, Iodine and Astatine 789

17.1	The Elements	789
17.1.1	Introduction	789
	Fluorine	789
	Chlorine	792
	Bromine	793
	Iodine	794
	Astatine	794
17.1.2	Abundance and distribution	795
17.1.3	Production and uses of the elements	796
17.1.4	Atomic and physical properties	800
17.1.5	Chemical reactivity and trends	804
	General reactivity and stereochemistry	804
	Solutions and charge-transfer complexes	806
17.2	Compounds of Fluorine, Chlorine, Bromine and Iodine	809
17.2.1	Hydrogen halides, HX	809
	Preparation and uses	809
	Physical properties of the hydrogen halides	812
	Chemical reactivity of the hydrogen halides	813
	The hydrogen halides as nonaqueous solvents	816
17.2.2	Halides of the elements	819
	Fluorides	820
	Chlorides, bromides and iodides	821
17.2.3	Interhalogen compounds	824
	Diatomic interhalogens, XY	824
	Tetra-atomic interhalogens, XY ₃	828
	Hexa-atomic and octa-atomic interhalogens, XF ₅ and IF ₇	832
17.2.4	Polyhalide anions	835
17.2.5	Polyhalonium cations XY _{2n} ⁺	839
17.2.6	Halogen cations	842
17.2.7	Oxides of chlorine, bromine and iodine	844
	Oxides of chlorine	844
	Oxides of bromine	850
	Oxides of iodine	851
17.2.8	Oxoacids and oxoacid salts	853
	General considerations	853
	Hypohalous acids, HOX, and hypohalites, XO ⁻	856
	Halous acids, HOXO, and halites, XO ₂ ⁻	859
	Halic acids, HOXO ₂ , and halates, XO ₃ ⁻	862
	Perhalic acid and perchalates	865
	Perchloric acid and perchlorates	865
	Perbromic acid and perbromates	871
	Periodic acids and periodates	872
17.2.9	Halogen oxide fluorides and related compounds	875
	Chlorine oxide fluorides	875
	Bromine oxide fluorides	880
	Iodine oxide fluorides	881
17.2.10	Halogen derivatives of oxoacids	883
17.3	The Chemistry of Astatine	885

Chapter 18	The Noble Gases: Helium, Neon, Argon, Krypton, Xenon and Radon	888
18.1	Introduction	888
18.2	The Elements	889
18.2.1	Distribution, production and uses	889
18.2.2	Atomic and physical properties of the elements	890
18.3	Chemistry of the Noble Gases	892
18.3.1	Clathrates	893
18.3.2	Compounds of xenon	893
18.3.3	Compounds of other noble gases	903
 Chapter 19	 Coordination and Organometallic Compounds	 905
19.1	Introduction	905
19.2	Types of Ligand	906
19.3	Stability of Coordination Compounds	908
19.4	The Various Coordination Numbers	912
19.5	Isomerism	918
	Conformational isomerism	918
	Geometrical isomerism	919
	Optical isomerism	919
	Ionization isomerism	920
	Linkage isomerism	920
	Coordination isomerism	920
	Polymerization isomerism	921
	Ligand isomerism	921
19.6	The Coordinate Bond	921
19.7	Organometallic Compounds	924
19.7.1	Monohapto ligands	925
19.7.2	Dihapto ligands	930
19.7.3	Trihapto ligands	933
19.7.4	Tetrahapto ligands	935
19.7.5	Pentahapto ligands	937
19.7.6	Hexahapto ligands	940
19.7.7	Heptahapto and octahapto ligands	941
 Chapter 20	 Scandium, Yttrium, Lanthanum and Actinium	 944
20.1	Introduction	944
20.2	The Elements	945
20.2.1	Terrestrial abundance and distribution	945
20.2.2	Preparation and uses of the metals	945
20.2.3	Properties of the elements	946
20.2.4	Chemical reactivity and trends	948
20.3	Compounds of Scandium, Yttrium, Lanthanum and Actinium	949
20.3.1	Simple compounds	949
20.3.2	Complexes	950
20.3.3	Organometallic compounds	953
 Chapter 21	 Titanium, Zirconium and Hafnium	 954
21.1	Introduction	954
21.2	The Elements	955
21.2.1	Terrestrial abundance and distribution	955
21.2.2	Preparation and uses of the metals	955
21.2.3	Properties of the elements	956
21.2.4	Chemical reactivity and trends	958
21.3	Compounds of Titanium, Zirconium and Hafnium	961
21.3.1	Oxides and sulfides	961

21.3.2	Mixed (or complex) oxides	962
21.3.3	Halides	964
21.3.4	Compounds with oxoanions	966
21.3.5	Complexes	967
	Oxidation state IV (d^0)	967
	Oxidation state III (d^1)	969
	Lower oxidation states	971
21.3.6	Organometallic compounds	972
Chapter 22	Vanadium, Niobium and Tantalum	976
22.1	Introduction	976
22.2	The Elements	977
22.2.1	Terrestrial abundance and distribution	977
22.2.2	Preparation and uses of the metals	977
22.2.3	Atomic and physical properties of the elements	978
22.2.4	Chemical reactivity and trends	979
22.3	Compounds of Vanadium, Niobium and Tantalum	981
22.3.1	Oxides	981
22.3.2	Polymetallates	983
22.3.3	Sulfides, selenides and tellurides	987
22.3.4	Halides and oxohalides	988
22.3.5	Compounds with oxoanions	993
22.3.6	Complexes	994
	Oxidation state V (d^0)	994
	Oxidation state IV (d^1)	994
	Oxidation state III (d^2)	996
	Oxidation state II (d^3)	998
22.3.7	The biochemistry of vanadium	999
22.3.8	Organometallic compounds	999
Chapter 23	Chromium, Molybdenum and Tungsten	1002
23.1	Introduction	1002
23.2	The Elements	1003
23.2.1	Terrestrial abundance and distribution	1003
23.2.2	Preparation and uses of the metals	1003
23.2.3	Properties of the elements	1004
23.2.4	Chemical reactivity and trends	1005
23.3	Compounds of Chromium, Molybdenum and Tungsten	1007
23.3.1	Oxides	1007
23.3.2	Isopolymetallates	1009
23.3.3	Heteropolymetallates	1013
23.3.4	Tungsten and molybdenum bronzes	1016
23.3.5	Sulfides, selenides and tellurides	1017
23.3.6	Halides and oxohalides	1019
23.3.7	Complexes of chromium, molybdenum and tungsten	1023
	Oxidation state VI (d^0)	1023
	Oxidation state V (d^1)	1024
	Oxidation state IV (d^2)	1025
	Oxidation state III (d^3)	1027
	Oxidation state II (d^4)	1031
23.3.8	Biological activity and nitrogen fixation	1035
23.3.9	Organometallic compounds	1037
Chapter 24	Manganese, Technetium and Rhenium	1040
24.1	Introduction	1040
24.2	The Elements	1041

Contents

xv

24.2.1	Terrestrial abundance and distribution	1041
24.2.2	Preparation and uses of the metals	1041
24.2.3	Properties of the elements	1043
24.2.4	Chemical reactivity and trends	1044
24.3	Compounds of Manganese, Technetium and Rhenium	1045
24.3.1	Oxides and chalcogenides	1045
24.3.2	Oxoanions	1049
24.3.3	Halides and oxohalides	1051
24.3.4	Complexes of manganese, technetium and rhenium	1054
	Oxidation state VII (d^0)	1054
	Oxidation state VI (d^1)	1055
	Oxidation state V (d^2)	1055
	Oxidation state IV (d^3)	1056
	Oxidation state III (d^4)	1057
	Oxidation state II (d^5)	1058
	Lower oxidation states	1061
24.3.5	The biochemistry of manganese	1061
24.3.6	Organometallic compounds	1062

Chapter 25 Iron, Ruthenium and Osmium 1070

25.1	Introduction	1070
25.2	The Elements Iron, Ruthenium and Osmium	1071
25.2.1	Terrestrial abundance and distribution	1071
25.2.2	Preparation and uses of the elements	1071
25.2.3	Properties of the elements	1074
25.2.4	Chemical reactivity and trends	1075
25.3	Compounds of Iron, Ruthenium and Osmium	1079
25.3.1	Oxides and other chalcogenides	1079
25.3.2	Mixed metal oxides and oxoanions	1081
25.3.3	Halides and oxohalides	1082
25.3.4	Complexes	1085
	Oxidation state VIII (d^0)	1085
	Oxidation state VII (d^1)	1085
	Oxidation state VI (d^2)	1085
	Oxidation state V (d^3)	1086
	Oxidation state IV (d^4)	1086
	Oxidation state III (d^5)	1088
	Oxidation state II (d^6)	1091
	Mixed valence compounds of ruthenium	1097
	Lower oxidation states	1098
25.3.5	The biochemistry of iron	1098
	Haemoglobin and myoglobin	1099
	Cytochromes	1101
	Iron-sulfur proteins	1102
25.3.6	Organometallic compounds	1104
	Carbonyls	1104
	Carbonyl hydrides and carbonylate anions	1105
	Carbonyl halides and other substituted carbonyls	1108
	Ferrocene and other cyclopentadienyls	1109

Chapter 26 Cobalt, Rhodium and Iridium 1113

26.1	Introduction	1113
26.2	The Elements	1113
26.2.1	Terrestrial abundance and distribution	1113
26.2.2	Preparation and uses of the elements	1114
26.2.3	Properties of the elements	1115
26.2.4	Chemical reactivity and trends	1116
26.3	Compounds of Cobalt, Rhodium and Iridium	1117

26.3.1	Oxides and sulfides	1117
26.3.2	Halides	1119
26.3.3	Complexes	1121
	Oxidation state IV (d^5)	1121
	Oxidation state III (d^6)	1122
	Oxidation state II (d^7)	1129
	Oxidation state I (d^8)	1133
	Lower oxidation states	1137
26.3.4	The biochemistry of cobalt	1138
26.3.5	Organometallic compounds	1139
	Carbonyls	1140
	Cyclopentadienyls	1143

Chapter 27 Nickel, Palladium and Platinum 1144

27.1	Introduction	1144
27.2	The Elements	1145
	27.2.1 Terrestrial abundance and distribution	1145
	27.2.2 Preparation and uses of the elements	1145
	27.2.3 Properties of the elements	1148
	27.2.4 Chemical reactivity and trends	1149
27.3	Compounds of Nickel, Palladium and Platinum	1150
	27.3.1 The Pd/H ₂ system	1150
	27.3.2 Oxides and chalcogenides	1151
	27.3.3 Halides	1152
	27.3.4 Complexes	1154
	Oxidation state IV (d^6)	1154
	Oxidation state III (d^7)	1155
	Oxidation state II (d^8)	1156
	Oxidation state I (d^9)	1166
	Oxidation state 0 (d^{10})	1166
	27.3.5 The biochemistry of nickel	1167
	27.3.6 Organometallic compounds	1167
	σ -Bonded compounds	1167
	Carbonyls	1168
	Cyclopentadienyls	1170
	Alkene and alkyne complexes	1170
	π -Allylic complexes	1171

Chapter 28 Copper, Silver and Gold 1173

28.1	Introduction	1173
28.2	The Elements	1174
	28.2.1 Terrestrial abundance and distribution	1174
	28.2.2 Preparation and uses of the elements	1174
	28.2.3 Atomic and physical properties of the elements	1176
	28.2.4 Chemical reactivity and trends	1177
28.3	Compounds of Copper, Silver and Gold	1180
	28.3.1 Oxides and sulfides	1181
	28.3.2 High temperature superconductors	1182
	28.3.3 Halides	1183
	28.3.4 Photography	1185
	28.3.5 Complexes	1187
	Oxidation state III (d^8)	1187
	Oxidation state II (d^9)	1189
	Electronic spectra and magnetic properties of copper(II)	1193
	Oxidation state I (d^{10})	1194
	Gold cluster compounds	1197
	28.3.6 Biochemistry of copper	1197
	28.3.7 Organometallic compounds	1199

Chapter 29	Zinc, Cadmium and Mercury	1201
29.1	Introduction	1201
29.2	The Elements	1202
29.2.1	Terrestrial abundance and distribution	1202
29.2.2	Preparation and uses of the elements	1202
29.2.3	Properties of the elements	1203
29.2.4	Chemical reactivity and trends	1205
29.3	Compounds of Zinc, Cadmium and Mercury	1208
29.3.1	Oxides and chalcogenides	1208
29.3.2	Halides	1211
29.3.3	Mercury(I)	1213
	Polycations of mercury	1214
29.3.4	Zinc(II) and cadmium(II)	1215
29.3.5	Mercury(II)	1217
	Hg ^{II} -N compounds	1218
	Hg ^{II} -S compounds	1220
	Cluster compounds involving mercury	1220
29.3.6	Organometallic compounds	1221
29.3.7	Biological and environmental importance	1224
Chapter 30	The Lanthanide Elements (Z = 58–71)	1227
30.1	Introduction	1227
30.2	The Elements	1229
30.2.1	Terrestrial abundance and distribution	1229
30.2.2	Preparation and uses of the elements	1230
30.2.3	Properties of the elements	1232
30.2.4	Chemical reactivity and trends	1235
30.3	Compounds of the Lanthanides	1238
30.3.1	Oxides and chalcogenides	1238
30.3.2	Halides	1240
30.3.3	Magnetic and spectroscopic properties	1242
30.3.4	Complexes	1244
	Oxidation state IV	1244
	Oxidation state III	1245
	Oxidation state II	1248
30.3.5	Organometallic compounds	1248
	Cyclopentadienides and related compounds	1248
	Alkyls and aryls	1249
Chapter 31	The Actinide and Transactinide Elements (Z = 90–112)	1250
31.1	Introduction	1250
	Superheavy elements	1253
31.2	The Actinide Elements	1253
31.2.1	Terrestrial abundance and distribution	1253
31.2.2	Preparation and uses of the actinide elements	1255
	Nuclear reactors and atomic energy	1256
	Nuclear fuel reprocessing	1260
31.2.3	Properties of the actinide elements	1262
31.2.4	Chemical reactivity and trends	1264
31.3	Compounds of the Actinides	1267
31.3.1	Oxides and chalcogenides of the actinides	1268
31.3.2	Mixed metal oxides	1269
31.3.3	Halides of the actinide elements	1269
31.3.4	Magnetic and spectroscopic properties	1272
31.3.5	Complexes of the actinide elements	1273
	Oxidation state VII	1273
	Oxidation state VI	1273
	Oxidation state V	1274
	Oxidation state IV	1275

	Oxidation state III	1277
	Oxidation state II	1278
	31.3.6 Organometallic compounds of the actinides	1278
31.4	The Transactinide Elements	1280
	31.4.1 Introduction	1280
	31.4.2 Element 104	1281
	31.4.3 Element 105	1282
	31.4.4 Element 106	1282
	31.4.5 Elements 107, 108 and 109	1283
	31.4.6 Elements 110, 111 and 112	1283
Appendix 1	Atomic Orbitals	1285
Appendix 2	Symmetry Elements, Symmetry Operations and Point Groups	1290
Appendix 3	Some Non-SI Units	1293
Appendix 4	Abundance of Elements in Crustal Rocks	1294
Appendix 5	Effective Ionic Radii	1295
Appendix 6	Nobel Prize for Chemistry	1296
Appendix 7	Nobel Prize for Physics	1300
Index		1305