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Inorganic Chemistry

Weller | Overton | Rourke | Armstrong

6TH EDITION



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Inorganic Chemistry

Sixth Edition

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藏书章

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The elements

Name	Symbol	Atomic number	Molar mass (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
Copernicium	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

Name	Symbol	Atomic number	Molar mass (g mol ⁻¹)
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

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 programme.

Acknowledgements

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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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 book's Online Resource Centre 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 following paragraphs describe the learning features of the text and Online Resource Centre 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.

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.

Notes on good practice

In some areas of inorganic chemistry, the nomenclature commonly in use can be confusing or archaic. To address this we have included brief 'notes on good practice' to help you avoid making common mistakes.

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.

(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.

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 (^{99}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 $^{99\text{m}}\text{Tc}$, where the 'm' indi-

cate has decayed within 24 hours. Consequently, $^{99\text{m}}\text{Tc}$ 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 $^{99\text{m}}\text{Tc}$. The half-life of ^{99}Mo is 66 hours, which makes it more convenient for transport and storage than $^{99\text{m}}\text{Tc}$ itself. Most commercial generators are based on ^{99}Mo in the form of the molybdate ion, $[\text{MoO}_4]^{2-}$, adsorbed on Al_2O_3 .

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.

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 Dmitri 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 $\uparrow$, in which case values for high-spin are quoted. Most

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 $1s$ orbitals, the $2s$ orbital, and the three $2p$ 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 $[\text{He}]2s^1$ and $[\text{He}]2s^2$, 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 *Self-tests* throughout each chapter and brief *Exercises* at the end of each chapter. You can find the answers on the *Online Resource Centre* and fully worked answers 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: 9780198701712) by Alen Hadzovic is available to accompany the text and provides complete solutions to the self-tests and end-of-chapter exercises.

Online Resource Centre

OXFORD UNIVERSITY PRESS online resource centres

Home > Chemistry > Weller, Overton, Rourke & Armstrong: Inorganic Chemistry 6e

3D rotatable molecular structures

Answers to self-tests and exercises

Tables for group theory

Videos of chemical reactions

Web links

Molecular modelling problems

Lecturer resources

Figures and tables from the book

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Figures and tables from the book

Available to download

Test bank

A bank of questions with which to test your students

The Online Resource Centre 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.oxfordtextbooks.co.uk/orc/ichem6e/

Please note that lecturer resources are available only to registered adopters of the textbook. To register, simply visit www.oxfordtextbooks.co.uk/orc/ichem6e/ and follow the appropriate links.

Student resources are openly available to all, without registration.

Materials on the online resource centre include:

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\[structure number\]](http://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\[figure number\]](http://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/\[chapter number\]](http://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 Online Resource Centre.

Videos of chemical reactions

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

Molecular modelling problems

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

Web links

There is a huge network of information available about inorganic chemistry on the web which can be bewildering to navigate. The web links guide you to a collection of websites and web resources related to inorganic chemistry, and are organized by chapter to aid navigation.

Group theory tables

Comprehensive group theory tables are available to download.

For registered adopters:

Figures and tables from the book

Lecturers 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).

Test bank

The test bank provides a ready-made bank of multiple-choice questions for each chapter, which can be used for assessing your students.

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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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Glossary of chemical abbreviations

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