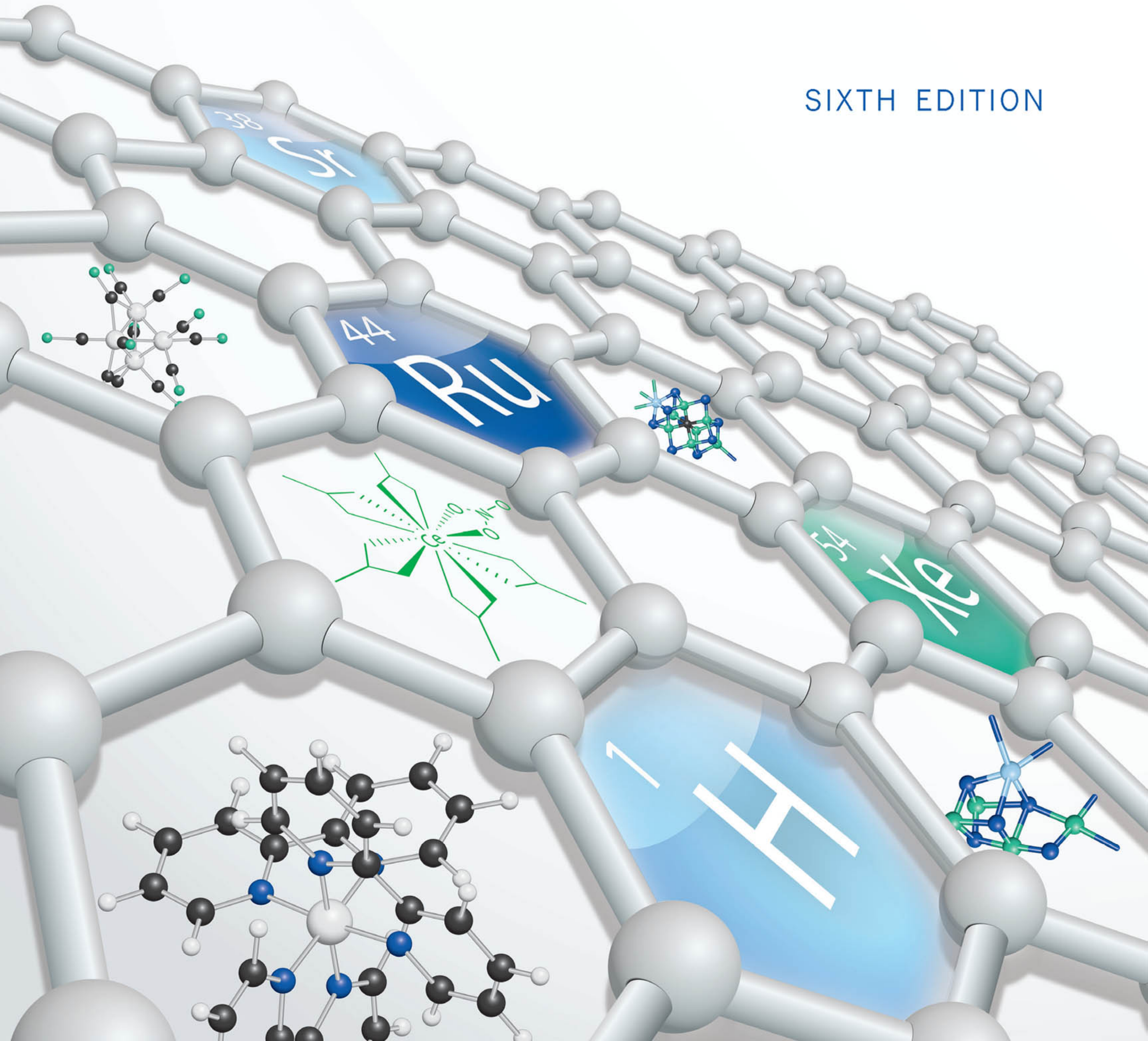
Inorganic Chemistry

Shriver | Weller | Overton | Rourke | Armstrong

SIXTH EDITION


38
Sr
44
Ru
Ce
O
N
O
54
Xe
1
H

PERIODIC TABLE OF THE ELEMENTS

Period	Group 1 I IA	2 II IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 III IIIA	14 IV IVA	15 V VA	16 VI VIA	17 VII VIIA	18 VIII VIIA
1	1 H hydrogen 1.0079 $1s^1$																	2 He helium 4.00 $1s^2$
2	3 Li lithium 6.94 $2s^1$	4 Be beryllium 9.01 $2s^2$											5 B boron 10.81 $2s^2 2p^1$	6 C carbon 12.01 $2s^2 2p^2$	7 N nitrogen 14.01 $2s^2 2p^3$	8 O oxygen 16.00 $2s^2 2p^4$	9 F fluorine 19.00 $2s^2 2p^5$	10 Ne neon 20.18 $2s^2 2p^6$
3	11 Na sodium 22.99 $3s^1$	12 Mg magnesium 24.31 $3s^2$											13 Al aluminium 26.98 $3s^2 3p^1$	14 Si silicon 28.09 $3s^2 3p^2$	15 P phosphorus 30.97 $3s^2 3p^3$	16 S sulfur 32.06 $3s^2 3p^4$	17 Cl chlorine 35.45 $3s^2 3p^5$	18 Ar argon 39.95 $3s^2 3p^6$
4	19 K potassium 39.10 $4s^1$	20 Ca calcium 40.08 $4s^2$	21 Sc scandium 44.96 $3d^1 4s^2$	22 Ti titanium 47.87 $3d^2 4s^2$	23 V vanadium 50.94 $3d^3 4s^2$	24 Cr chromium 52.00 $3d^5 4s^1$	25 Mn manganese 54.94 $3d^5 4s^2$	26 Fe iron 55.84 $3d^6 4s^2$	27 Co cobalt 58.93 $3d^7 4s^2$	28 Ni nickel 58.69 $3d^8 4s^2$	29 Cu copper 63.55 $3d^{10} 4s^1$	30 Zn zinc 65.41 $3d^{10} 4s^2$	31 Ga gallium 69.72 $4s^2 4p^1$	32 Ge germanium 72.64 $4s^2 4p^2$	33 As arsenic 74.92 $4s^2 4p^3$	34 Se selenium 78.96 $4s^2 4p^4$	35 Br bromine 79.90 $4s^2 4p^5$	36 Kr krypton 83.80 $4s^2 4p^6$
5	37 Rb rubidium 85.47 $5s^1$	38 Sr strontium 87.62 $5s^2$	39 Y yttrium 88.91 $4d^1 5s^2$	40 Zr zirconium 91.22 $4d^2 5s^2$	41 Nb niobium 92.91 $4d^4 5s^1$	42 Mo molybdenum 95.94 $4d^5 5s^1$	43 Tc technetium (98) $4d^5 5s^2$	44 Ru ruthenium 101.07 $4d^7 5s^1$	45 Rh rhodium 102.90 $4d^8 5s^1$	46 Pd palladium 106.42 $4d^{10}$	47 Ag silver 107.87 $4d^{10} 5s^1$	48 Cd cadmium 112.41 $4d^{10} 5s^2$	49 In indium 114.82 $5s^2 5p^1$	50 Sn tin 118.71 $5s^2 5p^2$	51 Sb antimony 121.76 $5s^2 5p^3$	52 Te tellurium 127.60 $5s^2 5p^4$	53 I iodine 126.90 $5s^2 5p^5$	54 Xe xenon 131.29 $5s^2 5p^6$
6	55 Cs caesium 132.91 $6s^1$	56 Ba barium 137.33 $6s^2$	57 La lanthanum 138.91 $5d^1 6s^2$	72 Hf hafnium 178.49 $5d^2 6s^2$	73 Ta tantalum 180.95 $5d^3 6s^2$	74 W tungsten 183.84 $5d^4 6s^2$	75 Re rhenium 186.21 $5d^5 6s^2$	76 Os osmium 190.23 $5d^6 6s^2$	77 Ir iridium 192.22 $5d^7 6s^2$	78 Pt platinum 195.08 $5d^9 6s^1$	79 Au gold 196.97 $5d^{10} 6s^1$	80 Hg mercury 200.59 $5d^{10} 6s^2$	81 Tl thallium 204.38 $6s^2 6p^1$	82 Pb lead 207.2 $6s^2 6p^2$	83 Bi bismuth 208.98 $6s^2 6p^3$	84 Po polonium (209) $6s^2 6p^4$	85 At astatine (210) $6s^2 6p^5$	86 Rn radon (222) $6s^2 6p^6$
7	87 Fr francium (223) $7s^1$	88 Ra radium (226) $7s^2$	89 Ac actinium (227) $6d^1 7s^2$	104 Rf rutherfordium (261) $6d^2 7s^2$	105 Db dubnium (262) $6d^3 7s^2$	106 Sg seaborgium (266) $6d^4 7s^2$	107 Bh bohrium (264) $6d^5 7s^2$	108 Hs hassium (277) $6d^6 7s^2$	109 Mt meitnerium (268) $6d^7 7s^2$	110 Ds darmstadtium (271) $6d^8 7s^2$	111 Rg roentgenium (272) $6d^{10} 7s^1$	112 Cp copernicum (277) $6d^{10} 7s^2$	113	114 Fl flerovium (289) $7s^2 7p^2$	115	116 Lv livermorium (293) $7s^2 7p^4$	117	118

6	58 Ce cerium 140.12 $4f^1 5d^1 6s^2$	59 Pr praseodymium 140.91 $4f^3 6s^2$	60 Nd neodymium 144.24 $4f^4 6s^2$	61 Pm promethium (145) $4f^5 6s^2$	62 Sm samarium 150.36 $4f^6 6s^2$	63 Eu europium 151.96 $4f^7 6s^2$	64 Gd gadolinium 157.25 $4f^7 5d^1 6s^2$	65 Tb terbium 158.93 $4f^9 6s^2$	66 Dy dysprosium 162.50 $4f^{10} 6s^2$	67 Ho holmium 164.93 $4f^{11} 6s^2$	68 Er erbium 167.26 $4f^{12} 6s^2$	69 Tm thulium 168.93 $4f^{13} 6s^2$	70 Yb ytterbium 173.04 $4f^{14} 6s^2$	71 Lu lutetium 174.97 $5d^1 6s^2$	Lanthanoids (lanthanides)
7	90 Th thorium 232.04 $6d^2 7s^2$	91 Pa protactinium 231.04 $5f^2 6d^1 7s^2$	92 U uranium 238.03 $5f^3 6d^1 7s^2$	93 Np neptunium (237) $5f^4 6d^1 7s^2$	94 Pu plutonium (244) $5f^6 7s^2$	95 Am americium (243) $5f^7 7s^2$	96 Cm curium (247) $5f^7 6d^1 7s^2$	97 Bk berkelium (247) $5f^9 7s^2$	98 Cf californium (251) $5f^{10} 7s^2$	99 Es einsteinium (252) $5f^{11} 7s^2$	100 Fm fermium (257) $5f^{12} 7s^2$	101 Md mendelevium (258) $5f^{13} 7s^2$	102 No nobelium (259) $5f^{14} 7s^2$	103 Lr lawrencium (262) $6d^1 7s^2$	Actinoids (actinides)

Molar masses (atomic weights) quoted to the number of significant figures given here can be regarded as typical of most naturally occuring samples-

The elements

Name	Symbol	Atomic number	Molar mass $(\mathrm{g\ mol^{-1}})$
Actinium	Ac	89	227
Aluminium (aluminum)	Al	13	26.98
Americium	Am	95	243
Antimony	Sb	51	121.76
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.33
Berkelium	Bk	97	247
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	264
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.41
Caesium (cesium)	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copernicum	Cp	112	277
Copper	Cu	29	63.55
Curium	Cm	96	247
Darmstadtium	Ds	110	271
Dubnium	Db	105	262
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	252
Erbium	Er	68	167.27
Europium	Eu	63	151.96
Fermium	Fm	100	257
Flerovium	Fl	114	289
Fluorine	F	9	19.00
Francium	Fr	87	223
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.64
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	269
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.008
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.22
Iron	Fe	26	55.84
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	262
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Livermorium	Lv	116	293
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitnerium	Mt	109	268
Mendelevium	Md	101	258
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	237
Nickel	Ni	28	58.69
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	259
Osmium	Os	76	190.23
Oxygen	O	8	16.00
Palladium	Pd	46	106.42
Phosphorus	P	15	30.97
Platinum	Pt	78	195.08
Plutonium	Pu	94	244
Polonium	Po	84	209
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	145
Protactinium	Pa	91	231.04
Radium	Ra	88	226
Radon	Rn	86	222
Rhenium	Re	75	186.21
Rhodium	Rh	45	102.91
Roentgenium	Rg	111	272
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	261
Samarium	Sm	62	150.36
Scandium	Sc	21	44.96
Seaborgium	Sg	106	266
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	98
Tellurium	Te	52	127.60
Terbium	Tb	65	158.93
Thallium	Tl	81	204.38
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.71
Titanium	Ti	22	47.87
Tungsten	W	74	183.84
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.29
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.41
Zirconium	Zr	40	91.22

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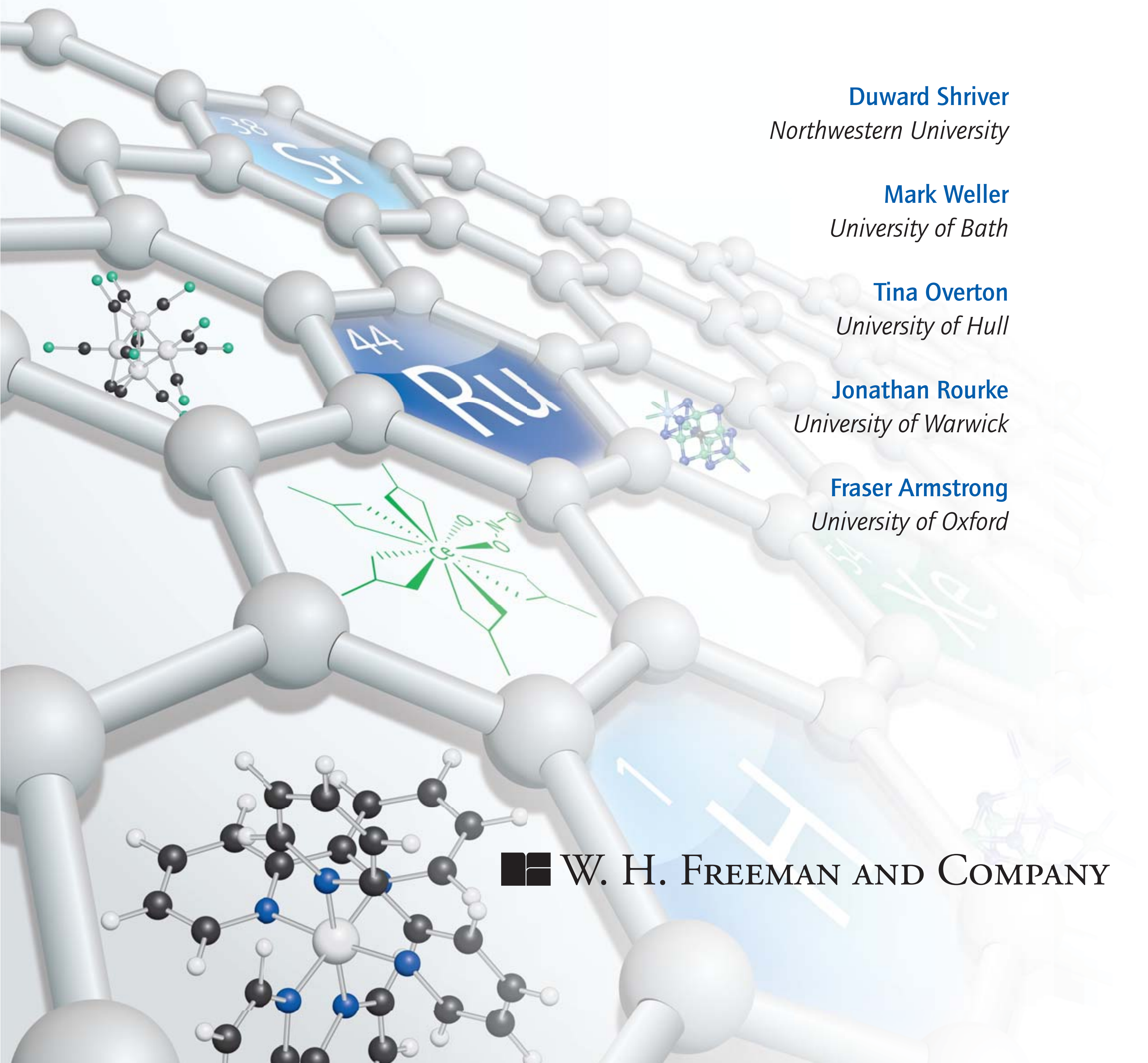

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Preface

Our aim in the sixth edition of *Inorganic Chemistry* is to provide a comprehensive and contemporary introduction to the diverse and fascinating subject of inorganic chemistry. Inorganic chemistry deals with the properties of all of the elements in the periodic table. These elements range from highly reactive metals, such as sodium, to noble metals, such as gold. The nonmetals include solids, liquids, and gases, and range from the aggressive oxidizing agent fluorine to unreactive gases such as helium. Although this variety and diversity are features of any study of inorganic chemistry, there are underlying patterns and trends which enrich and enhance our understanding of the discipline. These trends in reactivity, structure, and properties of the elements and their compounds provide an insight into the landscape of the periodic table and provide a foundation on which to build a detailed understanding.

Inorganic compounds vary from ionic solids, which can be described by simple applications of classical electrostatics, to covalent compounds and metals, which are best described by models that have their origin in quantum mechanics. We can rationalize and interpret the properties and reaction chemistries of most inorganic compounds by using qualitative models that are based on quantum mechanics, such as atomic orbitals and their use to form molecular orbitals. Although models of bonding and reactivity clarify and systematize the subject, inorganic chemistry is essentially an experimental subject. New inorganic compounds are constantly being synthesized and characterized through research projects especially at the frontiers of the subject, for example, organometallic chemistry, materials chemistry, nanochemistry, and bioinorganic chemistry. The products of this research into inorganic chemistry continue to enrich the field with compounds that give us new perspectives on structure, bonding, reactivity, and properties.

Inorganic chemistry has considerable impact on our everyday lives and on other scientific disciplines. The chemical industry is strongly dependent on it. Inorganic chemistry is essential to the formulation and improvement of modern materials such as catalysts, semiconductors, optical devices, energy generation and storage, superconductors, and advanced ceramics. The environmental and biological impacts of inorganic chemistry are also huge. Current topics in industrial, biological, and sustainable chemistry are mentioned throughout the book and are developed more thoroughly in later chapters.

In this new edition we have refined the presentation, organization, and visual representation. All of the book has been revised, much has been rewritten, and there is some completely new material. We have written with the student in mind, including some new pedagogical features and enhancing others.

The topics in Part 1, *Foundations*, have been updated to make them more accessible to the reader with more qualitative explanation accompanying the more mathematical treatments. Some chapters and sections have been expanded to provide greater coverage, particularly where the fundamental topic underpins later discussion of sustainable chemistry.

Part 2, *The elements and their compounds*, has been substantially strengthened. The section starts with an enlarged chapter which draws together periodic trends and cross references forward to the descriptive chapters. An enhanced chapter on hydrogen, with reference to the emerging importance of the hydrogen economy, is followed by a series of chapters traversing the periodic table from the s-block metals through the p block to the Group 18 gases. Each of these chapters is organized into two sections: *The essentials* describes the fundamental chemistry of the elements and *The detail* provides a more thorough, in-depth account. This is followed by a series of chapters discussing the fascinating chemistry of the d-block and, finally, the f-block elements. The descriptions of the chemical properties of each group of elements and their compounds are enriched with illustrations of current research and applications. The patterns and trends that emerge are rationalized by drawing on the principles introduced in Part 1.

Part 3, *Frontiers*, takes the reader to the edge of knowledge in several areas of current research. These chapters explore specialized subjects that are of importance to industry, materials science, and biology, and include catalysis, solid state chemistry, nanomaterials, metalloenzymes, and inorganic compounds used in medicine.

We are confident that this text will serve the undergraduate chemist well. It provides the theoretical building blocks with which to build knowledge and understanding of inorganic chemistry. It should help to rationalize the sometimes bewildering diversity of descriptive chemistry. It also takes the student to the forefront of the discipline with frequent discussion of the latest research in inorganic chemistry and should therefore complement many courses taken in the later stages of a program.

Acknowledgments

We have taken care to ensure that the text is free of errors. This is difficult in a rapidly changing field, where today's knowledge is soon replaced by tomorrow’s. Many of the figures in Chapters 26 and 27 were produced using PyMOL software (W.L. DeLano, The PyMOL Molecular Graphics System, DeLano Scientific, San Carlos, CA, USA, 2002). We thank colleagues past and present at Oxford University Press—Holly Edmundson, Jonathan Crowe, and Alice Mumford—and at W. H. Freeman—Heidi Bamatter, Jessica Fiorillo, and Dave Quinn—for their help and support during the writing of this text. Mark Weller would also like to thank the University of Bath for allowing him time to work on the text and numerous illustrations. We acknowledge and thank all those colleagues who so willingly gave their time and expertise to a careful reading of a variety of draft chapters.

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Nathan West, *University of the Sciences*
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About the book

Inorganic Chemistry provides numerous learning features to help you master this wide-ranging subject. In addition, the text has been designed so that you can either work through the chapters chronologically, or dip in at an appropriate point in your studies. The text's Book Companion Site provides further electronic resources to support you in your learning.

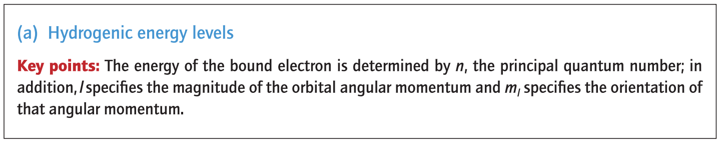
The material in this book has been logically and systematically laid out, in three distinct sections. Part 1, *Foundations,* outlines the underlying principles of inorganic chemistry, which are built on in the subsequent two sections. Part 2, *The elements and their compounds,* divides the descriptive chemistry into 'essentials' and 'detail', enabling you to easily draw out the key principles behind the reactions, before exploring them in greater depth. Part 3, *Frontiers,* introduces you to exciting interdisciplinary research at the forefront of inorganic chemistry.

The paragraphs below describe the learning features of the text and Book Companion Site in further detail.

Organizing the information

Key points

The key points outline the main take-home message(s) of the section that follows. These will help you to focus on the principal ideas being introduced in the text.

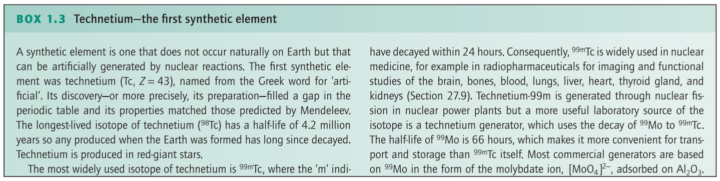


(a) Hydrogenic energy levels

Key points: The energy of the bound electron is determined by n, the principal quantum number; in addition, l specifies the magnitude of the orbital angular momentum and m_l specifies the orientation of that angular momentum.

Context boxes

Context boxes demonstrate the diversity of inorganic chemistry and its wide-ranging applications to, for example, advanced materials, industrial processes, environmental chemistry, and everyday life.



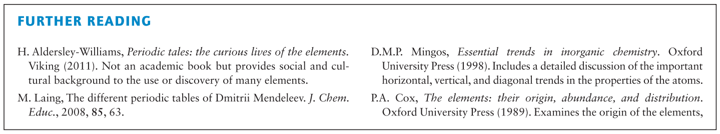
BOX 1.3 Technetium—the first synthetic element

A synthetic element is one that does not occur naturally on Earth but that can be artificially generated by nuclear reactions. The first synthetic element was technetium (Tc, $Z = 43$), named from the Greek word for 'artificial'. Its discovery—or more precisely, its preparation—filled a gap in the periodic table and its properties matched those predicted by Mendeleev. The longest-lived isotope of technetium (^{98}Tc) has a half-life of 4.2 million years so any produced when the Earth was formed has long since decayed. Technetium is produced in red-giant stars.

The most widely used isotope of technetium is ^{99m}Tc, where the 'm' indi- have decayed within 24 hours. Consequently, ^{99m}Tc is widely used in nuclear medicine, for example in radiopharmaceuticals for imaging and functional studies of the brain, bones, blood, lungs, liver, heart, thyroid gland, and kidneys (Section 27.9). Technetium-99m is generated through nuclear fission in nuclear power plants but a more useful laboratory source of the isotope is a technetium generator, which uses the decay of ^{99}Mo to ^{99m}Tc. The half-life of ^{99}Mo is 66 hours, which makes it more convenient for transport and storage than ^{99m}Tc itself. Most commercial generators are based on ^{99}Mo in the form of the molybdate ion, $[MoO_4]^{2-}$, adsorbed on Al_2O_3.

Further reading

Each chapter lists sources where further information can be found. We have tried to ensure that these sources are easily available and have indicated the type of information each one provides.



FURTHER READING

H. Aldersley-Williams, *Periodic tales: the curious lives of the elements.* Viking (2011). Not an academic book but provides social and cultural background to the use or discovery of many elements.

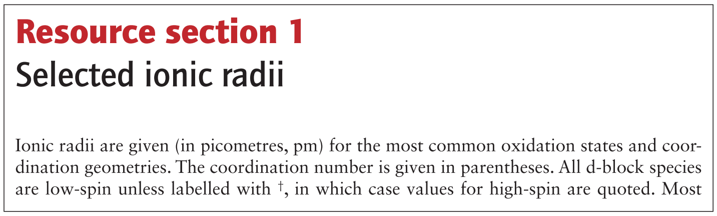
M. Laing, The different periodic tables of Dmitrii Mendeleev. *J. Chem. Educ.*, 2008, **85**, 63.

D.M.P. Mingos, *Essential trends in inorganic chemistry.* Oxford University Press (1998). Includes a detailed discussion of the important horizontal, vertical, and diagonal trends in the properties of the atoms.

P.A. Cox, *The elements: their origin, abundance, and distribution.* Oxford University Press (1989). Examines the origin of the elements,

Resource section

At the back of the book is a comprehensive collection of resources, including an extensive data section and information relating to group theory and spectroscopy.



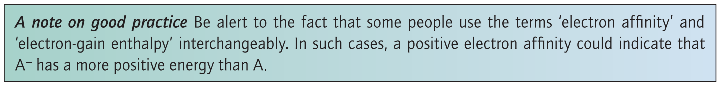
Resource section 1

Selected ionic radii

Ionic radii are given (in picometres, pm) for the most common oxidation states and coordination geometries. The coordination number is given in parentheses. All d-block species are low-spin unless labelled with †, in which case values for high-spin are quoted. Most

Notes on good practice

In some areas of inorganic chemistry the nomenclature commonly in use today can be confusing or archaic—to address this we have included short "notes on good practice" that make such issues clearer for the student.

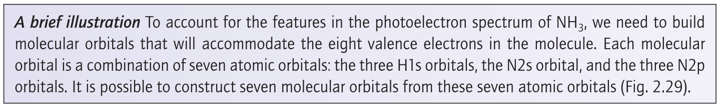


A note on good practice Be alert to the fact that some people use the terms 'electron affinity' and 'electron-gain enthalpy' interchangeably. In such cases, a positive electron affinity could indicate that A^- has a more positive energy than A.

Problem solving

Brief illustrations

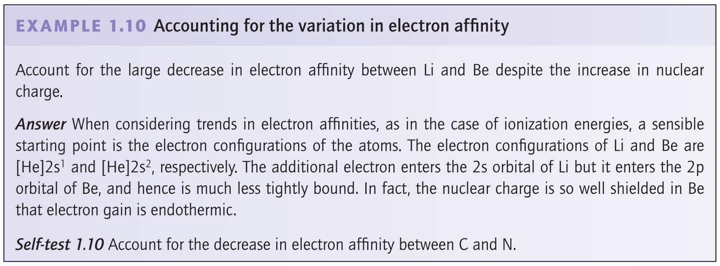
A *Brief illustration* shows you how to use equations or concepts that have just been introduced in the main text, and will help you to understand how to manipulate data correctly.



A brief illustration To account for the features in the photoelectron spectrum of NH_3, we need to build molecular orbitals that will accommodate the eight valence electrons in the molecule. Each molecular orbital is a combination of seven atomic orbitals: the three H1s orbitals, the N2s orbital, and the three N2p orbitals. It is possible to construct seven molecular orbitals from these seven atomic orbitals (Fig. 2.29).

Worked examples and Self-tests

Numerous worked *Examples* provide a more detailed illustration of the application of the material being discussed. Each one demonstrates an important aspect of the topic under discussion or provides practice with calculations and problems. Each *Example* is followed by a *Self-test* designed to help you monitor your progress.



EXAMPLE 1.10 Accounting for the variation in electron affinity

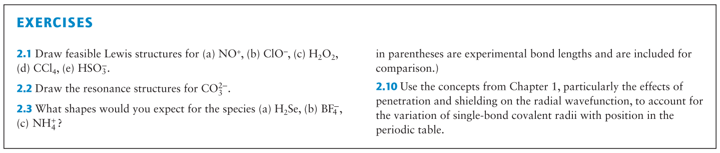
Account for the large decrease in electron affinity between Li and Be despite the increase in nuclear charge.

Answer When considering trends in electron affinities, as in the case of ionization energies, a sensible starting point is the electron configurations of the atoms. The electron configurations of Li and Be are $[He]2s^1$ and $[He]2s^2$, respectively. The additional electron enters the 2s orbital of Li but it enters the 2p orbital of Be, and hence is much less tightly bound. In fact, the nuclear charge is so well shielded in Be that electron gain is endothermic.

Self-test 1.10 Account for the decrease in electron affinity between C and N.

Exercises

There are many brief *Exercises* at the end of each chapter. You can find the answers on the Book Companion Site and fully worked solutions are available in the separate *Solutions manual*. The *Exercises* can be used to check your understanding and gain experience and practice in tasks such as balancing equations, predicting and drawing structures, and manipulating data.



EXERCISES

2.1 Draw feasible Lewis structures for (a) NO^+, (b) ClO^-, (c) H_2O_2, (d) CCl_4, (e) HSO_3^-.

2.2 Draw the resonance structures for CO_3^{2-}.

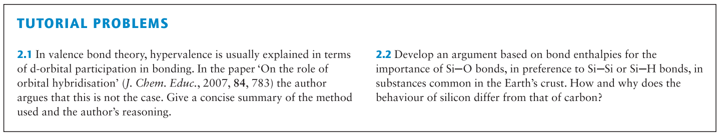
2.3 What shapes would you expect for the species (a) H_2Se, (b) BF_4^-, (c) NH_4^+?

in parentheses are experimental bond lengths and are included for comparison.)

2.10 Use the concepts from Chapter 1, particularly the effects of penetration and shielding on the radial wavefunction, to account for the variation of single-bond covalent radii with position in the periodic table.

Tutorial Problems

The *Tutorial Problems* are more demanding in content and style than the *Exercises* and are often based on a research paper or other additional source of information. Problem questions generally require a discursive response and there may not be a single correct answer. They may be used as essay type questions or for classroom discussion.



TUTORIAL PROBLEMS

2.1 In valence bond theory, hypervalence is usually explained in terms of d-orbital participation in bonding. In the paper 'On the role of orbital hybridisation' (*J. Chem. Educ.*, 2007, **84**, 783) the author argues that this is not the case. Give a concise summary of the method used and the author's reasoning.

2.2 Develop an argument based on bond enthalpies for the importance of Si—O bonds, in preference to Si—Si or Si—H bonds, in substances common in the Earth's crust. How and why does the behaviour of silicon differ from that of carbon?

Solutions Manual

A Solutions Manual (ISBN: 1-4641-2438-8) by Alen Hadzovic is available to accompany the text and provides complete solutions to the self-tests and end-of-chapter exercises.

Book Companion Site

The Book Companion Site to accompany this book provides a number of useful teaching and learning resources to augment the printed book, and is free of charge.

The site can be accessed at: www.whfreeman.com/ichem6e

Please note that instructor resources are available only to registered adopters of the textbook. To register, simply visit www.whfreeman.com/ichem6e and follow the appropriate links.

Student resources are openly available to all, without registration.

Materials on the Book Companion Site include:

UNIVERSITY OF LIVERPOOL
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Information
Quick links
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Visit the ChemTube3D news page>

ChemTube3D contains interactive 3D animations and structures, with supporting information for some of the most important topics covered during an undergraduate chemistry degree.

Explore the various sections using the menu bar above to find the content of interest to you.

Please send any feedback to Nick Greeves

Jmol uses Java - if you would like to make sure that your machine is up to date check here

The JISC funded iChem3D project investigated the use of and developed ChemTube3D

New facebook group started - join here

Molecular photobooth gallery

To download the guides for creating 3D animations, 3D crystallography structures and animated 3D polymers click here

ChemTube3D news - Browser advice - Please use Firefox, Safari, Chrome or Opera. Internet Explorer 9 works in Compatibility Mode only

New VSEPR pages and enhanced atomic orbital pages added to support the publication of Chemistry^3 2nd edition by Burrows et al. (OUP)

NEW sections Diels-Alder reaction regio- and endo stereoselectivity, stereospecificity, Aromatic Heterocycles and Anomeric Effect

Enantioselective reactions including chiral auxiliaries, enantioselective reagents, metal catalysts and organocatalysts

Press release: 364,000 visitors from 194 countries in 2012, up 38% on 2011. >2000 visitors in a single November 2012 day!

3D rotatable molecular structures

Numbered structures can be found online as interactive 3D structures. Type the following URL into your browser, adding the relevant structure number: www.chemtube3d.com/weller/[chapter number]S[structure number]. For example, for structure 10 in Chapter 1, type www.chemtube3d.com/weller/1S10.

Those **figures** with an asterisk (*) in the caption can also be found online as interactive 3D structures. Type the following URL into your browser, adding the relevant figure number: www.chemtube3d.com/weller/[chapter number]F[figure number]. For example, for Figure 4 in chapter 7, type www.chemtube3d.com/weller/7F04.

Visit www.chemtube3d.com/weller/[chapter number] for all 3D resources organized by chapter.

Answers to Self-tests and Exercises

There are many *Self-tests* throughout each chapter and brief *Exercises* at the end of each chapter. You can find the answers on the Book Companion Site.

Videos of chemical reactions

Video clips showing demonstrations of a variety of inorganic chemistry reactions are available for certain chapters of the book.

Molecular modeling problems

Molecular modeling problems are available for almost every chapter, and are written to be performed using the popular *Spartan Student*™ software. However, they can also be completed using any electronic structure program that allows Hartree–Fock, density functional, and MP2 calculations.

Group theory tables

Comprehensive group theory tables are available to download.

For registered adopters:

Figures and tables from the book

Instructors can find the artwork and tables from the book online in ready-to-download format. These can be used for lectures without charge (but not for commercial purposes without specific permission).

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Glossary of chemical abbreviations

Ac	acetyl, CH_3CO
acac	acetylacetonato
aq	aqueous solution species
bpy	2,2′-bipyridine
cod	1,5-cyclooctadiene
cot	cyclooctatetraene
Cy	cyclohexyl
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
cyclam	tetraazacyclotetradecane
dien	diethylenetriamine
DMSO	dimethylsulfoxide
DMF	dimethylformamide
η	hapticity
edta	ethylenediaminetetraacetato
en	ethylenediamine (1,2-diaminoethane)
Et	ethyl
gly	glycinato
Hal	halide
^{i}Pr	isopropyl
L	a ligand
μ	signifies a bridging ligand
M	a metal
Me	methyl
mes	mesityl, 2,4,6-trimethylphenyl
Ox	an oxidized species
ox	oxalato
Ph	phenyl
phen	phenanthroline
py	pyridine
Red	a reduced species
Sol	solvent, or a solvent molecule
soln	nonaqueous solution species
^{t}Bu	tertiary butyl
THF	tetrahydrofuran
TMEDA	*N*, *N*,N′,*N*′-tetramethylethylenediamine
trien	2,2′,2″-triaminotriethylene
X	generally halogen, also a leaving group or an anion
Y	an entering group

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PART 1
Foundations

The eight chapters in this part of the book lay the foundations of inorganic chemistry. The first three chapters develop an understanding of the structures of atoms, molecules, and solids. Chapter 1 introduces the structure of atoms in terms of quantum theory and describes important periodic trends in their properties. Chapter 2 develops molecular structure in terms of increasingly sophisticated models of covalent bonding. Chapter 3 describes ionic bonding, the structures and properties of a range of typical solids, the role of defects in materials, and the electronic properties of solids. The next two chapters focus on two major types of reactions. Chapter 4 explains how acid–base properties are defined, measured, and applied across a wide area of chemistry. Chapter 5 describes oxidation and reduction, and demonstrates how electrochemical data can be used to predict and explain the outcomes of reactions in which electrons are transferred between molecules. Chapter 6 shows how a systematic consideration of the symmetry of molecules can be used to discuss the bonding and structure of molecules and help interpret data from some of the techniques described in Chapter 8. Chapter 7 describes the coordination compounds of the elements. We discuss bonding, structure, and reactions of complexes, and see how symmetry considerations can provide useful insight into this important class of compounds. Chapter 8 provides a toolbox for inorganic chemistry: it describes a wide range of the instrumental techniques that are used to identify and determine the structures and compositions of inorganic compounds.

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Atomic structure

1

This chapter lays the foundations for the explanation of the trends in the physical and chemical properties of all inorganic compounds. To understand the behaviour of molecules and solids we need to understand atoms: our study of inorganic chemistry must therefore begin with a review of their structures and properties. We start with a discussion of the origin of matter in the solar system and then consider the development of our understanding of atomic structure and the behaviour of electrons in atoms. We introduce quantum theory qualitatively and use the results to rationalize properties such as atomic radii, ionization energy, electron affinity, and electronegativity. An understanding of these properties allows us to begin to rationalize the diverse chemical properties of the more than 110 elements known today.

The structures of hydrogenic atoms

1.1 Spectroscopic information
1.2 Some principles of quantum mechanics
1.3 Atomic orbitals

Many-electron atoms

1.4 Penetration and shielding
1.5 The building-up principle
1.6 The classification of the elements
1.7 Atomic properties

Further reading

Exercises

Tutorial problems

The observation that the universe is expanding has led to the current view that about 14 billion years ago the currently visible universe was concentrated into a point-like region that exploded in an event called the **Big Bang**. With initial temperatures immediately after the Big Bang of about 10^9 K, the fundamental particles produced in the explosion had too much kinetic energy to bind together in the forms we know today. However, the universe cooled as it expanded, the particles moved more slowly, and they soon began to adhere together under the influence of a variety of forces. In particular, the **strong force**, a short-range but powerful attractive force between nucleons (protons and neutrons), bound these particles together into nuclei. As the temperature fell still further, the **electromagnetic force**, a relatively weak but long-range force between electric charges, bound electrons to nuclei to form atoms, and the universe acquired the potential for complex chemistry and the existence of life (Box 1.1).

About two hours after the start of the universe, the temperature had fallen so much that most of the matter was in the form of H atoms (89 per cent) and He atoms (11 per cent). In one sense, not much has happened since then for, as Fig. 1.1 shows, hydrogen and helium remain overwhelmingly the most abundant elements in the universe. However, nuclear reactions have formed a wide assortment of other elements and have immeasurably enriched the variety of matter in the universe, and thus given rise to the whole area of chemistry (Boxes 1.2 and 1.3).

Table 1.1 summarizes the properties of the subatomic particles that we need to consider in chemistry. All the known elements—by 2012, 114, 116, and 118 had been confirmed, although not 115 or 117, and several more are candidates for confirmation—that are formed from these subatomic particles are distinguished by their **atomic number**, Z, the number of protons in the nucleus of an atom of the element. Many elements have a number of **isotopes**, which are atoms with the same atomic number but different atomic masses. These isotopes are distinguished by the **mass number**, A, which is the total number of protons and neutrons in the nucleus. The mass number is also sometimes termed more appropriately the **nucleon number**. Hydrogen, for instance, has three isotopes. In each

Those **figures** with an asterisk (*) in the caption can be found online as interactive 3D structures. Type the following URL into your browser, adding the relevant figure number: www.chemtube3d.com/weller/[chapter number]F[figure number]. For example, for Figure 4 in chapter 7, type www.chemtube3d.com/weller/7F04.

Many of the **numbered structures** can also be found online as interactive 3D structures: visit www.chemtube3d.com/weller/[chapter number] for all 3D resources organized by chapter.

BOX 1.1 Nucleosynthesis of the elements

The earliest stars resulted from the gravitational condensation of clouds of H and He atoms. This gave rise to high temperatures and densities within them, and fusion reactions began as nuclei merged together.

Energy is released when light nuclei fuse together to give elements of higher atomic number. Nuclear reactions are very much more energetic than normal chemical reactions because the ***strong force*** which binds protons and neutrons together is much stronger than the electromagnetic force that binds electrons to nuclei. Whereas a typical chemical reaction might release about 10^3 kJ mol^{-1}, a nuclear reaction typically releases a million times more energy, about 10^9 kJ mol^{-1}.

Elements up to $Z = 26$ were formed inside stars. Such elements are the products of the nuclear fusion reactions referred to as 'nuclear burning'. The burning reactions, which should not be confused with chemical combustion, involved H and He nuclei and a complicated fusion cycle catalysed by C nuclei. The stars that formed in the earliest stages of the evolution of the cosmos lacked C nuclei and used noncatalysed H-burning. Nucleosynthesis reactions are rapid at temperatures between 5 and 10 MK (where 1 MK = 10^6 K). Here we have another contrast between chemical and nuclear reactions, because chemical reactions take place at temperatures a hundred thousand times lower. Moderately energetic collisions between species can result in chemical change, but only highly vigorous collisions can provide the energy required to bring about most nuclear processes.

Heavier elements are produced in significant quantities when hydrogen burning is complete and the collapse of the star's core raises the density there to 10^8 kg m^{-3} (about 10^5 times the density of water) and the temperature to 100 MK. Under these extreme conditions, helium burning becomes viable.

The high abundance of iron and nickel in the universe is consistent with these elements having the most stable of all nuclei. This stability is expressed in terms of the **binding energy**, which represents the difference in energy between the nucleus itself and the same numbers of individual protons and neutrons. This binding energy is often presented in terms of a difference in mass between the nucleus and its individual protons and neutrons because, according to Einstein's theory of relativity, mass and energy are related by $E = mc^2$, where c is the speed of light. Therefore, if the mass of a nucleus differs from the total mass of its components by $\Delta m = m_{\text{nucleons}} - m_{\text{nucleus}}$, then its binding energy is $E_{\text{bind}} = (\Delta m)c^2$. The binding energy of ^{56}Fe, for example, is the difference in energy between the ^{56}Fe nucleus and 26 protons and 30 neutrons. A positive binding energy corresponds to a nucleus that has a lower, more favourable, energy (and lower mass) than its constituent nucleons.

Figure B1.1 shows the binding energy per nucleon, E_{bind}/A (obtained by dividing the total binding energy by the number of nucleons), for all the elements. Iron and nickel occur at the maximum of the curve, showing that their nucleons are bound more strongly than in any other nuclide. Harder to see from the graph is an alternation of binding energies as the atomic number varies from even to odd, with even-Z nuclides slightly more stable than their odd-Z neighbours. There is a corresponding alternation in cosmic abundances, with nuclides of even atomic number being marginally more abundant than those of odd atomic number. This stability of even-Z nuclides is attributed to the lowering of energy by the pairing of nucleons in the nucleus.

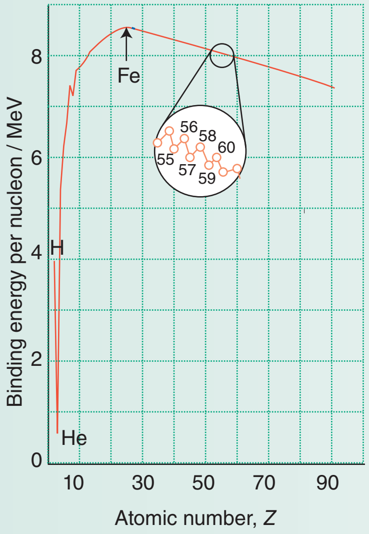

Figure B1.1 Nuclear binding energies. The greater the binding energy, the more stable is the nucleus. Note the alternation in stability shown in the inset.

case $Z=1$, indicating that the nucleus contains one proton. The most abundant isotope has $A=1$, denoted ^{1}H, its nucleus consisting of a single proton. Far less abundant (only 1 atom in 6000) is deuterium, with $A=2$. This mass number indicates that, in addition to a proton, the nucleus contains one neutron. The formal designation of deuterium is ^{2}H, but it is commonly denoted D. The third, short-lived, radioactive isotope of hydrogen is tritium, ^{3}H or T. Its nucleus consists of one proton and two neutrons. In certain cases it is helpful to display the atomic number of the element as a left suffix; so the three isotopes of hydrogen would then be denoted $^1_1$H, $^2_1$H, and $^3_1$H.

The structures of hydrogenic atoms

The organization of the periodic table is a direct consequence of periodic variations in the electronic structure of atoms. Initially, we consider hydrogen-like or **hydrogenic atoms**, which have only one electron and so are free of the complicating effects of electron–electron repulsions. Hydrogenic atoms include ions such as He$^+$ and C^{5+} (found in stellar interiors) as well as the hydrogen atom itself. Then we use the concepts these atoms introduce to build up an approximate description of the structures of **many-electron atoms** (or **polyelectron atoms**).

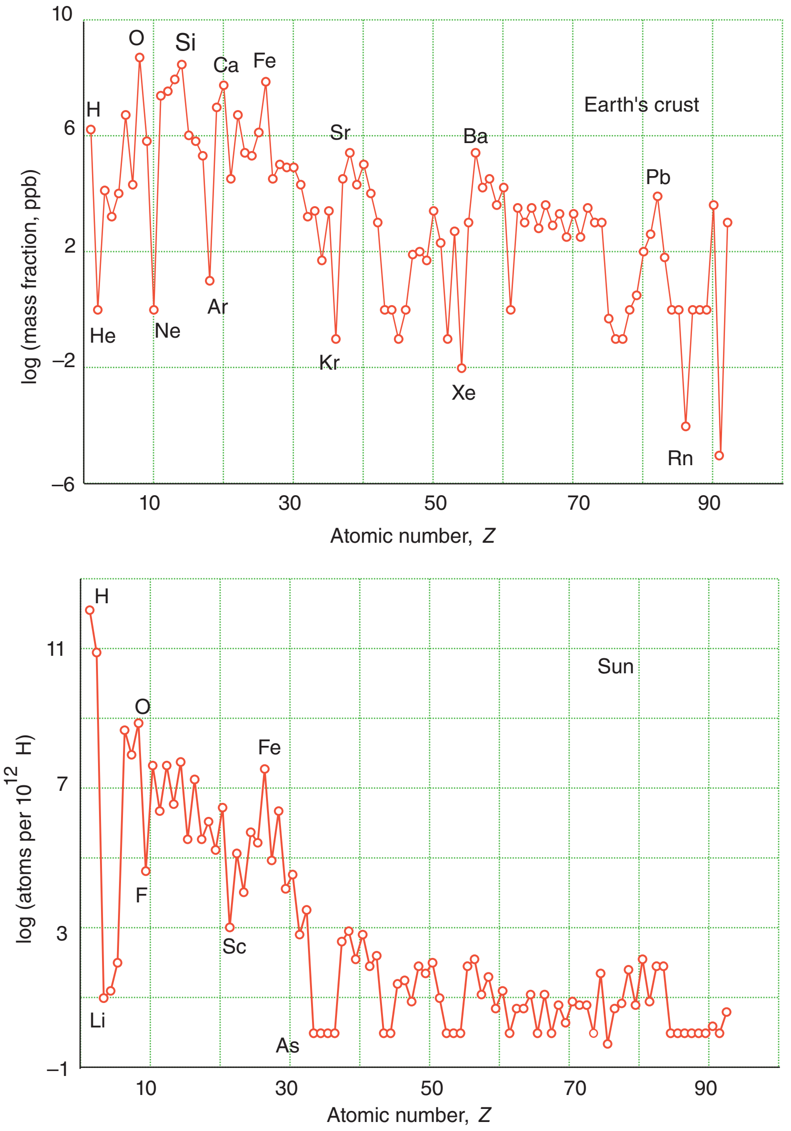

Figure 1.1 The abundances of the elements in the Earth's crust and the Sun. Elements with odd *Z* are less stable than their neighbours with even *Z*.

BOX 1.2 Nuclear fusion and nuclear fission

If two nuclei with mass numbers lower than 56 merge to produce a new nucleus with a larger nuclear binding energy, the excess energy is released. This process is called **fusion**. For example, two neon-20 nuclei may fuse to give a calcium-40 nucleus:

$$2\,{}^{20}_{10}\text{Ne} \rightarrow {}^{40}_{20}\text{Ca}$$

The value of the binding energy per nucleon, E_{bind}/A, for Ne is approximately 8.0 MeV. Therefore, the total binding energy of the species on the left-hand side of the equation is $2\times20\times8.0$ MeV$=$320 MeV. The value of E_{bind}/A for Ca is close to 8.6 MeV and so the total energy of the species on the right-hand side is 40×8.6 MeV$=$344 MeV. The difference in the binding energies of the products and reactants is therefore 24 MeV.

For nuclei with $A>56$, binding energy can be released when they split into lighter products with higher values of E_{bind}/A. This process is called fission. For example, uranium-236 can undergo fission into (among many other modes) xenon-140 and strontium-93 nuclei:

$${}^{236}_{92}\text{U} \rightarrow {}^{140}_{54}\text{Xe} + {}^{93}_{38}\text{Sr} + 3\,{}^{1}_{0}\text{n}$$

The values of E_{bind}/A for ^{236}U, ^{140}Xe, and ^{93}Sr nuclei are 7.6, 8.4, and 8.7 MeV, respectively. Therefore, the energy released in this reaction is $(140\times8.4)+(93\times8.7)-(236\times7.6)$ MeV$=$191.5 MeV for the fission of each ^{236}U nucleus.

Fission can also be induced by bombarding heavy elements with neutrons:

$${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow \text{fission products} + \text{neutrons}$$

The kinetic energy of fission products from ^{235}U is about 165 MeV and that of the neutrons is about 5 MeV, and the γ-rays produced have an energy of about 7 MeV. The fission products are themselves radioactive and decay by β-, γ-, and X-radiation, releasing about 23 MeV. In a nuclear fission reactor the neutrons that are not consumed by fission are captured with the release of about 10 MeV. The energy produced is reduced by about 10 MeV which escapes from the reactor as radiation, and about 1 MeV which remains as undecayed fission products in the spent fuel. Therefore, the total energy produced for one fission event is about 200 MeV, or 32 pJ. It follows that about 1 W of reactor heat (where 1 W$=$1 J s^{-1}) corresponds to about

3.1×10^{10} fission events per second. A nuclear reactor producing 3 GW has an electrical output of approximately 1 GW and corresponds to the fission of 3 kg of ^{235}U per day.

The use of nuclear power is controversial in large part on account of the risks associated with the highly radioactive, long-lived, spent fuel. The declining stocks of fossil fuels, however, make nuclear power very attractive as it is estimated that stocks of uranium could last for hundreds of years. The cost of uranium ores is currently very low and one small pellet of uranium oxide generates as much energy as three barrels of oil or 1 tonne of coal. The use of nuclear power would also drastically reduce the rate of emission of greenhouse gases. The environmental drawback with nuclear power is the storage and disposal of radioactive waste and the public's continued nervousness about possible nuclear accidents, including Fukushima in 2011, and misuse in pursuit of political ambitions.

BOX 1.3 Technetium—the first synthetic element

A synthetic element is one that does not occur naturally on Earth but that can be artificially generated by nuclear reactions. The first synthetic element was technetium (Tc, $Z=43$), named from the Greek word for 'artificial'. Its discovery—or more precisely, its preparation—filled a gap in the periodic table and its properties matched those predicted by Mendeleev. The longest-lived isotope of technetium (^{98}Tc) has a half-life of 4.2 million years so any produced when the Earth was formed has long since decayed. Technetium is produced in red-giant stars.

The most widely used isotope of technetium is ^{99m}Tc, where the 'm' indicates a metastable isotope. Technetium-99m emits high-energy γ-rays but has a relatively short half-life of 6.01 hours. These properties make the isotope particularly attractive for use *in vivo* as the γ-ray energy is sufficient for it to be detected outside the body and its half-life means that most of it will have decayed within 24 hours. Consequently, ^{99m}Tc is widely used in nuclear medicine, for example in radiopharmaceuticals for imaging and functional studies of the brain, bones, blood, lungs, liver, heart, thyroid gland, and kidneys (Section 27.9). Technetium-99m is generated through nuclear fission in nuclear power plants but a more useful laboratory source of the isotope is a technetium generator, which uses the decay of ^{99}Mo to ^{99m}Tc. The half-life of ^{99}Mo is 66 hours, which makes it more convenient for transport and storage than ^{99m}Tc itself. Most commercial generators are based on ^{99}Mo in the form of the molybdate ion, $[MoO_4]^{2-}$, adsorbed on Al_2O_3. The $[^{99}MoO_4]^{2-}$ ion decays to the pertechnetate ion, $[^{99m}TcO_4]^{2-}$, which is less tightly bound to the alumina. Sterile saline solution is washed through a column of the immobilized ^{99}Mo and the ^{99m}Tc solution is collected.

Table 1.1 Subatomic particles of relevance to chemistry

Particle	Symbol	Mass/m_u*	Mass number	Charge/e†	Spin
Electron	e^-	5.486×10^{-4}	0	-1	½
Proton	p	1.0073	1	$+1$	½
Neutron	n	1.0087	1	0	½
Photon	γ	0	0	0	1
Neutrino	ν	*c.* 0	0	0	½
Positron	e^+	5.486×10^{-4}	0	$+1$	½
α particle	α	[${}^{2}_{4}He^{2+}$ nucleus]	4	$+2$	0
β particle	β	[e^- ejected from nucleus]	0	-1	½
γ photon	γ	[electromagnetic radiation from nucleus]	0	0	1

* Masses are expressed relative to the atomic mass constant, $m_u = 1.6605\times10^{-27}$ kg.

† The elementary charge is $e = 1.602\times10^{-19}$ C.

1.1 Spectroscopic information

Key point: Spectroscopic observations on hydrogen atoms suggest that an electron can occupy only certain energy levels and that the emission of discrete frequencies of electromagnetic radiation occurs when an electron makes a transition between these levels.

Electromagnetic radiation is emitted when an electric discharge is applied to hydrogen gas. When passed through a prism or diffraction grating, this radiation is found to consist of a series of components: one in the ultraviolet region, one in the visible region, and several in the infrared region of the electromagnetic spectrum (Fig. 1.2 ; Box 1.4). The nineteenth-century spectroscopist Johann Rydberg found that all the wavelengths (λ, lambda) can be described by the expression

$$\frac{1}{\lambda}=R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \tag{1.1}$$

where R is the **Rydberg constant**, an empirical constant with the value 1.097×10^7 m^{-1}. The n are integers, with $n_1=1, 2,\ldots$ and $n_2=n_1+1, n_1+2,\ldots$. The series with $n_1=1$ is called the **Lyman series** and lies in the ultraviolet. The series with $n_1=2$ lies in the visible region and is called the **Balmer series**. The infrared series include the **Paschen series** ($n_1=3$) and the **Brackett series** ($n_1=4$).

The structure of the spectrum is explained if it is supposed that the emission of radiation takes place when an electron makes a transition from a state of energy $-hcR/n_2^2$ to a state of energy $-hcR/n_1^2$ and that the difference, which is equal to $hcR(1/n_1^2-1/n_2^2)$, is carried away as a photon of energy hc/λ. By equating these two energies, and cancelling hc, we obtain eqn 1.1. The equation is often expressed in terms of wavenumber $\tilde{\nu}$, where $\tilde{\nu}=1/\lambda$. The wavenumber gives the number of wavelengths in a given distance. So a wavenumber of 1 cm^{-1} denotes one complete wavelength in a distance of 1 cm. A related term is the frequency, ν, which is the number of times per second that a wave travels through a complete cycle. It is expressed in units of hertz (Hz), where 1 Hz$=$1 s^{-1}. Wavelength and frequency for electromagnetic radiation are related by the expression $\nu=c/\lambda$, with c, the speed of light,$=2.998\times10^8$ m s^{-1}.

A note on good practice Although wavelength is usually expressed in nano- or picometers, wavenumbers are usually expressed in cm^{-1}, or reciprocal centimetres.

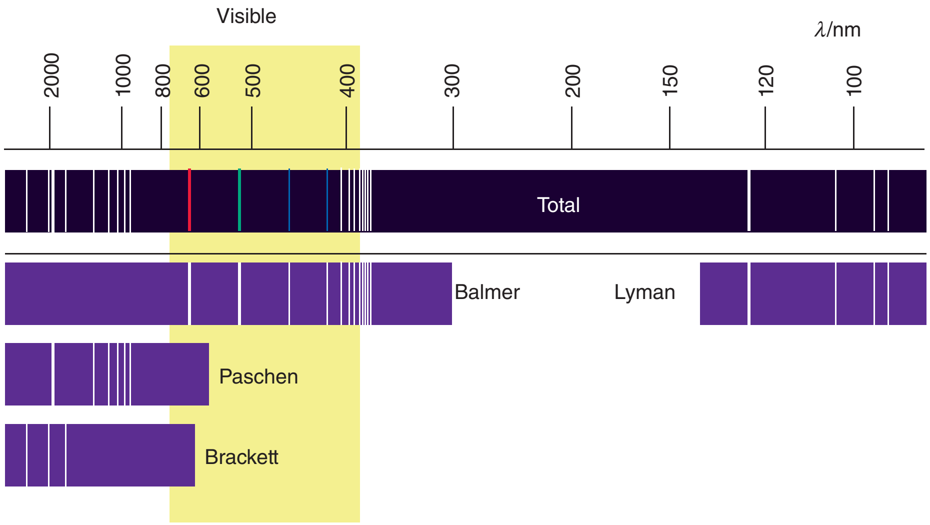

Figure 1.2 The spectrum of atomic hydrogen and its analysis into series.

BOX 1.4 Sodium street lights

The emission of light when atoms are excited is put to good use in lighting streets in many parts of the world. The widely used yellow street lamps are based on the emission of light from excited sodium atoms.

Low pressure sodium (LPS) lamps consist of a glass tube coated with indium tin oxide (ITO). The indium tin oxide reflects infrared and ultraviolet light but transmits visible light. Two inner glass tubes hold solid sodium and a small amount of neon and argon, the same mixture as found in neon lights. When the lamp is turned on the neon and argon emit a red glow which heats the sodium metal. Within a few minutes, the sodium starts to vaporize and the electrical discharge excites the atoms and they re-emit the energy as yellow light.

One advantage of these lamps over other types of street lighting is that they do not lose light output as they age. They do, however, use more energy towards the end of their life, which may make them less attractive from environmental and economic perspectives.

The question these observations raise is why the energy of the electron in the atom is limited to the values $-hcR/n^2$ and why R has the value observed. An initial attempt to explain these features was made by Niels Bohr in 1913 using an early form of quantum theory in which he supposed that the electron could exist in only certain circular orbits. Although he obtained the correct value of R, his model was later shown to be untenable as it conflicted with the version of quantum theory developed by Erwin Schrödinger and Werner Heisenberg in 1926.

EXAMPLE 1.1 Predicting the wavelength of lines in the atomic spectrum of hydrogen

Predict the wavelengths of the first three lines in the Balmer series.

Answer For the Balmer series, $n_1=2$ and $n_2=3, 4, 5, 6, \ldots$. If we substitute into equation 1.1 we obtain $\frac{1}{\lambda}=R\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$ for the first line, which gives $1/\lambda=1513\ 888\ \text{m}^{-1}$ or $\lambda=661$ nm. Using values of $n_2=4$ and 5 for the next two lines gives values for λ of 486 and 434 nm, respectively.

Self-test 1.1 Predict the wavenumber and wavelength of the second line in the Paschen series.

1.2 Some principles of quantum mechanics

Key points: Electrons can behave as particles or as waves; solution of the Schrödinger equation gives wavefunctions, which describe the location and properties of electrons in atoms. The probability of finding an electron at a given location is proportional to the square of the wavefunction. Wavefunctions generally have regions of positive and negative amplitude, and may undergo constructive or destructive interference with one another.

In 1924, Louis de Broglie suggested that because electromagnetic radiation could be considered to consist of particles called photons yet at the same time exhibit wave-like properties, such as interference and diffraction, then the same might be true of electrons. This dual nature is called **wave–particle duality**. An immediate consequence of duality is that it is impossible to know the linear momentum (the product of mass and velocity) and the location of an electron (or any other particle) simultaneously. This restriction is the content of Heisenberg's **uncertainty principle**, that the product of the uncertainty in momentum and the uncertainty in position cannot be less than a quantity of the order of Planck's constant (specifically, $\frac{1}{2}\hbar$, where $\hbar=h/2\pi$).

Schrödinger formulated an equation that took account of wave–particle duality and accounted for the motion of electrons in atoms. To do so, he introduced the **wavefunction**, ψ (psi), a mathematical function of the position coordinates x, y, and z which describes the behaviour of an electron. The **Schrödinger equation**, of which the wavefunction is a solution, for an electron free to move in one dimension is

$$\overbrace{-\frac{\hbar^2}{2m_e}\frac{d^2\psi}{dx^2}}^{\text{Kinetic energy contribution}} + \overbrace{V(x)\psi(x)}^{\text{Potential energy contribution}} + = \overbrace{E\psi(x)}^{\text{Total energy}} \qquad (1.2)$$

where m_e is the mass of an electron, V is the potential energy of the electron, and E is its total energy. The Schrödinger equation is a second-order differential equation that can be solved exactly for a number of simple systems (such as a hydrogen atom) and can be solved numerically for many more complex systems (such as many-electron atoms and molecules). However, we shall need only qualitative aspects of its solutions. The generalization of eqn 1.2 to three dimensions is straightforward, but we do not need its explicit form.

One crucial feature of eqn 1.2 and its analogues in three dimensions and the imposition of certain requirements ('boundary conditions') is that physically acceptable solutions exist only for certain values of E. Therefore, the **quantization** of energy, the fact that an electron can possess only certain discrete energies in an atom, follows naturally from the Schrödinger equation.

A wavefunction contains all the dynamical information possible about the electron, including where it is and how fast it is travelling. As Heisenberg's uncertainty principle means it is impossible to know all this information simultaneously, this leads naturally to the concept of the probability of finding an electron at a given location. Specifically, the probability of finding an electron at a given location is proportional to the square of the wavefunction at that point, ψ^2. According to this interpretation, there is a high probability of finding the electron where ψ^2 is large, and the electron will not be found where ψ^2 is zero (Fig. 1.3). The quantity ψ^2 is called the **probability density** of the electron. It is a 'density' in the sense that the product of ψ^2 and the infinitesimal volume element $d\tau = dxdydz$ (where τ is tau) is proportional to the probability of finding the electron in that volume. The probability is *equal* to $\psi^2 d\tau$ if the wavefunction is 'normalized'. A normalized wavefunction is one that is scaled so that the total probability of finding the electron somewhere is 1. The wavefunction of an electron in an atom is called an **atomic orbital**. To help keep track of the relative signs of different regions of a wavefunction, in illustrations we label regions of opposite sign with dark and light shading corresponding to + and − signs, respectively.

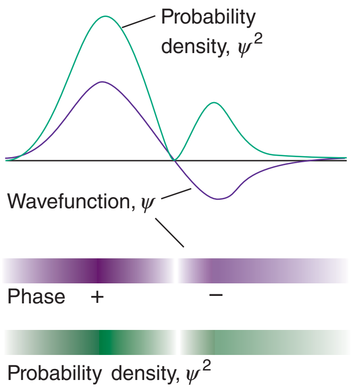

Figure 1.3 The Born interpretation of the wavefunction is that its square is a probability density. There is zero probability density at a node. The shaded bars represent the values of the wavefunction and the probability density, respectively.

Like other waves, wavefunctions in general have regions of positive and negative amplitude, or sign. The sign of the wavefunction is of crucial importance when two wavefunctions spread into the same region of space and interact. Then a positive region of one wavefunction may add to a positive region of the other wavefunction to give a region of enhanced amplitude. This enhancement is called **constructive interference** (Fig. 1.4a). It means that where the two wavefunctions spread into the same region of space, such as occurs when two atoms are close together, there may be a significantly enhanced probability of finding the electrons in that region. Conversely, a positive region of one wavefunction may be cancelled by a negative region of the second wavefunction (Fig. 1.4b). This **destructive interference** between wavefunctions reduces the probability that an electron will be found in that region. As we shall see, the interference of wavefunctions is of great importance in the explanation of chemical bonding.

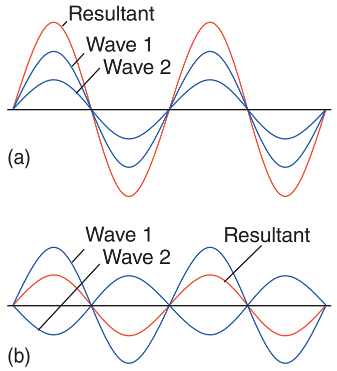

Figure 1.4 Wavefunctions interfere where they spread into the same region of space. (a) If they have the same sign in a region, they interfere constructively and the total wavefunction has an enhanced amplitude in the region. (b) If the wavefunctions have opposite signs, then they interfere destructively, and the resulting superposition has a reduced amplitude.

1.3 Atomic orbitals

Chemists use hydrogenic atomic orbitals to develop models that are central to the interpretation of inorganic chemistry, and we shall spend some time describing their shapes and significance.

(a) Hydrogenic energy levels

Key points: The energy of the bound electron is determined by *n*, the principal quantum number; in addition, *l* specifies the magnitude of the orbital angular momentum and m_l specifies the orientation of that angular momentum.

Each of the wavefunctions obtained by solving the Schrödinger equation for a hydrogenic atom is uniquely labelled by a set of three integers called **quantum numbers**. These quantum numbers are designated n, l, and m_l: n is called the **principal quantum number**, l is the **orbital angular momentum quantum number** (formerly the 'azimuthal quantum number'), and m_l is called the **magnetic quantum number**. Each quantum number specifies a physical property of the electron: n specifies the energy, l labels the magnitude of the orbital angular momentum, and m_l labels the orientation of that angular momentum. The value of n also indicates the size of the orbital, with larger-n, high-energy orbitals, more diffuse than low-n, compact, tightly bound, low-energy orbitals. The value of l also indicates the angular shape of the orbital, with the number of lobes increasing as l increases. The value of m_l also indicates the orientation of these lobes.

The allowed energies are specified by the principal quantum number, n. For a hydrogenic atom of atomic number Z, they are given by

$$E_n = -\frac{hcRZ^2}{n^2} \tag{1.3}$$

with $n = 1, 2, 3, \ldots$ and

$$R = \frac{m_e e^4}{8h^3 c\varepsilon_0^2} \tag{1.4}$$