

# Descriptive Inorganic Chemistry

Sixth Edition

**Geoff Rayner-Canham**  
**Tina Overton**

											2 He
						5 B	6 C	7 N	8 O	9 F	10 Ne
						13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

< 1%

1-10%

>10-25%

>25-50%

>50%

1      2

# Periodic Table of the Elements\*

1

1 <b>H</b> 1.0079
-------------------------

2

3 <b>Li</b> 6.94	4 <b>Be</b> 9.01
------------------------	------------------------

Metals

3

11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31
--------------------------	--------------------------

3

4

5

6

7

8

9

4

19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.88	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93
-------------------------	--------------------------	--------------------------	--------------------------	-------------------------	--------------------------	--------------------------	--------------------------	--------------------------

5

37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.94	43 <b>Tc</b>	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.91
--------------------------	--------------------------	-------------------------	--------------------------	--------------------------	--------------------------	-----------------	---------------------------	---------------------------

6

55 <b>Cs</b> 132.91	56 <b>Ba</b> 137.34	71 <b>Lu</b> 174.97	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.95	74 <b>W</b> 183.85	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2
---------------------------	---------------------------	---------------------------	---------------------------	---------------------------	--------------------------	--------------------------	--------------------------	--------------------------

7

87 <b>Fr</b> 223	88 <b>Ra</b> 226.03	103 <b>Lr</b>	104 <b>Rf</b>	105 <b>Db</b>	106 <b>Sg</b>	107 <b>Bh</b>	108 <b>Hs</b>	109 <b>Mt</b>
------------------------	---------------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------

57 <b>La</b> 138.91	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.91	60 <b>Nd</b> 144.24	61 <b>Pm</b>
89 <b>Ac</b> 227.03	90 <b>Th</b> 232.04	91 <b>Pa</b> 231.04	92 <b>U</b> 238.03	93 <b>Np</b>

\*Molar masses quoted to the number of significant figures given here can be regarded as typical of most naturally occurring samples.

			13	14	15	16	17	18	
									2 He 4.00
Nonmetals									
Metalloids →			5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18	
10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95	
28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80	
46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30	
78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po 210	85 At 210	86 Rn 222	
110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo	
62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	Lanthanoids
94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	Actinoids

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# DESCRIPTIVE INORGANIC CHEMISTRY





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SIXTH EDITION

**Geoff Rayner-Canham**

Grenfell Campus, Memorial University  
Corner Brook, Newfoundland, Canada

**Tina Overton**

University of Hull, UK

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76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo	
62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
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# What Is Descriptive Inorganic Chemistry?

**D**escriptive inorganic chemistry was traditionally concerned with the properties of the elements and their compounds. Now, in the renaissance of the subject, the properties are being linked with explanations for the formulas and structures of compounds together with an understanding of the chemical reactions they undergo. In addition, we are no longer looking at inorganic chemistry as an isolated subject but as a part of essential scientific knowledge with applications throughout science and our lives. And it is because of a need for greater contextualization that we have added more relevance by means of the new chapter openers: **CONTEXT**.

In many colleges and universities, descriptive inorganic chemistry is offered as a sophomore or junior course. In this way, students come to know something of the fundamental properties of important and interesting elements and their compounds. Such knowledge is important for careers not only in pure or applied chemistry but also in pharmacy, medicine, geology, environmental science, and other scientific fields. This course can then be followed by a junior or senior course that focuses on the theoretical principles and the use of spectroscopy to a greater depth than is covered in a descriptive text. In fact, the theoretical course builds nicely on the descriptive background. Without the descriptive grounding, however, the theory becomes sterile, uninteresting, and irrelevant.

This book was written to pass on to another generation our fascination with descriptive inorganic chemistry. Thus, the comments of the readers, both students and instructors, will be sincerely appreciated. Our current e-mail addresses are: [grcanham@grenfell.mun.ca](mailto:grcanham@grenfell.mun.ca) and [T.L.Overton@hull.ac.uk](mailto:T.L.Overton@hull.ac.uk).



# PREFACE

**Descriptive Inorganic chemistry goes beyond academic interest; it is an important part of our lives.**

The role of inorganic chemistry in our lives is increasing. Thus, the sixth edition of *Descriptive Inorganic Chemistry* now has the following improvements:

**Context:** Each chapter opens with a *Context*, an aspect of inorganic chemistry which impinges on us in one way or another. Each of these contexts is intended to be thought-provoking and also ties in with an aspect of the chapter content.

**Worked Examples:** Sprinkled throughout the chapters, we have added *Worked Examples*, so that students can see how content relates to principles.

**New Discoveries:** In addition to some reorganization of content and an increased use of subheadings, we have added new discoveries to show that descriptive inorganic chemistry is alive and well as the twenty-first century progresses.

**Predominance Diagrams:** To provide a visual display of which species of an element or ion are present under specific conditions, comparative predominance diagrams have been added, where appropriate.

## **Chapter 1: The Electronic Structure of the Atom: A Review**

Addition of discussion of f-orbitals.

## **Chapter 2: The Structure of the Periodic Table**

Inclusion of relativistic effects.

Improved discussion of electron affinity patterns.

## **Chapter 3: Covalent Bonding and Molecular Spectroscopy**

VSEPR theory now precedes molecular orbital theory.

Improvement of spectroscopy discussion.

## **Chapter 4: Metallic Bonding and Alloys**

Expansion of discussion on alloys.

Addition of subsection on quasicrystals.

## **Chapter 5: Ionic Bonding and Solid-State Structures**

Consolidation of solid-state structures into this one chapter.

Addition of a section on crystal defects and nonstoichiometric compounds.

## **Chapter 6: Why Compounds Exist—Inorganic Thermodynamics**

Discussion on nonexistent compounds.

New section on lattice energies and comparative ion sizes and charges.

## **Chapter 7: Solvent Systems and Acid-Bases Behavior**

Revised section on acid-base reactions of oxides.

**Chapter 8: Oxidation and Reduction**

Improved discussion of Frost diagrams.  
Improved discussion of Pourbaix diagrams.

**Chapter 9: Periodic Patterns**

Revised section on the “knight’s move” relationship.  
Revised section on the lanthanoid relationships.

**Chapter 10: Hydrogen**

New section on the trihydrogen ion.

**Chapter 11: The Group 1 Elements: The Alkali Metals**

Restructuring of chapter.

**Chapter 12: The Group 2 Elements: The Alkaline Earth Metals**

Restructuring of chapter.

**Chapter 13: The Group 13 Elements**

Minor changes.

**Chapter 14: The Group 14 Elements**

Revised comparison of carbon and silicon.  
Additional subsection in carbides on MAX phases.

**Chapter 15: The Group 15 Elements: The Pnictogens**

Revised comparison of nitrogen and phosphorus.  
Additional discussion of nitrogen species such as pentazole.

**Chapter 16: The Group 16 Elements: The Chalcogens**

Additional subsections on octaoxygen and dihydrogen dioxide.  
New section on oxygen and the atmosphere.

**Chapter 17: The Group 17 Elements: The Halogens**

Restructuring of chapter.

**Chapter 18: The Group 18 Elements: The Noble Gases**

New section on compounds of helium, argon, and krypton.  
New section on other xenon compounds.

**Chapter 19: Transition Metal Complexes**

More detailed discussion on crystal field theory.  
New section on reaction mechanisms.

**Chapter 20: The 3d Transition Metals**

New section on the V-Cr-Mn triad.  
New section on the Fe-Co-Ni triad.

**Chapter 21: The 4d and 5d Transition Metals**

Restructuring of chapter.

**Chapter 22: The Group 12 Elements**

Updating of chapter.

**Chapter 23: Organometallic Chemistry**

Updating of chapter.

**Chapter 24: The Rare Earth, Actinoid, and Postactinoid Elements—web**

Updating of chapter.

## ANCILLARY SUPPORT

### Student Support Resources

#### Book Companion Site

The *Descriptive Inorganic Chemistry* Book Companion Site, [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e), contains the following student friendly materials:

- **Chapter 24** Although the lanthanoids, actinoids, and postactinoid elements are of interest and of increasing importance, as few instructors cover these elements, the chapter is only available on-line.
- **Appendices 9 and 10** To save space and paper, these lengthy appendices are also available on the Book Companion Site.
- **Video Demos** Chemistry is a visual subject, thus over 60 video demos are on-line to match reactions described in the text. The text has a margin symbol to identify where there is a corresponding video demo.
- **Laboratory Experiments** A series of experimental exercises are available to enable students to see a selection of the chemical reactions described in the text.

#### Student Solutions Manual

The *Student Solutions Manual*, ISBN: 1-4641-2560-0, contains the answers to the odd-numbered end-of-chapter questions.

#### The CourseSmart e-Textbook

The CourseSmart e-Textbook provides the full digital text, along with tools to take notes, search, and highlight passages. A free app allows access to CourseSmart e-Textbooks and Android and Apple devices, such as the iPad. They can also be downloaded to your computer and accessed without an Internet connection, removing any limitations for students when it comes to reading digital text. The CourseSmart e-Textbook can be purchased at [www.coursesmart.com](http://www.coursesmart.com).

### Instructor Resources

#### Book Companion Site

The password-protected instructor side of the Book Companion Site contains the *Instructor's Solutions Manual*, with answers to the even-numbered end-of-chapter questions, as well as all the illustrations and tables in the book, in .jpg and PowerPoint format.





## Correlation of Descriptive Inorganic Chemistry, 6<sup>th</sup> Edition, with American Chemical Society Guidelines Committee on Professional Training, Inorganic Chemistry Supplement 2012

Each topic from the ACS guidelines listed below is followed by the corresponding chapter(s) in *Descriptive Inorganic Chemistry*, 6th edition, [DIC6] in brackets.

- Atomic Structure. Spectra and orbitals, ionization energy, electron affinity, shielding and effective nuclear charge. [DIC6, Chapter 1]
- Covalent Molecular Substances. Geometries (symmetry point groups), valence bond theory (hybridization,  $\sigma$ ,  $\pi$ ,  $\delta$  bonds), molecular orbital theory (homonuclear and heteronuclear diatomics, multicentered MO, electron-deficient molecules,  $\pi$ -donor and acceptor ligands). [DIC6, Chapter 3 (and parts of 13 and 21)]
- Main Group Elements. Synthesis, structure, physical properties, variations in bonding motifs, acid-base character, and reactivities of the elements and their compounds. [DIC6, Chapters 2, 6 through 18, 22]
- Transition Elements and Coordination Chemistry. Ligands, coordination number, stereochemistry, bonding motifs, nomenclature; ligand field and molecular orbital theories, Jahn-Teller effects, magnetic properties, electronic spectroscopy (term symbols and spectrochemical series), thermodynamic aspects (formation constants, hydration enthalpies, chelate effect), kinetic aspects (ligand substitution, electron transfer, fluxional behavior), lanthanides, and actinides. [DIC6, Chapters 19, 20, 21, 24]
- Organometallic Chemistry. Metal carbonyls, hydrocarbon and carbocyclic ligands, 18-electron rule (saturation and unsaturation), synthesis and properties, patterns of reactivity (substitution, oxidative-addition and reductive-elimination, insertion and deinsertion, nucleophilic attack on ligands, isomerization, stereochemical nonrigidity). [DIC6, Chapter 23]
- Solid-State Materials. Close packing in metals and metal compounds, metallic bonding, band theory, magnetic properties, conductivity, semiconductors, insulators, and defects. [DIC6, Chapters 4 and 5]
- Special Topics. Catalysis and important industrial processes, bioinorganic chemistry, condensed materials containing chain, ring, sheet, cage, and network structures, supramolecular structures, nanoscale structures and effects, surface chemistry, environmental and atmospheric chemistry. [DIC6, Topics incorporated throughout]



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## DEDICATION

Chemistry is a human endeavor. New discoveries are the result of the work of enthusiastic individuals and groups of individuals who want to explore the molecular world. We hope that you, the reader, will come to share our own fascination with inorganic chemistry. We have chosen to dedicate this book to two persons who, for very different reasons, never did receive the ultimate accolade of a Nobel Prize.

### Henry Moseley (1887–1915)

Although Mendeleev is identified as the discoverer of the periodic table, his version was based on an increase in atomic mass. In some cases, the order of elements had to be reversed to match properties with location. It was a British scientist, Henry Moseley, who put the Periodic Table on a much firmer footing by discovering that, upon bombardment with electrons, each element emitted X-rays of characteristic wavelengths. The wavelengths fitted a formula related by an integer number unique to each element. We now know that number to be the number of protons. With the establishment of the atomic number of an element, chemists at last knew the fundamental organization of the periodic table. Sadly, Moseley was killed at the battle of Gallipoli in the First World War. Thus, one of the brightest scientific talents of the twentieth century died at the age of 27. The famous American scientist Robert Milliken commented: “Had the European War had no other result than the snuffing out of this young life, that alone would make it one of the most hideous and most irreparable crimes in history.” Unfortunately, Nobel Prizes are only awarded to living scientists. In 1924, there was the claim of the discovery of element 43, and it was named moseleyum; however, the claim was disproved by the very method that Moseley had pioneered.





### Lise Meitner (1878–1968)

In the 1930s, scientists were bombarding atoms of heavy elements such as uranium with subatomic particles to try to make new elements and extend the periodic table. The Austrian scientist Lise Meitner had shared leadership with Otto Hahn of the German research team working on the synthesis of new elements. They thought they had discovered nine new elements. Shortly after the claimed discovery, Meitner was forced to flee Germany because of her Jewish ancestry, and she settled in Sweden. Hahn reported to her that one of the new elements behaved chemically just like barium. During a famous “walk in the snow” with her nephew, the physicist Otto Frisch, Meitner realized that an atomic nucleus could break in two just like a drop of water. No wonder the element formed behaved like barium: it was barium! Thus, was born the concept of nuclear fission. She informed Hahn of her proposal. When Hahn wrote the research paper on the work, he barely mentioned the vital contribution of Meitner and Frisch. As a result, Hahn and his colleague, Fritz Strassmann, received the Nobel Prize. Meitner’s flash of genius was ignored. Only recently has Meitner received the acclaim she deserved by naming an element after her, element 109, meitnerium.

### Additional reading

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Sime, R.L., *Lise Meitner: A Life in Physics*, University of California Press, Berkeley, CA, 1996.

Weeks M.E., and Leicester, H.M. Discovery of the Elements, *Journal of Chemical Education*, Easton, PA, 7th edition, 1968.

# THE ELECTRONIC STRUCTURE OF THE ATOM: A Review

## CHAPTER 1

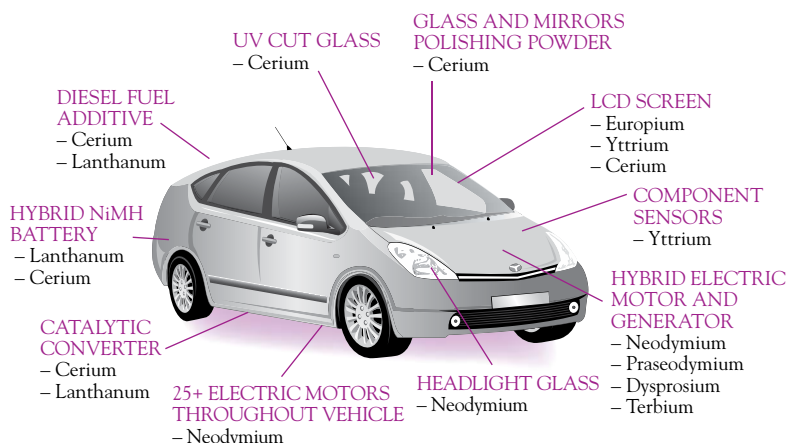
						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

To understand the behavior of inorganic compounds, we need to study the nature of chemical bonding. Bonding, in turn, relates to the behavior of electrons in the constituent atoms. Our coverage of inorganic chemistry, therefore, starts with a survey of the quantum (probability) model's applications to the electron configurations of atoms and ions. We will show how these configurations can be used to explain patterns and trends in common physical properties of atoms.

- 1.1 A Review of the Quantum Model
- 1.2 Shapes of the Atomic Orbitals
- 1.3 The Polyelectronic Atom
- 1.4 Ion Electron Configurations
- 1.5 Magnetic Properties of Atoms

### Context: The Importance of the Lanthanoids

The cover design of this sixth edition of *Descriptive Inorganic Chemistry* highlights the lack of recycling of most of the metallic elements. In particular, very little of the elements from lanthanum to lutetium—the lanthanoids—is reclaimed. Yet we are depending more and more on the unique properties of each of these metals to serve vital niche roles in our electronic-based civilization. For example, hybrid and all-electric vehicles rely on what are called *nickel-metal hydride* batteries for the energy storage. The metal is, in fact, lanthanum, and a hybrid vehicle battery typically contains between 10 and 15 kilograms of lanthanum. The hybrid electric motor and generator itself contains neodymium,



The lanthanoid elements (and yttrium) used in a typical hybrid vehicle.



praseodymium, dysprosium, and terbium; each metal performing a vital function. The figure above shows the wide-ranging use of the lanthanoids (and yttrium) in a typical hybrid vehicle.

All modern high-performance magnets depend upon alloys containing neodymium, whether they are tiny magnets in the ear-pieces for audio devices or giant magnets in the turbines of commercial wind turbines. The brilliance of color displays for computers and televisions is commonly the result of emission from europium ions (for red), terbium ions (for green), and cerium ions (for blue). There are also many medical applications for these elements. For example, gadolinium gives a strong image in a magnetic resonance imaging (MRI) scan. Thus, to see a finer structure of blood vessels (and of tumors), an intravenous injection of a gadolinium(III) compound is administered to a patient prior to performing an MRI scan.

The common feature of these elements is that, progressing from lanthanum to lutetium, the 4f orbitals are being filled. Thus, in this chapter, we will not only review the s, p, and d orbitals which you have encountered in lower level courses, but also introduce you to the f orbitals.

## 1.1 A Review of the Quantum Model

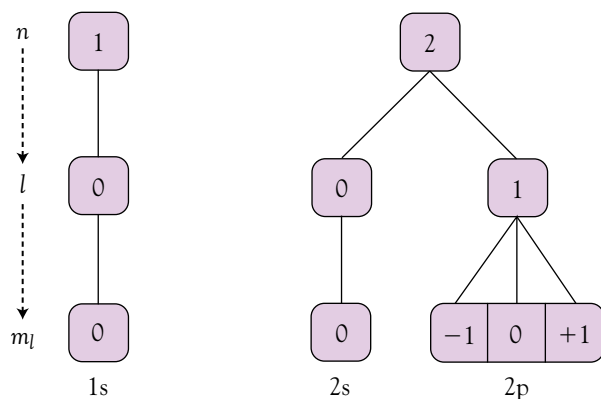
The quantum model of atomic structure was derived from the work of Louis de Broglie. De Broglie showed that, just as electromagnetic waves could be treated as streams of particles (photons), moving particles could exhibit wavelike properties. Thus, it was equally valid to picture electrons either as particles or as waves. Using this wave-particle duality, Erwin Schrödinger developed a partial differential equation to represent the behavior of an electron around an atomic nucleus.

The derivation of the equation and the method of solving it are in the realm of physics and physical chemistry, but the solution itself is of great importance to inorganic chemists. We should always keep in mind, however, that the wave equation is simply a mathematical formula. We attach meanings to the solution simply because most people need concrete images to think about subatomic phenomena. The conceptual models that we create in our macroscopic world cannot hope to reproduce the subatomic reality.

### Quantum Numbers

There are a number of solutions to a wave equation. Each solution describes a different orbital and, hence, a different probability distribution for an electron in that orbital. Each of these orbitals is uniquely defined by a set of three integers:  $n$ ,  $l$ , and  $m_l$ .

In addition to the three quantum numbers derived from the original theory, a fourth quantum number had to be defined to explain the results of an experiment in 1922. In this experiment, Otto Stern and Walther Gerlach found that passing a beam of silver atoms through a magnetic field caused about half the atoms to be deflected in one direction and the other half in the opposite direction. Other investigators proposed that the observation was the result of two different electronic spin orientations. The atoms possessing an electron with



**FIGURE 1.1** The possible sets of quantum numbers for  $n = 1$  and  $n = 2$ .

one spin were deflected one way, and the atoms whose electron had the opposite spin were deflected in the opposite direction. This spin quantum number was assigned the symbol  $m_s$ .

The possible values of the quantum numbers are defined as follows:

$n$ , the *principal quantum number*, can have all positive integer values from 1 to  $\infty$ .

$l$ , the *angular momentum quantum number*, can have all integer values from  $(n - 1)$  to 0.

$m_l$ , the *magnetic quantum number*, can have all integer values from  $+l$  through 0 to  $-l$ .

$m_s$ , the *spin quantum number*, can have values of  $+\frac{1}{2}$  and  $-\frac{1}{2}$ .

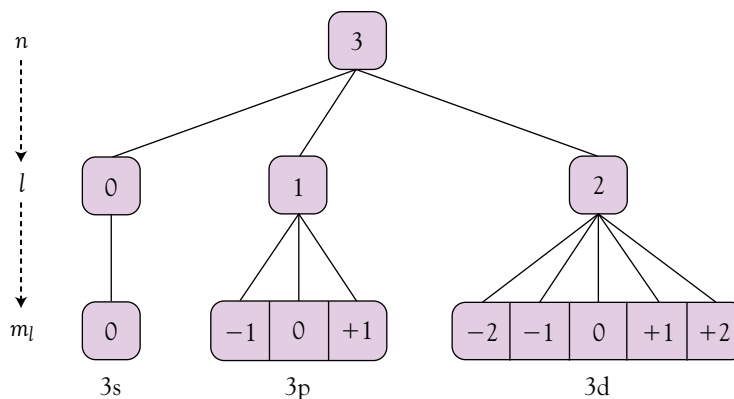
### Values of Quantum Numbers

When the value of the principal quantum number is 1, there is only one possible set of quantum numbers  $n$ ,  $l$ , and  $m_l$  (1, 0, 0), whereas for a principal quantum number of 2, there are four sets of quantum numbers (2, 0, 0; 2, 1,  $-1$ ; 2, 1, 0; 2, 1,  $+1$ ). This situation is shown diagrammatically in Figure 1.1. To identify the electron orbital that corresponds to each set of quantum numbers, we use the value of the principal quantum number  $n$ , followed by a letter for the angular momentum quantum number  $l$ . Thus, when  $n = 1$ , there is only the 1s orbital.

When  $n = 2$ , there is one 2s orbital and three 2p orbitals (corresponding to the  $m_l$  values of  $+1$ , 0, and  $-1$ ). The letters s, p, d, and f are derived from categories of the spectral lines: sharp, principal, diffuse, and fundamental. The correspondences are shown in Table 1.1.

**TABLE 1.1** Correspondence between angular momentum number  $l$  and orbital designation

$l$ Value	Orbital designation
0	s
1	p
2	d
3	f

**FIGURE 1.2** The possible sets of quantum numbers for  $n = 3$ .

When the principal quantum number is  $n = 3$ , there are nine sets of quantum numbers (Figure 1.2). These sets correspond to one 3s, three 3p, and five 3d orbitals. A similar diagram for the principal quantum number  $n = 4$  would show 16 sets of quantum numbers, corresponding to one 4s, three 4p, five 4d, and seven 4f orbitals (Table 1.2).

**TABLE 1.2** Correspondence between angular momentum number  $l$  and number of orbitals

$l$ Value	Number of orbitals
0	1
1	3
2	5
3	7

Theoretically, we can go on and on, but as we will see, the f orbitals represent the limit of orbital types among the elements of the periodic table for atoms in their electronic ground states.

**WORKED EXAMPLE 1.1**

Give the set of quantum numbers that describe the 4d orbitals.

**Answer**

The 4d orbital must have a principal quantum number  $n = 4$ .

For d orbitals,  $l = 2$  and therefore  $m_l = -2, -1, 0, +1, +2$ . ■

**1.2 Shapes of the Atomic Orbitals**

Representing the solutions to a wave equation on paper is not an easy task. In fact, we would need four-dimensional graph paper (if it existed) to display the complete solution for each orbital. As a realistic alternative, we break the wave equation into two parts: a radial part and an angular part.

Each of the three quantum numbers derived from the wave equation represents a different aspect of the orbital:

The principal quantum number  $n$  indicates the size of the orbital.

The angular momentum quantum number  $l$  represents the shape of the orbital.

The magnetic quantum number  $m_l$  represents the spatial direction of the orbital.

The spin quantum number  $m_s$  has little physical meaning; it merely allows two electrons to occupy the same orbital.

It is the value of the principal quantum number and, to a lesser extent the angular momentum quantum number, which determines the energy of the electron. Although the electron may not literally be spinning, it behaves as if it were, and it has the magnetic properties expected for a spinning particle.

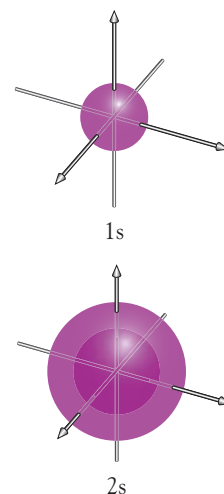
### The s Orbitals

The s orbitals are spherically symmetrical about the atomic nucleus. As the principal quantum number increases, the electron tends to be found farther from the nucleus. To express this idea in a different way, we say that, as the principal quantum number increases, the orbital becomes more diffuse. A unique feature of electron behavior in an s orbital is that there is a finite probability of finding the electron close to, and even within, the nucleus. This penetration by s orbital electrons plays a role in atomic radii (see Chapter 2) and as a means of studying nuclear structure.

An orbital diagram is used to indicate the probability of finding an electron at any point in space. We define a location where an electron is most probably found as an area of high *electron density*. Conversely, locations with a low probability are called areas of low electron density. Orbital diagrams of the angular functions of the 1s and 2s orbitals of an atom are compared in Figure 1.3. In both cases, the tiny nucleus is located at the center of the spheres. These spheres represent the region in which there is a 99 percent probability of finding an electron. The total probability cannot be represented, for the probability of finding an electron drops to zero only at an infinite distance from the nucleus.

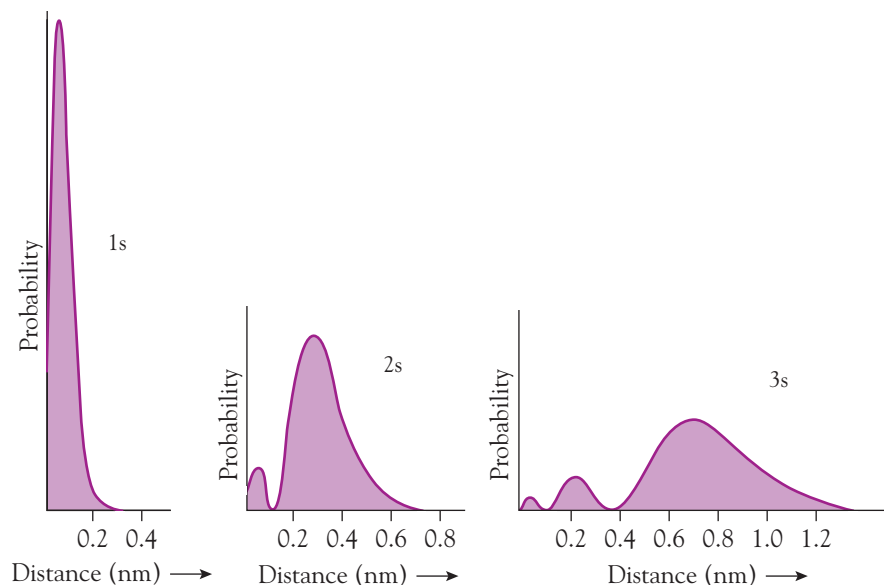
The probability of finding the electron within an orbital will always be positive (since the probability is derived from the square of the wave function and squaring a negative makes a positive). However, when we discuss the bonding of atoms, we find that the sign related to the original wave function has importance. For this reason, it is conventional to superimpose the sign of the wave function on the representation of each atomic orbital. For an s orbital, the sign is positive.

In addition to the considerable difference in size between the 1s and the 2s orbitals, the 2s orbital has, at a certain distance from the nucleus, a spherical surface on which the electron density is zero. A surface on which the probability of finding an electron is zero is called a *nodal surface*. When the principal



**FIGURE 1.3** Representations of the shapes and comparative sizes of the 1s and 2s orbitals (computer-generated representations by Andrzej Okuniewski).

**FIGURE 1.4** The variation of the radial density distribution function with distance from the nucleus for electrons in the 1s, 2s, and 3s orbitals of a hydrogen atom.



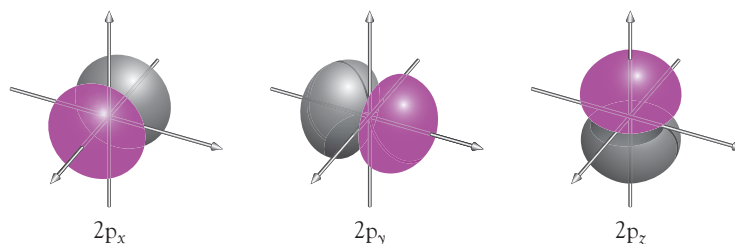
quantum number increases by 1, the number of nodal surfaces also increases by 1. We can visualize nodal surfaces more clearly by plotting a graph of the radial density distribution function as a function of distance from the nucleus for any direction. Figure 1.4 shows plots for the 1s, 2s, and 3s orbitals. These plots show that the electron tends to be farther from the nucleus as the principal quantum number increases. The areas under all three curves are the same.

### The p Orbitals

Unlike the s orbitals, the p orbitals consist of two separate volumes of space (lobes), with the nucleus located between the two lobes. Because there are three p orbitals, we assign each orbital a direction according to Cartesian coordinates:  $p_x$ ,  $p_y$ , and  $p_z$ . Figure 1.5 shows representations of the three 2p orbitals. At right angles to the axis of higher probability, there is a nodal plane through the nucleus. For example, the  $2p_z$  orbital has a nodal plane in the  $xy$  plane. In terms of wave function sign, one lobe is positive and the other negative.

If we compare graphs of electron density as a function of atomic radius for the 2s orbital and a 2p orbital (the latter plotted along the axis of higher

**FIGURE 1.5** Representations of the shapes of the  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals (computer-generated representations by Andrzej Okuniewski).

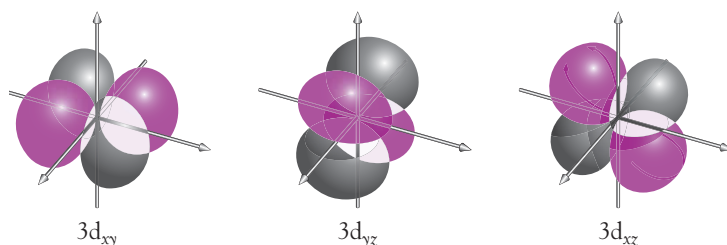


probability), we find that the 2s orbital has a much greater electron density close to the nucleus than does the 2p orbital (Figure 1.6). Conversely, the second maximum of the 2s orbital is farther out than the single maximum of the 2p orbital. However, the mean distance of maximum probability is the same for both orbitals.

Like the s orbitals, the p orbitals develop additional nodal surfaces within the orbital structure as the principal quantum number increases. Thus, a 3p orbital does not look exactly like a 2p orbital since it has an additional nodal surface. However, the detailed differences in orbital shapes for a particular angular momentum quantum number are of little relevance in the context of introductory inorganic chemistry.

### The d Orbitals

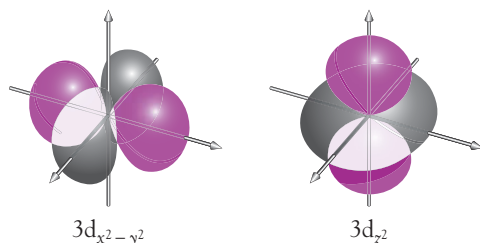
The five d orbitals have more complex shapes. Three of them are located between the Cartesian axes, and the other two are oriented along the axes. In all cases, the nucleus is located at the intersection of the axes. Three orbitals each have four lobes that are located between pairs of axes (Figure 1.7). These orbitals are identified as  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ . The other two d orbitals,  $d_{z^2}$  and  $d_{x^2-y^2}$ , are shown in Figure 1.8. The  $d_{z^2}$  orbital looks somewhat similar to a  $p_z$  orbital (see Figure 1.5), except that it has an additional doughnut-shaped ring of high electron density in the  $xy$  plane. The  $d_{x^2-y^2}$  orbital is identical to the  $d_{xy}$  orbital but has been rotated through  $45^\circ$ .



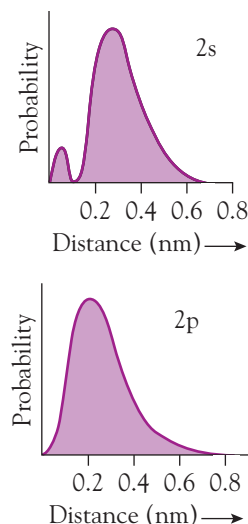
**FIGURE 1.7** Representations of the shapes of the  $3d_{xy}$ ,  $3d_{xz}$ , and  $3d_{yz}$  orbitals (computer-generated representations by Andrzej Okuniewski).

### The f Orbitals

In the opening section of the chapter, we saw that the elements corresponding to the filling of the 4f orbitals are of great importance in our lives. The f orbitals are

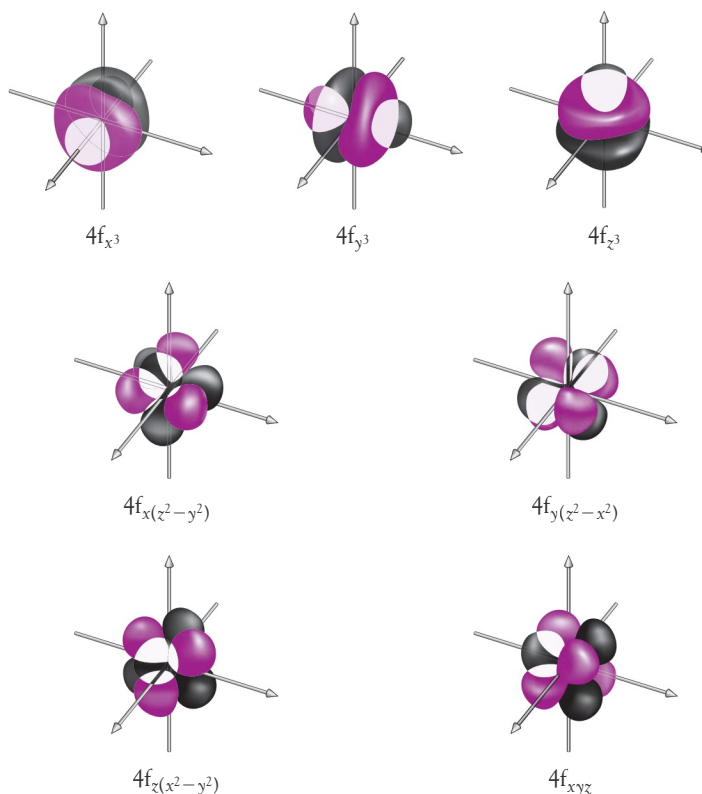


**FIGURE 1.8** Representations of the shapes of the  $3d_{x^2-y^2}$  and  $3d_{z^2}$  orbitals (computer-generated representations by Andrzej Okuniewski).



**FIGURE 1.6** The variation of the radial density distribution function with distance from the nucleus for electrons in the 2s and 2p orbitals of a hydrogen atom.

**FIGURE 1.9** Representations of the shapes of the cubic set of the seven f orbitals (computer-generated representations by Andrzej Okuniewski).



even more complex than the d orbitals. There are seven f orbitals, as there are seven possible  $m_l$  values corresponding to  $l = 3$ . Orbitals are mathematical constructs derived from the wave equation, and particularly for the f orbitals, there are different sets of solutions each set giving rise to a different-shaped set of f orbitals. In Figure 1.9, the cubic set of f orbitals is shown as it logically relates to the d orbitals. First, there is a set of three orbitals,  $f_x^3$ ,  $f_y^3$ , and  $f_z^3$ , which resemble the  $d_{z^2}$  orbital with lobes along one axis, but with two “doughnut rings” for the f orbitals. Then the other four orbitals of the cubic set have eight lobes each, the first three being identical, but with the lobes rotated  $45^\circ$  from each other:  $f_x(z^2 - y^2)$ ,  $f_y(z^2 - x^2)$ , and  $f_z(x^2 - y^2)$ . The fourth of the eight-lobed f electrons is the  $f_{xyz}$  which has all eight lobes between all of the axes.

### 1.3 The Polyelectronic Atom

In our model of the polyelectronic atom, the electrons are distributed among the orbitals of the atom according to the *Aufbau* (German: building-up) *principle*. This simple idea proposes that, when the electrons of an atom are all in the ground state, they occupy the orbitals of lowest energy, thereby minimizing the atom’s total electronic energy. Thus, the configuration of an atom can be described simply by adding electrons one by one until the total number required for the element has been reached.

Before starting to construct electron configurations, we need to take into account a second rule: the *Pauli's exclusion principle*. According to this rule, no two electrons in an atom may possess identical sets of the four quantum numbers. Thus, there can be only one orbital of each three-quantum-number set per atom, and each orbital can hold only two electrons—one with  $m_s = +\frac{1}{2}$  and the other with  $m_s = -\frac{1}{2}$ .

### Filling the s Orbitals

The simplest configuration is that of the hydrogen atom. According to the Aufbau principle, the single electron will be located in the 1s orbital. This configuration is the ground state of the hydrogen atom. Adding energy would raise the electron to one of the many higher energy states. These configurations are referred to as excited states. In the diagram of the ground state of the hydrogen atom (Figure 1.10), a half-headed arrow is used to indicate the direction of electron spin. The electron configuration is written as  $1s^1$ , with the superscript “1” indicating the number of electrons in that orbital.

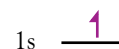
With a two-electron atom (helium), there is a choice: the second electron could go in the 1s orbital (Figure 1.11a) or the next higher energy orbital, the 2s orbital (Figure 1.11b). Although it might seem obvious that the second electron would enter the 1s orbital, it is not so simple. If the second electron entered the 1s orbital, it would be occupying the same volume of space as the electron already in that orbital. The very strong electrostatic repulsions, the *pairing energy*, would discourage the occupancy of the same orbital. However, by occupying an orbital with a high probability closer to the nucleus, the second electron will experience a much greater nuclear attraction. As the nuclear attraction is greater than the inter-electron repulsion, the actual configuration will be  $1s^2$ .

In the lithium atom the 1s orbital is filled by two electrons, and the third electron must be in the next higher energy orbital, the 2s orbital. Thus, lithium has the configuration of  $1s^2 2s^1$ . For beryllium, a fourth electron needs to be added to the electron configuration. As for the helium case above, the energy separation of an s and its corresponding p orbitals is greater than the pairing energy. Thus, the electron configuration of beryllium will be  $1s^2 2s^2$  rather than  $1s^2 2s^1 2p^1$ .

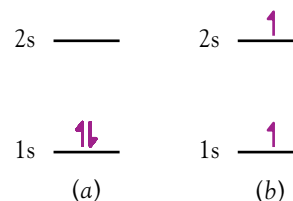
### Filling the p Orbitals

Boron marks the beginning of the filling of the 2p orbitals. A boron atom has an electron configuration of  $1s^2 2s^2 2p^1$ . Because the p orbitals are degenerate (that is, they all have the same energy), it is impossible to decide which one of the three orbitals contains the electron.

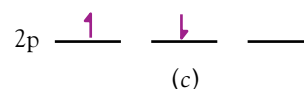
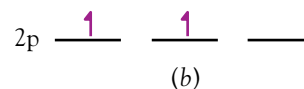
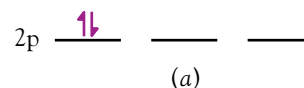
Carbon is the second ground-state atom with electrons in the p orbitals. Its electron configuration provides another challenge. There are three possible arrangements of the two 2p electrons (Figure 1.12): (a) both electrons in one orbital, (b) two electrons with parallel spins in different orbitals, and (c) two electrons with opposed spins in different orbitals. On the basis of electron repulsions, the first possibility (a) can be rejected immediately. The



**FIGURE 1.10** Electron configuration of a hydrogen atom.



**FIGURE 1.11** Two possible electron configurations for helium.



**FIGURE 1.12** Possible 2p electron configurations for carbon.



decision between the other two possibilities is less obvious and requires a deeper knowledge of quantum theory. In fact, if the two electrons have parallel spins, there is a zero probability of their occupying the same space. However, if the spins are opposed, there is a finite possibility that the two electrons will occupy the same region in space, thereby resulting in some repulsion and a higher energy state. Hence, the parallel spin situation (*b*) will have the lowest energy. This preference for unpaired electrons with parallel spins has been formalized in *Hund's rule*: When filling a set of degenerate orbitals, the number of unpaired electrons will be maximized, and these electrons will have parallel spins.

After the completion of the 2p electron set at neon ( $1s^2 2s^2 2p^6$ ), the 3s and 3p orbitals start to fill. Rather than write the full electron configurations, a shortened form can be used. In this notation, the inner electrons are represented by the noble gas symbol having that configuration. Thus, magnesium, whose full electron configuration would be written as  $1s^2 2s^2 2p^6 3s^2$ , can be represented as having a neon noble gas core, and its configuration is written as  $[\text{Ne}]3s^2$ . An advantage of the noble gas core representation is that it emphasizes the outermost (valence) electrons, and it is these electrons that are involved in chemical bonding. Then filling the 3p orbitals brings us to argon.

### Filling the d Orbitals

It is at this point that the 3d and 4s orbitals start to fill. The simple orbital energy level concept breaks down because the energy levels of the 4s and 3d orbitals are very close. What becomes most important is not the minimum energy for a single electron but the configuration that results in the least number of inter-electron repulsions for all the electrons. For potassium, this is  $[\text{Ar}]4s^1$ ; for calcium,  $[\text{Ar}]4s^2$ .

In general, the lowest overall energy for each transition metal is obtained by filling the s orbitals first; the remaining electrons then occupy the d orbitals. Although there are minor fluctuations in configurations throughout the d-block and f-block elements, the following order can be used as a guide:



Figure 1.13 shows the elements organized by order of orbital filling.

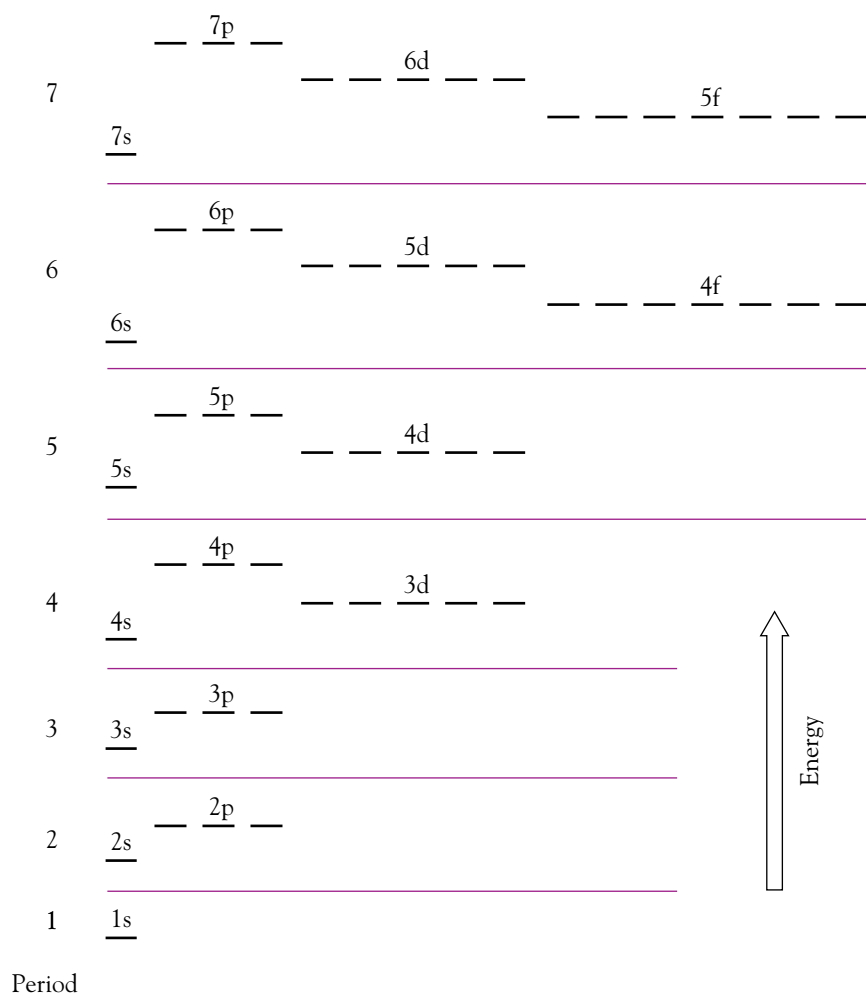
This order is shown as an energy-level diagram in Figure 1.14. The orbitals fill in this order because the energy differences between the s, p, d, and f orbitals of the same principal quantum number become so great beyond  $n = 2$  that they overlap with the orbitals of the following principal quantum numbers. It is important to note that Figure 1.14 shows the filling order, not the order for any particular element. For example, for elements beyond zinc, electrons in the 3d orbitals are far lower in energy than those in the 4s orbitals. Thus, at this point, the 3d orbitals have become “inner” orbitals and have no role in chemical bonding. Hence, their precise ordering is unimportant.

Although these are the generalized rules, to illustrate how this delicate balance changes with increasing numbers of protons and electrons, the outer

[illegible]

**FIGURE 1.13** In this version of the periodic table, the chemical elements are organized in order of orbital filling.

**FIGURE 1.14** Representation of the comparative energies of the atomic orbitals for filling order purposes.



electrons in each of the Group 3 to Group 12 elements are listed here. These configurations are not important in themselves, but they do show how close the  $ns$  and  $(n - 1)d$  electrons are in energy.

Atom	Configuration	Atom	Configuration	Atom	Configuration
Sc	$4s^2 3d^1$	Y	$5s^2 4d^1$	Lu	$6s^2 5d^1$
Ti	$4s^2 3d^2$	Zr	$5s^2 4d^2$	Hf	$6s^2 5d^2$
V	$4s^2 3d^3$	Nb	$5s^1 4d^4$	Ta	$6s^2 5d^3$
Cr	$4s^1 3d^5$	Mo	$5s^1 4d^5$	W	$6s^2 5d^4$
Mn	$4s^2 3d^5$	Tc	$5s^2 4d^5$	Re	$6s^2 5d^5$
Fe	$4s^2 3d^6$	Ru	$5s^1 4d^7$	Os	$6s^2 5d^6$
Co	$4s^2 3d^7$	Rh	$5s^1 4d^8$	Ir	$6s^2 5d^7$
Ni	$4s^2 3d^8$	Pd	$5s^0 4d^{10}$	Pt	$6s^1 5d^9$
Cu	$4s^1 3d^{10}$	Ag	$5s^1 4d^{10}$	Au	$6s^1 5d^{10}$
Zn	$4s^2 3d^{10}$	Cd	$5s^2 4d^{10}$	Hg	$6s^2 5d^{10}$

For certain elements, the lowest energy is obtained by shifting one or both of the s electrons to d orbitals. Looking at the first series in isolation would lead to the conclusion that there is some preference for a half-full or full set of d orbitals by chromium and copper. However, it is more accurate to say that the inter-electron repulsion between the two s electrons is sufficient in several cases to result in an  $s^1$  configuration.

### Filling the f Orbitals

For the elements from lanthanum (La) to ytterbium (Yb), the situation is even more fluid because the 6s, 5d, and 4f orbitals all have similar energies. For example, lanthanum has a configuration of  $[\text{Xe}]6s^25d^1$ , whereas the next element, cerium has the configuration of  $[\text{Xe}]6s^24f^15d^1$ . The most interesting electron configuration in this row is that of gadolinium,  $[\text{Xe}]6s^25d^14f^7$ , rather than the predicted  $[\text{Xe}]6s^24f^8$ . This configuration provides more evidence of the importance of inter-electron repulsion in the determination of electron configuration when adjacent orbitals have similar energies. Analogous complexities occur among the elements from actinium (Ac) to nobelium (No), in which the 7s, 6d, and 5f orbitals have close energies.

#### WORKED EXAMPLE 1.2

Just as half-filled p orbitals and half-filled d orbitals have an energetic advantage, so it is also true for f orbital filling. Hence deduce the electron configuration of curium (Cm).

#### Answer

Strictly following the energy level filling order would give curium an electron configuration of  $[\text{Rn}]7s^25f^8$ . However, taking into account the half-filled orbital stability, the electron configuration of curium would be:  $[\text{Rn}]7s^25f^76d^1$ . ■

## 1.4 Ion Electron Configurations

### The Main Group Elements

For the main group elements of the early periods, the electron configurations of the simple ions can be predicted quite readily. Thus, metals tend to lose all the electrons in the outer orbital set. This situation is illustrated for the *isoelectronic* series (same electron configuration) of sodium, magnesium, and aluminum cations:

Atom	Electron configuration	Ion	Electron configuration
Na	$[\text{Ne}]3s^1$	$\text{Na}^+$	$[\text{Ne}]$
Mg	$[\text{Ne}]3s^2$	$\text{Mg}^{2+}$	$[\text{Ne}]$
Al	$[\text{Ne}]3s^23p^1$	$\text{Al}^{3+}$	$[\text{Ne}]$

Nonmetals gain electrons to complete the outer orbital set. This situation is shown for nitrogen, oxygen, and fluorine anions:

Atom	Electron configuration	Ion	Electron configuration
N	[He]2s <sup>2</sup> 2p <sup>3</sup>	N <sup>3-</sup>	[Ne]
O	[He]2s <sup>2</sup> 2p <sup>4</sup>	O <sup>2-</sup>	[Ne]
F	[He]2s <sup>2</sup> 2p <sup>5</sup>	F <sup>-</sup>	[Ne]

Some of the later main group metals form two ions with different charges. For example, lead forms Pb<sup>2+</sup> and (rarely) Pb<sup>4+</sup>. The 2+ charge can be explained by the loss of the 6p electrons only (the “inert pair” effect, which we discuss in Chapter 9, Section 9.6), whereas the 4+ charge results from loss of both 6s and 6p electrons:

Atom	Electron configuration	Ion	Electron configuration
Pb	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>2</sup>	Pb <sup>2+</sup>	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup>
		Pb <sup>4+</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup>

Notice that the electrons of the higher principal quantum number are lost first. This rule is found to be true for all the elements. For example, zinc always forms an ion of 2+ charge:

Atom	Electron configuration	Ion	Electron configuration
Zn	[Ar]4s <sup>2</sup> 3d <sup>10</sup>	Zn <sup>2+</sup>	[Ar]3d <sup>10</sup>

### The Transition Metals

For the transition metals, the s electrons are always lost first when a metal cation is formed. That is, for the transition metal cations, the (*n* − 1)d orbitals are always lower in energy than the *ns* orbitals. For the first transition period, a charge of 2+, representing the loss of the two 4s electrons, is common for the metals from manganese to copper. In addition to a 2+ ion, iron also forms an ion with a charge of 3+. It is tempting to ascribe the formation of the 3+ ion to a process in which inter-electron repulsion “forces out” the only paired d electron:

Atom	Electron configuration	Ion	Electron configuration
Fe	[Ar]4s <sup>2</sup> 3d <sup>6</sup>	Fe <sup>2+</sup>	[Ar]3d <sup>6</sup>
		Fe <sup>3+</sup>	[Ar]3d <sup>5</sup>

It is dangerous, however, to read too much into the electron configurations of atoms as a means of predicting the ion charges. The series of nickel, palladium, and platinum illustrate this point: they have different configurations as atoms, yet their common ionic charges and corresponding ion electron configurations are similar:

Atom	Electron configuration	Ion	Electron configuration
Ni	[Ar]4s <sup>2</sup> 3d <sup>8</sup>	Ni <sup>2+</sup>	[Ar]3d <sup>8</sup>
Pd	[Kr]5s <sup>0</sup> 4d <sup>10</sup>	Pd <sup>2+</sup> , Pd <sup>4+</sup>	[Kr]4d <sup>8</sup> , [Kr]4d <sup>6</sup>
Pt	[Xe]6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>9</sup>	Pt <sup>2+</sup> , Pt <sup>4+</sup>	[Xe]4f <sup>14</sup> 5d <sup>8</sup> , [Xe]4f <sup>14</sup> 5d <sup>6</sup>

## The Lanthanoids

For the lanthanoids, too, it is the electrons of the higher principal quantum number which are lost first. Whereas for the 3d transition metals, the most common ion charge is 2+; for the lanthanoids, 3+ is consistently the most common charge for all of them. The explanation for the predominance of the 3+ charge relates to the lattice energy of the compounds, as we will see in Chapter 6, Inorganic Thermodynamics. The two common lanthanoid ions which are exceptions to the rule are those of cerium(IV) and europium(II). As examples, the electron configurations for four of the lanthanoids: lanthanum, cerium, europium, and lutetium are listed as follows:

Atom	Electron configuration	Ion	Electron configuration
La	$[\text{Xe}]6s^2 4f^0 5d^1$	$\text{La}^{3+}$	$[\text{Xe}]4f^0$
Ce	$[\text{Xe}]6s^2 4f^1 5d^1$	$\text{Ce}^{3+}, \text{Ce}^{4+}$	$[\text{Xe}]4f^1, [\text{Xe}]4f^0$
Eu	$[\text{Xe}]6s^2 4f^7$	$\text{Eu}^{2+}, \text{Eu}^{3+}$	$[\text{Xe}]4f^7, [\text{Xe}]4f^6$
Lu	$[\text{Xe}]6s^2 4f^{14} 5d^1$	$\text{Lu}^{3+}$	$[\text{Xe}]4f^{14}$

### WORKED EXAMPLE 1.3

Suggest why silver commonly forms an ion of +1 charge.

#### Answer

Analogous to copper, silver has an electron configuration of  $[\text{Kr}]5s^1 4d^{10}$ . By losing the  $5s^1$  electron, the +1 silver ion will retain its complete  $4d^{10}$  electron set. ■

### WORKED EXAMPLE 1.4

What is the highest possible ion charge for tungsten?

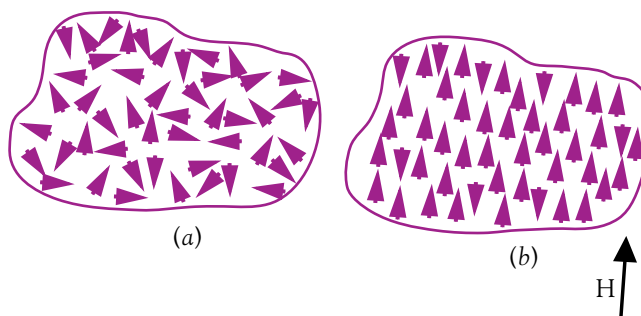
#### Answer

Tungsten (W) has the electron configuration:  $[\text{Xe}]6s^2 4f^{14} 5d^4$ . The f electrons are always retained; thus, the highest possible charge would result from the loss of the  $6s^2$  and  $5d^4$  electrons. This loss would give an ion charge of +6. ■

## 1.5 Magnetic Properties of Atoms

In the discussions of electron configuration, we saw that some atoms possess unpaired electrons. The presence of unpaired electrons in the atoms of an element can be determined easily from the element's magnetic properties. If atoms containing only spin-paired electrons are placed in a magnetic field, they are weakly repelled by the field. This phenomenon is called *diamagnetism*.

**FIGURE 1.15** Behavior of paramagnetic materials without (a) and with (b) an applied field.



Conversely, atoms containing one or more unpaired electrons are attracted by the magnetic field. This behavior of unpaired electrons is named *paramagnetism*. The attraction of each unpaired electron is many times stronger than the repulsion of all the spin-paired electrons in that atom.

To explain paramagnetism in simple terms, we can visualize the electron as a particle spinning on its axis and generating a magnetic moment, just as an electric current flowing through a wire does. This permanent magnetic moment results in an attraction into the stronger part of the field. When electrons have their spins paired, the magnetic moments cancel each other. As a result, the paired electrons are weakly repelled by the lines of force of the magnetic field. In paramagnetic materials, application of a magnetic field aligns some of the normally randomly oriented electron spins with the applied magnetic field (Figure 1.15a and b). It is this alignment that results in the attraction of the material into the magnetic field. We will encounter this phenomenon again in our discussions of covalent bonding and the bonding in transition metal compounds.

## KEY IDEAS

- The properties of an electron in an atom can be defined in terms of four quantum numbers.
- There are a variety of shapes of orbitals (s, p, d, f) as defined by the angular momentum quantum number.
- Electrons in the ground state of an atom fill the orbitals of lowest energy.
- For the transition metals, the energies of the  $ns$  and  $(n - 1)d$  orbitals are very similar.
- For the lanthanoids, the energies of the  $ns$ ,  $(n - 1)d$ , and  $(n - 2)f$  orbitals are very similar.
- In the formation of a cation, the electrons in the orbitals of highest principal quantum number are lost first.
- Paramagnetic behavior in a magnetic field indicates the presence of unpaired electrons.

## EXERCISES

**1.1** Define the following terms: (a) nodal surface; (b) Pauli's exclusion principle; (c) paramagnetic.

**1.2** Define the following terms: (a) orbital; (b) degenerate; (c) Hund's rule.

**1.3** Construct a quantum number tree for the principal quantum number  $n = 4$  similar to that depicted for  $n = 3$  in Figure 1.2.

**1.4** Determine the lowest value of  $n$  for which  $m_l$  can (theoretically) have a value of  $+4$ .

- 1.5** Identify the orbital that has  $n = 5$  and  $l = 1$ .
- 1.6** Identify the orbital that has  $n = 6$  and  $l = 0$ .
- 1.7** How does the quantum number  $n$  relate to the properties of an orbital?
- 1.8** How does the quantum number  $l$  relate to the properties of an orbital?
- 1.9** Explain concisely why carbon has two electrons in different p orbitals with parallel spins rather than the other possible arrangements.
- 1.10** Explain concisely why beryllium has a ground-state electron configuration of  $1s^2 2s^2$  rather than  $1s^2 2s^1 2p^1$ .
- 1.11** Write noble gas core ground-state electron configurations for atoms of (a) sodium; (b) nickel; (c) copper.
- 1.12** Write noble gas core ground-state electron configurations for atoms of (a) calcium; (b) chromium; (c) lead.
- 1.13** Write noble gas core ground-state electron configurations for ions of (a) potassium; (b) scandium  $3+$ ; (c) copper  $2+$ .
- 1.14** Write noble gas core ground-state electron configurations for ions of (a) chlorine; (b) cobalt  $2+$ ; (c) manganese  $4+$ .
- 1.15** Predict the common charges of the ions of thallium. Explain your reasoning in terms of electron configurations.
- 1.16** Predict the common charges of the ions of tin. Explain your reasoning in terms of electron configurations.
- 1.17** Predict the common charge of the silver ion. Explain your reasoning in terms of electron configurations.
- 1.18** Predict the highest possible charge of a zirconium ion. Explain your reasoning in terms of electron configurations.
- 1.19** Write the noble gas core ground-state electron configurations for the  $3+$  ion of gadolinium (Gd).
- 1.20** Write the noble gas core ground-state electron configurations for the  $3+$  ion of ytterbium (Yb). What other ion is ytterbium likely to form?
- 1.21** Use diagrams similar to Figure 1.11 to determine the number of unpaired electrons in atoms of (a) oxygen; (b) magnesium; (c) chromium.
- 1.22** Use diagrams similar to Figure 1.11 to determine the number of unpaired electrons in atoms of (a) nitrogen; (b) silicon; (c) iron.
- 1.23** Write the electron configuration expected for element 113 and the configurations for the two cations that it is most likely to form.
- 1.24** Which of the following species are hydrogen-like? (a)  $\text{He}^+$ ; (b)  $\text{He}^-$ ; (c)  $\text{Li}^+$ ; (d)  $\text{Li}^{2+}$ .

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## BEYOND THE BASICS

- 1.25** The next set of orbitals after the f orbitals are the g orbitals. How many g orbitals would there be? What would be the lowest principal quantum number  $n$  that would possess g orbitals? Deduce the atomic number of the first element at which g orbitals would begin to be filled on the basis of the patterns of the d and f orbitals.
- 1.26** An alternative to the Schrödinger wave equation is the Dirac wave equation. Using online sources, research the Dirac wave equation and contrast it with the Schrödinger wave equation.
- 1.27** In Figure 1.12, the elements are organized logically according to the order of orbital filling. Identify two disadvantages of organizing the elements in this way.
- 1.28** In Section 1.3, gadolinium is mentioned as having an electron configuration that deviates from the lanthanoid pattern. Which element in the actinoids should show a similar deviation? What would be its electron configuration?
- 1.29** A philosophical question: Does an orbital exist even if it does not contain an electron? Discuss.

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

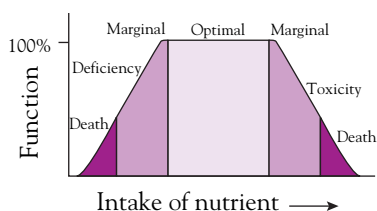


For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

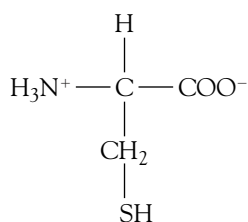




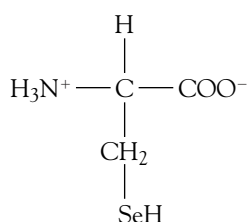




**FIGURE 2.1** Variation of response with intake dose, Bertrand's rule.



(a)



(b)

**FIGURE 2.2** The structures of the amino acids: (a) cysteine; (b) selenocysteine.

One Brazil nut contains our daily nutritional requirement of selenium.

elements are still unknown. As biochemical techniques become more sophisticated, more elements may be added to the list of those required.

For almost all the essential elements, there is a range of intake that is optimum, whereas below and above that range some harmful effects are experienced. This principle is known as *Bertrand's rule* (Figure 2.1). Many people are aware of the Bertrand rule in the context of iron intake. Too little iron can cause anemia, yet children also have died after consuming their parents' iron supplement pills.

The range of optimum intake varies tremendously from element to element. One of the narrow ranges is that of selenium, for which the optimum intake is between  $50 \text{ g} \cdot \text{day}^{-1}$  and  $200 \text{ g} \cdot \text{day}^{-1}$ . Less than  $17 \text{ g} \cdot \text{day}^{-1}$  will cause severe health problems, such as Kashan's disease, whereas chronic selenosis ensues from intake levels above  $1600 \text{ g} \cdot \text{day}^{-1}$ . There is strong evidence that those with levels of selenium toward the higher end of the nutritional range have lower risks of death from a variety of types of cancer. Also, there seems to be a lower incidence of arthritis among those with higher blood levels of selenium.

So what does selenium do? One of the common amino acids is sulfur-containing cysteine (Figure 2.2a). Selenium, the element below sulfur in the periodic table, forms an analogous amino acid, selenocysteine (Figure 2.2b). In addition to cysteine, for health, we need small concentrations of selenocysteine. The difference between the seleno–amino acids and sulfur–amino acids is that selenium has a higher reduction potential than sulfur, enabling the selenium-containing enzymes to function better as antioxidants. It is the antioxidant role which is believed to cause the beneficial effect. Generally, the levels in food are enough to protect against diseases that may result from too little selenium. Most of the daily intake of selenium comes from eating grains, cereals, and meat.

## 2.1 Organization of the Modern Periodic Table

In the modern periodic table, the elements are placed in order of increasing atomic number (the number of protons). Since the Russian chemist Dmitri Mendeleev (pronounced men-deh-lay'-ef) devised the first periodic table in 1869, there have been numerous designs over the years, but the two most common are the long form and the short form. The long form (Figure 2.3) shows all the elements in numerical order.

**FIGURE 2.3** The long form of the periodic table.

																H																	He
Li	Be																			B	C	N	O	F	Ne								
Na	Mg																			Al	Si	P	S	Cl	Ar								
K	Ca																	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr																	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuh	Uuo		

Main					1s		Main	1s
2s							2p	
3s					Transition		3p	
4s					3d		4p	
5s					4d		5p	
6s	4f	Lanthanoids			5d		6p	
7s	5f	Actinoids			6d		7p	

**FIGURE 2.4** Electron orbital filling sequence in the periodic table.

The start of a new period always corresponds to the introduction of the first electron into the s orbital of a new principal quantum number. In a particular period, the principal quantum number of the p orbitals is the same as that of the s orbitals, whereas the d orbitals are one less and the f orbitals are two less. The number of elements in each period corresponds to the number of electrons required to fill those orbitals (Figure 2.4).

Each group contains elements of similar electron configuration. For example, all Group 1 elements have an outer electron that is  $ns^1$ , where  $n$  is the principal quantum number. Although elements in a group have similar properties, it is important to realize that each element is unique. Thus, although nitrogen and phosphorus are sequential elements in the same group, nitrogen gas is very unreactive and phosphorus is so reactive that it spontaneously reacts with the oxygen in the air.

Because the long form of the periodic table is a very elongated diagram and because the elements from lanthanum to ytterbium and from actinium to nobelium show similar chemical behavior, the short form displays these two sets of elements in rows beneath the remainder of the table and the resulting space is closed up. Figure 2.5 shows this more compact, short form of the table.

Chemists disagree about the choice of elements to be placed in Group 3 for Periods 6 and 7. Some consider lanthanum (element 57) and actinium (element 89) to be the correct choices, while others believe lutetium (element 71)

																		18
																		He
1	2																	
Li	Be																	
Na	Mg	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Lanthanoids *	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Actinoids **	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

**FIGURE 2.5** Short form of the periodic table displaying the group numbers. Main group elements are mauve.

and lawrencium (element 103) belong there. The electron configurations of the contenders are shown in the following list:

Atom	Electron configuration	Atom	Electron configuration
La	$[\text{Xe}]6s^25d^1$	Lu	$[\text{Xe}]6s^24f^{14}5d^1$
Ac	$[\text{Rn}]7s^26d^1$	Lr	$[\text{Rn}]7s^25f^{14}6d^1$

Both arguments have their merits. The La-Ac supporters argue that the configurations match those of the elements above: scandium ( $[\text{Ar}]4s^23d^1$ ) and yttrium ( $[\text{Kr}]5s^24d^1$ ). The Lu-Lr supporters point out that all the other transition metals of Period 6 have  $4f^{14}$  in their configurations and those of Period 7 have  $5f^{14}$  in their configurations, making the Lu-Lr pair more consistent.

According to the recommendations of the International Union of Pure and Applied Chemistry (IUPAC), the main and transition groups of elements are numbered from 1 to 18. This system replaces the old system of using a mixture of Roman numerals and letters, a notation that caused confusion because of differences in numbering between North America and the rest of the world. For example, in North America, IIIB referred to the group containing scandium, whereas in the rest of the world, this designation was used for the group starting with boron. Numerical designations are not used for the series of elements from lanthanum (La) to ytterbium (Yb) and from actinium (Ac) to nobelium (No) because there is much more resemblance in properties within each of those rows of elements than vertically in groups.

Groups 1 and 2 and 13 through 18 represent the *main group elements*, and these groups correspond to the filling of the s and p orbitals. Groups 4 through 11, corresponding to the filling of the d orbitals, are classified as the *transition metals*. The discussion of the main groups will be discussed most fully in this text because it is these elements that cover the widest range of chemical and physical properties. The elements of Group 12, although sometimes included among the transition metals, have a very different chemistry from that series; hence, Group 12 will be considered separately. Several of the main groups have been given specific names: *alkali metals* (Group 1), *alkaline earth metals* (Group 2), *pnictogens* (a lesser-used term for Group 15), *chalcogens* (a lesser-used term for Group 16), *halogens* (Group 17), and *noble gases* (Group 18). The elements in Group 11 are sometimes called the *coinage metals*.

The elements corresponding to the filling of the 4f orbitals are called the *lanthanoids*, and those corresponding to the filling of the 5f orbitals are called the *actinoids*. These elements used to be named the lanthanides and actinides, respectively, but the *-ide* ending more correctly means a negative ion, such as oxide or chloride. For a few years, the IUPAC was suggesting the names lanthanons and actinons, but because the ending *-on* is preferred for nonmetals (and the lanthanoids and actinoids are all metallic elements), the *-oid* ending is now recommended. The chemistry of the elements of Group 3, scandium (Sc), yttrium (Y), and lutetium (Lu), more closely resembles that of the lanthanoids than that of the transition metals. For this reason, these three elements are usually discussed together with the lanthanoid elements, lanthanum to ytterbium

Four lanthanoid elements were named after the small Swedish town of Ytterby, where the elements were first discovered. These elements are yttrium, ytterbium, terbium, and erbium.

(see Chapter 24). There is, in fact, a collective name for the Group 3 and lanthanoid elements: the *rare earth elements*.

Although the elements in the periodic table are arranged according to electron structure, we make an exception for helium ( $1s^2$ ). Rather than placing it with the other  $ns^2$  configuration elements, the alkaline earth metals, it is placed with the other noble gases (of configuration  $ns^2np^6$ ) because of chemical similarities (see Figure 2.4). Hydrogen is even more of a problem. Although some versions of the periodic table show it as a member of Group 1 or Group 17 or both, its chemistry is unlike either that of the alkali metals or the halogens (see Chapter 10). For this reason, it is placed on its own in the tables in this text to indicate its chemical uniqueness.

## 2.2 Existence of the Elements

To understand why there are so many elements and to explain the pattern of the abundances of the elements, we must look at the most widely accepted theory of the origin of the universe. This is the Big Bang Theory, which assumes that the universe started from a single point. About one second after the universe came into existence, the temperature had dropped to about  $10^{10}$  K, enabling protons and neutrons to exist. During the next three minutes, hydrogen-1, hydrogen-2, helium-3, helium-4, beryllium-7, and lithium-7 nuclei formed. (The number following the hyphen represents the *mass number*, the sum of protons and neutrons, of that isotope.) After these first few minutes, the universe had expanded and cooled below the temperature at which nuclear fusion reactions could occur. At this time, as is still true today, most of the universe consisted of hydrogen-1 and some helium-4.

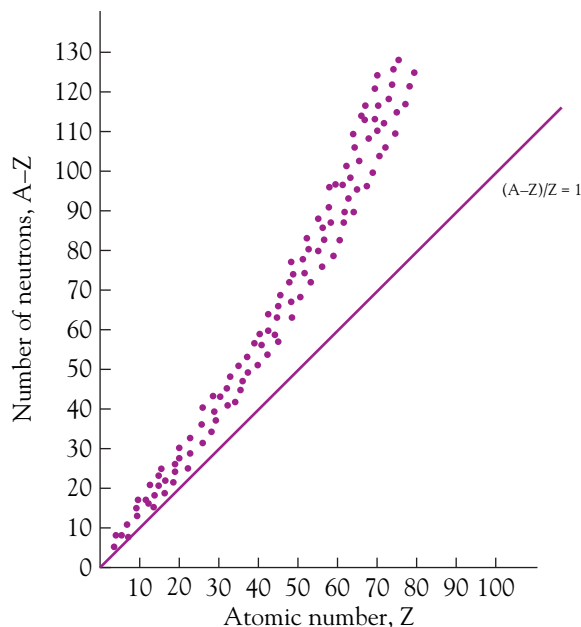
Through gravitational effects, the atoms became concentrated in small volumes of space; indeed, the compression was great enough to cause exothermic nuclear reactions. These volumes of space we call *stars*. In the stars, hydrogen nuclei are fused to give more helium-4 nuclei. About 10 percent of the helium in the present universe has come from hydrogen fusion within stars. As the larger stars become older, build-up of helium-4 and additional gravitational collapse cause the helium nuclei to combine to form beryllium-8, carbon-12, and oxygen-16. At the same time, the fragile helium-3, beryllium-7, and lithium-7 are destroyed. For most stars, oxygen-16 and traces of neon-20 are the largest (highest atomic number) elements produced. However, the temperature of the very massive stars increases to a maximum as high as  $10^9$  K, and their density increases to about  $10^6 \text{ g}\cdot\text{cm}^{-3}$ . Under these conditions, the tremendous repulsion between the high positive charges of carbon and oxygen nuclei can be overcome, a condition leading to the formation of all the elements up to iron. However, iron is the limit because, beyond iron, synthesis (fusion) is endothermic rather than exothermic.

When the more massive elements have accumulated in the core of the star and the energy from nuclear syntheses is no longer balancing the enormous gravitational forces, a catastrophic collapse occurs, followed by an unimaginable

## 2.3 Stability of the Elements and Their Isotopes

The fact that the number of stable elements is limited can be explained by recalling that the nucleus contains positively charged protons. Repulsive forces exist between the protons, just like the repulsive forces between electrons, discussed in Chapter 1. We can visualize the neutrons simply as material separating the positive charges. Figure 2.7 shows that, as the number of protons increases, the number of neutrons in the most common isotope of each element

																H																	He
Li		Be																B	C	N	O	F	Ne										
Na		Mg																Al	Si	P	S	Cl	Ar										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo																
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb																				
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No																				



**FIGURE 2.7** The change in the neutron-proton ratio with increasing atomic number.

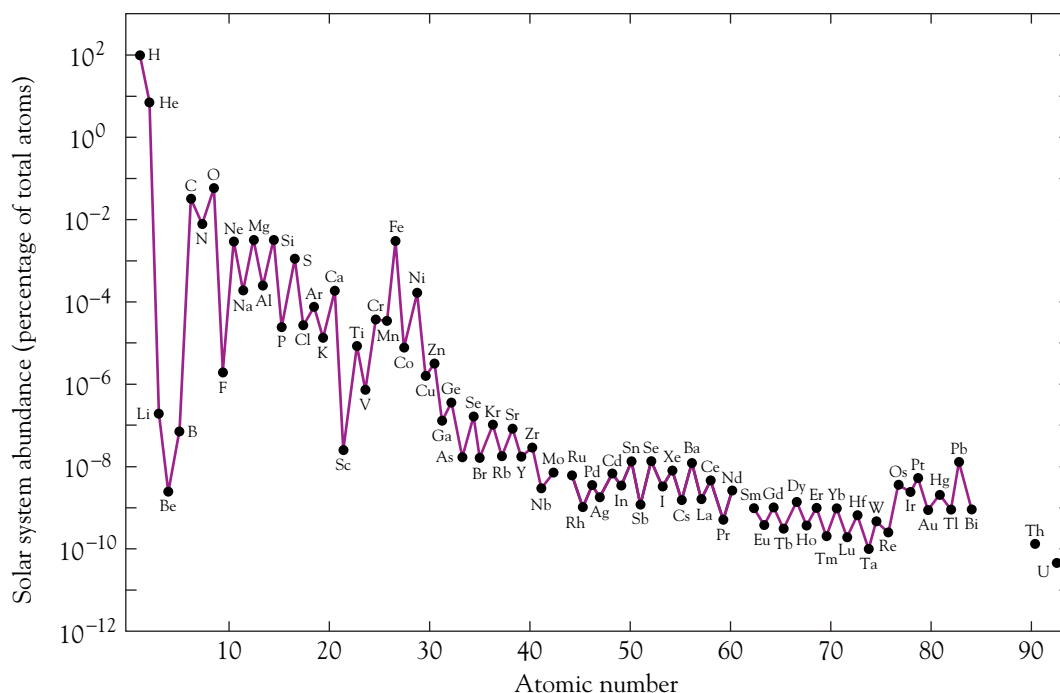
increases at a faster rate. Beyond the 126 protons of lead, the number of positive charges in the nucleus becomes too large to maintain nuclear stability, and the repulsive forces prevail. All the subsequent elements only form radioactive isotopes.

To gain a better understanding of the nucleus, we can devise a quantum (or shell) model of the nucleus. Just as Neils Bohr visualized electrons as existing in quantum levels, so we can visualize layers of protons and neutrons (together called the *nucleons*). Thus, within the nucleus, protons and neutrons will independently fill energy levels corresponding to the principal quantum number  $n$ . However, the angular momentum quantum number  $l$  is not limited as it is for electrons. In fact, for nucleons, the filling order starts with 1s, 1p, 2s, 1d. . . . Each nuclear energy level is controlled by the same magnetic quantum number rules as electrons, so there are one s level, three p levels, and five d levels. Both nucleons have spin quantum numbers that can be  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

### Nuclear Spin Pairing

Different from electron behavior, spin pairing is an important factor for nucleons. In fact, of the 273 stable nuclei, only four have odd numbers of both protons and neutrons. Elements with even numbers of protons tend to have large numbers of stable isotopes, whereas those with odd numbers of protons tend to have one or, at most, two stable isotopes. For example, cesium (55 protons) has just one stable isotope, whereas barium (56 protons) has seven stable isotopes. Technetium and promethium, the only elements before bismuth to exist only as radioactive isotopes, both have odd numbers of protons.





**FIGURE 2.8** Solar system abundances of the elements as percentages on a logarithmic scale. [Adapted from P.A. Cox, *The Elements* (Oxford, UK: Oxford University Press, 1989), p. 17.]

The greater stability of even numbers of protons in nuclei can be related to the abundance of elements on Earth. As well as the decrease of abundance with increasing atomic number, we see that elements with odd numbers of protons have an abundance about one-tenth that of their even-numbered neighbors (Figure 2.8).

### Nuclear Shells

Using the Meyer-Jensen Shell Model, we find that, for nuclei, completed quantum levels contain 2, 8, 20, 28, 50, 82, and 126 nucleons of one kind (compared with 2, 10, 18, 36, 54, and 86 for electrons). Thus, the first completed quantum level corresponds to the  $1s^2$  configuration, the next with the  $1s^21p^6$  configuration, and the following one with  $1s^21p^62s^21d^{10}$ . These levels are filled independently for protons and for neutrons. We find that, just like the quantum levels of electrons, completed nucleon levels confer a particular stability on a nucleus. For example, the decay of all naturally occurring radioactive elements beyond lead results in the formation of lead isotopes, all of which have 82 protons.

The influence of the filled energy levels is apparent in the patterns among stable isotopes. Thus, tin, with 50 protons, has the largest number of stable isotopes (10). Similarly, there are seven different elements with isotopes containing

## The Origin of the Shell Model of the Nucleus

The proposal that the nucleus might have a structure came much later than Bohr's work on electron energy levels. Of the contributors to the discovery, the physicist Maria Goeppert Mayer probably accomplished the most crucial work. In 1946, Mayer was studying the abundances of the different elements in the universe, and she noticed that certain nuclei were far more abundant than those of their neighbors in the periodic table. The higher abundances had to reflect a greater stability of those particular nuclei. She realized that the stability could be explained by considering that the protons and neutrons were not just a solid core but were themselves organized in energy levels just like the electrons.

Mayer published her ideas, but the picture was not complete. She could not understand why the numbers of nucleons to complete each energy level were 2, 8, 20, 28, 50, 82, and 126. After her working on the problem for three years, the flash of inspiration came one evening and she was able to derive theoretically the quantum levels and sublevels. Another physicist, Hans Jensen, read her ideas on the shell model of the nucleus and, in the same year as Mayer, independently came up with the same theoretical results. Mayer and Jensen met and collaborated to write the definitive book (*Elementary Theory of Nuclear Shell Structure*) on the nuclear structure of the atom. Becoming good friends, Mayer and Jensen shared the 1963 Nobel Prize in physics for their discovery of the structure of the nucleus.

82 neutrons (isotones) and six different elements with isotopes containing 50 neutrons.

If the possession of a completed quantum level of one nucleon confers stability to the nucleus, then we might expect that nuclei with filled levels for both nucleons—so-called doubly magic nuclei—would be even more favored. This is indeed the case. In particular, helium-4 with  $1s^2$  configurations of both protons and neutrons is the second most common isotope in the universe, and the helium-4 nucleus (the  $\alpha$ -particle) is ejected in many nuclear reactions. Similarly, it is the next doubly completed nucleus, oxygen-16 (8p, 8n), that makes up 99.8 percent of oxygen on this planet. Calcium follows the trend with 97 percent of the element being calcium-40 (20p, 20n). As we saw in Figure 2.8, the number of neutrons increases more rapidly than that of protons. Thus, the doubly stable isotope is lead-208 (82p, 126n). This is the most massive stable isotope of lead and the most common in nature.

## Synthesis of New Elements

A goal of both chemists and physicists has been the synthesis of new chemical elements. To accomplish this, a target of a high atomic number element is bombarded with atoms of a neutron-rich element whose combined atomic number is that of the desired element. In addition to the common doubly magic isotope of calcium, calcium-40, about 0.2% of natural calcium is neutron-rich doubly magic calcium-48 (20p, 28n). With a neutron-proton ratio of 1.4, calcium-48 has been the key to synthesizing many new elements. Using calcium-48 nuclei as projectiles, nuclear physicists have claimed the synthesis of element 114 (Fl) from plutonium-244, element 115 (Uup) from americium-243, element 116 (Lv) from curium-248, element 117 (Uus) from berkelium-249, and element 118 (Uuo) from californium-249.

## 2.4 Classifications of the Elements

## Metals and Nonmetals

**FIGURE 2.9** Classification of the elements into gases (mauve), liquids (black), and solids (white) at 25°C.

																H																		He
Li		Be																		B	C	N	O	F	Ne									
Na		Mg																		Al	Si	P	S	Cl	Ar									
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																	
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																	
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo																	
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb																					
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No																					

flattened into sheets (*malleability*) or to be pulled into wires (*ductility*) is sometimes cited as a common property of metals, but some of the transition metals are quite brittle. High thermal conductivity is common among the elements we call metals, but diamond, a nonmetal, has one of the highest thermal conductivities of any element. So that classification is not valid either.

High three-dimensional electrical conductivity is the best criterion of a metal. We have to stipulate three rather than two dimensions because graphite, an allotrope of carbon, has high electrical conductivity in two dimensions. There is a difference of  $10^2$  in conductivity between the best electrical conducting metal (silver) and the worst (plutonium). But even plutonium has an electrical conductivity about  $10^5$  times better than the best conducting nonmetallic element. To be precise, though, the SATP conditions of 25°C and 100 kPa have to be stipulated because below 18°C, the stable allotrope of tin is nonelectrically conducting. Furthermore, under readily obtainable pressures, iodine becomes electrically conducting. A more specific physical criterion is the temperature dependence of the electrical conductivity, for the conductivity of metals decreases with increasing temperature, whereas that of nonmetals increases.

### Metalloids

Some nonmetal elements on the border region of the metal-nonmetal divide have some properties which are more metal-like. Such elements were originally called *metalloids*, but in more recent times, the term *semimetal* became more accepted. Unfortunately, physicists have now appropriated the term semimetal to identify elements and compounds with semiconductor properties. Therefore, it seems wise to revert to the use of the term metalloid to avoid confusion.

The question arises, then, which criteria should be used to determine membership of the metalloid category. Intermediate behavior between metals and nonmetals is obviously the focus, but of what? For example, there are certainly elements with values of electronegativity and ionization energy in between the values for typical metals and for typical nonmetals. Whatever the property measured, most inorganic chemists agree that boron, silicon, germanium, arsenic, antimony, and tellurium can be assigned this ambiguous status of metalloids (Figure 2.10). One characteristic of metalloids is that they are solids having at least two allotropes with significantly different structures and electrical conductivities. To illustrate, germanium has one allotrope with the same structure as diamond and another with the same structure as one of the metallic allotropes of tin. Some chemists also include selenium as a metalloid. Selenium would fit as a metalloid using the allotrope criterion in that selenium has three allotropes of very different structures and physical properties.

### Weak Metals

Even then, the division of elements into three categories is a simplification. There is a subgroup of the metals, those closest to the metalloid borderline, that exhibit some chemical behavior that is more typical of the metalloids, particularly formation of anionic species. These eight *chemically weak metals* are beryllium, aluminum, zinc, gallium, tin, lead, bismuth, and polonium. As an

**FIGURE 2.10** Classification of the elements into metals (white), weak metals (mauve), metalloids (black), and nonmetals (pale mauve).

																H																		He
Li	Be																	B	C	N	O	F	Ne											
Na	Mg																	Al	Si	P	S	Cl	Ar											
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																	
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																	
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo																	
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb																					
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No																					

example of one of the anionic species, we can choose aluminum. In very basic solution, as we see in Chapter 13, aluminum forms aluminates,  $\text{Al}(\text{OH})_4^-(aq)$  (sometimes written as  $\text{AlO}_2^-(aq)$ ). The other chemically weak metals similarly form beryllates, zincates, gallates, stannates, plumbates, antimonates, bismuthates, and polonates.

The term *chemically weak metals* defines this cluster of elements according to chemical criteria, differentiating them from “normal” metals. To confuse matters, overlapping with the term *weak metals*, the terms *post-transition metal* and *poor metal* are sometimes used in the literature. However, these categories refer to periodic table locations. Thus post-transition metal refers to all the metals of Groups 12 to 16, while poor metals are specifically the metals of the p-block elements (Groups 13 to 16).

## Bioinorganic Chemistry Implications

In bioinorganic chemistry, one of the fascinating areas is that of element substitution. For example, a group of marine organisms, the tunicates (sea squirts) often contain very high concentrations of vanadium. It seems that, if necessary, these organisms are able to utilize niobium, the element below vanadium in the periodic table, for the same biochemical functions. Certain bacteria, which normally utilize molybdenum in some of their enzymes, utilize tungsten-containing enzymes instead when the bacteria are in high-temperature environments. It is believed that the tungsten-containing enzymes can survive and function as thermophiles.

In the d block of the periodic table, all of the elements are metals, so it is not quite so surprising that an organism can choose to utilize a different metal from the same Group if that different element has advantages under certain conditions. The opening Context section in this chapter focused on the selenoamino acids which have essential roles in living organisms, different than those of the sulfur analogs. Descending any of the groups in the p block involves crossing from nonmetal through to metal. The question then becomes: what about going one more down the chalcogen series to tellurium. Are there analogous tellurium amino acids? Looking at Figure 2.10, we see that tellurium is a

## Medicinal Inorganic Chemistry: An Introduction

Inorganic chemistry affects our lives directly in two ways. First, as we discuss at the beginning of this chapter, many chemical elements are required for the functioning of living organisms. Second, inorganic elements and compounds have been used as medicines since earliest times. Periodically in this text, we give examples of the use of inorganic compounds as medicinal substances, but it is useful to provide an overview.

Many inorganic compounds have been used as medicines through the ages. For example, a fashionable habit in European countries during the late nineteenth and early twentieth centuries was to “take the waters” at spa cities. In some cases, the springs were mineral-rich; for example, the water in Vichy, France (now available bottled), is rich in magnesium ion, which acts as a potent laxative. That water, therefore, should only be drunk in small quantities. The solid salt, magnesium sulfate heptahydrate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , has the same effect. It was named Epsom salts after the town in England where it was first discovered. During the nineteenth century, one British hospital was giving 2.5 tonnes per year to its patients!

Some cultures practice geophagy, the eating of soil—usually clay. Clays are a complex class of minerals, as we discuss in Chapter 14. One form of clay is kaolin—a substance that is known for its absorptive abilities. Several types of tablets to combat stomach upsets employ kaolin, which is believed to be able to surface-absorb toxins produced by ingested harmful bacteria. Other clays and soils

can supply trace nutrients. However, persistent clay eating is not advised since the clay can line the stomach and prevent nutrient adsorption. Also, many natural clays contain high concentrations of harmful elements, such as lead.

Inorganic medicinal chemistry can appear in the most unusual contexts. For example, religious statues made from the mineral realgar, diarsenic disulfide ( $\text{As}_2\text{S}_2$ ), were popular among devotees of the Chinese Taoist religion. Handling the statues was believed to restore health. In this particular case, chemistry rather than faith might have contributed, for many people in tropical areas suffer from internal parasites and handling the statues would result in arsenic absorption through the skin, which was enough to kill the parasites but not enough to kill the devotee.

In the following chapters, we mention a few of the many modern medicinal applications of inorganic compounds:

Antacids (Chapter 7)

Lithium in the treatment of bipolar disorder (Chapter 11)

Boron neutron capture therapy (Chapter 13)

Platinum complexes as anticancer agents (Chapter 19)

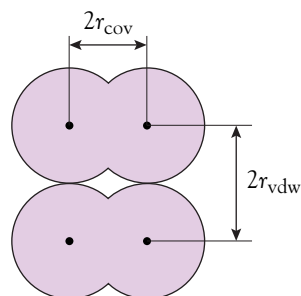
Technetium as a radiopharmaceutical (Chapter 21)

Gold in the treatment of rheumatoid arthritis (Chapter 21)

metalloid. However, though scientists like to make categories, there is no more a firm boundary between nonmetal and metalloid than there is for the simplistic metal/nonmetal “divide.” So recent research has shown that there are indeed telluro-cysteine and telluro-methionine. In fact, a certain fungus fed tellurium rather than sulfur quite happily synthesizes the tellurium analogs!

## 2.5 Periodic Properties: Atomic Radius

One of the most systematic periodic properties is atomic radius. What is the meaning of atomic size? Because the electrons can be defined only in terms of probability, there is no real boundary to an atom. Nevertheless, there are two common ways in which we can define atomic radius. The *covalent radius*,  $r_{\text{cov}}$ , is defined as the half-distance between the nuclei of two atoms of the same element joined in a single covalent bond. The *van der Waals radius*,  $r_{\text{vdw}}$ , is defined as the half-distance



**FIGURE 2.11** Comparison of the covalent radius,  $r_{\text{cov}}$ , and the van der Waals radius,  $r_{\text{vdw}}$ .

The largest atom in the periodic table is francium.

between the nuclei of two atoms of neighboring molecules (Figure 2.11). Furthermore, for the metallic elements, it is possible to measure a *metallic radius*: the half-distance between the nuclei of two neighboring atoms in the solid metal.

Covalent radii are experimental values, and there are significant variations in the numbers for each element. For example, if the atom is in a polar covalent molecule, there will also be an ionic component to the bonding, making the bond length shorter. Among other factors, the covalent radius depends upon the bond order, and for transition metal ions, the number of unpaired electrons. Some values in tables are obtained only from extrapolation of trends. For example, many general chemistry texts list covalent radii for all the noble gases. However, since isolable compounds of helium, neon, and argon have never been synthesized, it is obvious these values are, at best, rough estimates or theoretical values. Likewise, covalent radii for metallic elements are of limited validity and the values cited are often those of the metallic radius. Figure 2.12 provides some of the more reliable values of covalent radii (in picometers,  $10^{-12}$  m) for the Group 17 elements and for the covalently-bonding elements of Period 2. Though the numerical values may differ between sources, the trend is always the same: with few exceptions, radii decrease from left to right across a period and increase descending a group.

To explain these trends, we must examine the model of the atom. Let us start with lithium. A lithium atom contains three protons, and its electron configuration is  $1s^2 2s^1$ . The apparent size of the atom is determined by the size of the outermost orbital containing electrons: in this case, the 2s orbital. The electron in the 2s orbital is shielded from the full attraction of the protons by the electrons in the 1s orbital (Figure 2.13). Hence, the *effective nuclear charge*,  $Z_{\text{eff}}$ , felt by the 2s electron will be much less than 3 and closer to 1. The electrons in the inner orbitals will not completely shield the 2s electron; however, because the volumes of the 2s and 1s orbitals overlap, the  $Z_{\text{eff}}$  will be slightly greater than 1. In fact, its value can be estimated as 1.3 charge units.

A beryllium nucleus has four protons, and the electron configuration of beryllium is  $1s^2 2s^2$ . There will be two factors to consider in estimating atomic radius: the increased  $Z_{\text{eff}}$  as a result of the increased number of protons and the repulsions between the two negative electrons themselves. Each 2s electron will experience the higher  $Z_{\text{eff}}$  since each 2s electron, having the same average distance from the nucleus, will offer little shielding to the other. It has been found that the nuclear attraction is more significant than the inter-electron repulsion; hence, there will be a contraction of the 2s orbitals.

**FIGURE 2.12** Covalent radii (pm) of a typical group and short period.

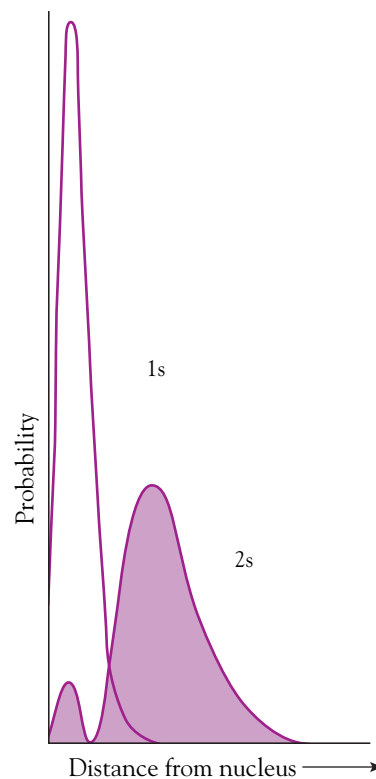
Be 106	B 88	C 77	N 70	O 66	F 64
					Cl 99
					Br 114
					I 133



Proceeding across the period, the contraction continues and we can explain this trend in terms of the effect of  $Z_{\text{eff}}$ . The  $Z_{\text{eff}}$  increases as a result of the increasing nuclear charge and has a greater and greater effect on the electrons that are being added to orbitals (s and p of the same principal quantum number) that overlap substantially. In other words, we can consider the value of  $Z_{\text{eff}}$  for the outer electrons to determine the apparent outer orbital size and hence the radii of the atoms across a period.

Descending a group, the atoms become larger (see Figure 2.12). This trend is also explainable in terms of the increasing size of the orbitals and the influence of the shielding effect. Let us compare a lithium atom (three protons) with the larger sodium atom (11 protons). Because of the greater number of protons, one might expect the greater nuclear charge to cause sodium to have the smaller atomic radius. However, sodium has 10 “inner” electrons,  $1s^2 2s^2 2p^6$ , shielding the electron in the  $3s^1$  orbital. As a result, the 3s electron will feel a much reduced nuclear attraction. Thus, the outermost orbital of sodium will be quite large (radially diffuse), accounting for the larger measured covalent radius of sodium than that of lithium.

There are a few minor variations in the smooth trend. For example, gallium has the same covalent radius (126 pm) as aluminum, the element above it. If we compare the electron configurations—aluminum is  $[\text{Ne}]3s^2 3p^1$  and gallium is  $[\text{Ar}]4s^2 3d^{10} 4p^1$ —we see that gallium has not 8 but 18 protons in its nucleus; these extra protons correspond to the 10 electrons filling the 3d orbitals. However, the 3d orbitals do not shield outer orbitals very well. Thus, the 4p electrons are exposed to a higher  $Z_{\text{eff}}$  than expected. As a result, the radius is reduced to a value similar to that of the preceding member of the group.



**FIGURE 2.13** The variation of electron probability with distance from the nucleus for electrons in 1s and 2s orbitals.

## Slater's Rules

Up to now, we have used  $Z_{\text{eff}}$  in qualitative terms. In 1930, J. C. Slater proposed a set of empirical rules to semiquantify the concept of effective nuclear charge. He proposed a formula that related  $Z_{\text{eff}}$  to the actual nuclear charge,  $Z$ :

$$Z_{\text{eff}} = Z - \sigma_s$$

where  $\sigma_s$  is called *Slater's screening constant*. Slater derived a series of empirical rules for the calculation of  $\sigma_s$ . To use this series of rules, we must order the orbitals by principal quantum number; that is, 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, and so on.

To find the screening constant for a particular electron, the rules are as follows:

1. All electrons in orbitals of greater principal quantum number contribute zero.
2. Each electron in the same principal quantum number contributes 0.35, except when the electron studied is in a d or an f orbital; then the electrons in the s and p orbitals count 1.00 each.
3. Electrons in the  $(n - 1)$  principal quantum level contribute 0.85 each, except when the electron studied is in a d or f orbital; then the electrons count 1.00 each.
4. All electrons in the lesser principal quantum levels count 1.00 each.



**WORKED EXAMPLE 2.1**

Calculate the Slater effective nuclear charge on one of the 3p electrons in the ground-state silicon atom.

**Answer**

The electron configuration of the silicon atom is  $1s^2 2s^2 2p^6 3s^2 3p^2$ . So there are three other electrons with the same principal quantum number: eight electrons in the  $(n - 1)$  principal quantum level and two electrons in the  $(n - 2)$  principal quantum level. Thus, the Slater screening constant is:

$$\sigma_s = (5 \times 0.35) + (8 \times 0.85) + (2 \times 1.00) = 9.85$$

And,  $Z_{\text{eff}} = Z - \sigma_s = (14 - 9.85) = 4.15$ .

The Slater effective nuclear charge on a 3p electron of a silicon atom is 4.15 charge units. ■

**Clementi and Raimondi Values of Effective Nuclear Charge**

Although the results of calculations using Slater's rules provide a more quantitative feel for the concept of effective nuclear charge, their simplicity makes them less than perfect. In particular, the rules assume that both s and p electrons in the same principal quantum number experience the same nuclear charge. From the orbital diagrams that we discussed in Chapter 1, this is obviously not the case. Using calculations based on the atomic wave functions, E. Clementi and D. L. Raimondi derived more precise values for effective nuclear charge, some of which are shown in Table 2.1. The Clementi and Raimondi values do indeed show a small but significant difference in effective nuclear charge for the more penetrating s electrons compared with the p electrons in the same principal quantum number. Note that the increasing  $Z_{\text{eff}}$  on the outermost electrons along the period correlates well with the trend of decreasing atomic radii.

**Relativistic Effects**

There is a contraction in radius for the elements in the sixth period and beyond compared with that predicted from classic calculations. We can explain this in terms of a shortcoming of the Schrödinger wave equation: that it fails to take into account the effects of relativity on the electrons. This simplification is acceptable for the lower mass elements, but toward the bottom of the periodic table, relativistic effects cannot be ignored. For example, the 1s electrons of

**TABLE 2.1** Values of effective nuclear charge for electrons in second period elements according to Clementi and Raimondi

Element	Li	Be	B	C	N	O	F	Ne
<i>Z</i>	3	4	5	6	7	8	9	10
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76

mercury have been estimated to travel at over half the velocity of light. Such a speed results in about a 20 percent increase in mass and hence an approximately 20 percent decrease in orbital size for these electrons.

This reduction in size is particularly apparent for s orbitals, as electrons in these orbitals have high probabilities close to the nucleus. The p orbitals experience a similar but lesser contraction. The d and f orbitals do not penetrate the core and, with the contraction of the s and p orbitals, they are more strongly shielded from the nucleus. As a result, the d and f orbitals expand. However, the outermost orbitals that determine atomic radius are usually s and p; hence, the net effect is a shrinkage in radius among the later-period elements. As we see in later chapters, the relativistic effect can also be used to explain anomalies in the chemistry of the more massive elements.

## 2.6 Periodic Properties: Ionization Energy

One pattern explicable in terms of electron configuration is that of ionization energy. Usually we are interested in the *first ionization energy*; that is, the energy needed to remove one electron from the outermost occupied orbital of a free atom X:

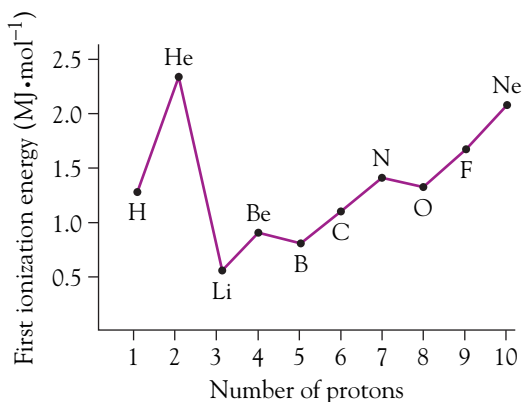


### Period Trends in Ionization Energy

Unlike the molecule-dependent values of covalent radii, ionization energies can be measured with great precision. Figure 2.14 shows the first ionization energies for Period 1 and Period 2 elements.

The explanation for the substantial increase from hydrogen to helium ( $1314 \text{ kJ}\cdot\text{mol}^{-1}$  to  $2368 \text{ kJ}\cdot\text{mol}^{-1}$ ) involves the second proton in the nucleus. Each electron in the 1s orbital of helium is only slightly shielded by the other. Thus, the nuclear attraction,  $Z_{\text{eff}}$ , on each electron is almost twice that for the electron of the hydrogen atom. In fact, there is a good correlation between the measured first ionization energy of an atom and the calculated value of  $Z_{\text{eff}}$  for the outermost electron.

In the lithium atom, the ionizing 2s electron is shielded from the nuclear attraction by the two electrons in the 1s orbital. With a weaker attraction to



**FIGURE 2.14** First ionization energies ( $\text{MJ}\cdot\text{mol}^{-1}$ ) for the elements in Periods 1 and 2.

overcome, the energy needed should be much less, and that is what we find experimentally. The first ionization energy of beryllium is higher than that of lithium, and again we use the concept of little shielding between electrons in the same orbital set—in this case, the 2s orbital—to explain this result.

The slight drop in ionization energy for boron shows a phenomenon that is not apparent from a comparison of covalent radii; it is an indication that the s orbitals do partially shield the corresponding p orbitals. This effect is not unexpected; we show in Chapter 1 that the s orbitals penetrate closer to the nucleus than do the matching p orbitals. Following boron, the trend of increasing ionization energy resumes as the  $Z_{\text{eff}}$  increases and the additional electrons are placed in the same p orbital set.

The final deviation from the trend comes with oxygen. The drop in first ionization energy here can only be explained in terms of inter-electron repulsions. That is, the one paired electron can be lost more readily than would otherwise be the case, leaving the oxygen ion with an electron configuration of  $1s^2 2s^2 2p^3$ . Beyond oxygen, the steady rise in first ionization energy continues to the completion of Period 2. Again, this pattern is expected as a result of the increase in  $Z_{\text{eff}}$ .

Looking at a long period, such as that from potassium to bromine (Figure 2.15), we see a similar pattern as the short periods, with the ionization energy of scandium only slightly greater than that of calcium as a result of the shielding of the single 3d electron by the  $4s^2$  electrons. The ionization energy rises slowly across the transition metals. Once the filling of the 4p orbitals commences, we find that the ionization energy for gallium is quite low; in fact, similar to that of calcium. The sudden drop can be explained by the electrons in the 3d orbitals becoming part of the core and hence more effective at shielding. Also, the lower ionization energy of selenium compared with arsenic can be explained in terms of the loss of one electron from the  $4p^4$  of selenium will result in the half-full p orbital set.

### Group Trends in Ionization Energy

Proceeding down a group, the first ionization energy generally decreases. Using the same argument as that for the increase in atomic radius, we conclude that the inner orbitals shield the electrons in the outer orbitals and the successive outer orbitals themselves are larger. For example, compare lithium and sodium again. Although the number of protons has increased from 3 in lithium to 11 in sodium, sodium has 10 shielding inner electrons. Thus, the  $Z_{\text{eff}}$  for the outermost electron of each atom will be essentially the same. At the same time, the volume occupied by the electron in the 3s orbital of sodium will be significantly larger (thus, on average, the electron will be farther from the nucleus) than that occupied by the electron in the 2s orbital of lithium. Hence, the 3s electron of sodium will require less energy to ionize than the 2s electron of lithium. A

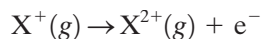
K 0.42	Ca 0.59	Sc 0.63	•••	Cu 0.75	Zn 0.91	Ga 0.58	Ge 0.76	As 0.95	Se 0.94	Br 1.14	Kr 1.35
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**FIGURE 2.15** First ionization energies ( $\text{MJ}\cdot\text{mol}^{-1}$ ) for the main group elements in Period 3.

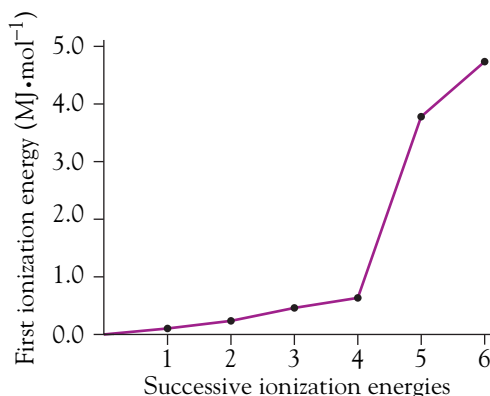
similar trend is apparent among the halogen atoms, although the values themselves are much higher than those of the alkali metals (Figure 2.16).

### Successive Ionization Energies

We can also gain information from looking at successive ionizations of an element. For example, the *second ionization energy* corresponds to the process



Carbon, electron configuration  $1s^2 2s^2 2p^2$ , provides a simple example of such trends (Figure 2.17). The 2p electrons, being shielded by the 1s electrons and partially by the 2s electrons, are comparatively easy to remove. To remove each of the 2s electrons requires more energy. Then, to remove each of the 1s electrons requires very much greater energy. The lesser value for removing the fifth electron compared to the sixth can be accounted for by two factors: First, there are always electron-electron repulsions when two electrons occupy the same orbital; second, even within the same orbital, one electron does partially shield the other electron.



F
1.68
Cl
1.26
Br
1.14
I
1.01
At
0.91

**FIGURE 2.16** First ionization energies ( $\text{MJ}\cdot\text{mol}^{-1}$ ) for the elements in Group 17.

**FIGURE 2.17** Successive ionization energies ( $\text{MJ}\cdot\text{mol}^{-1}$ ) for carbon.

### WORKED EXAMPLE 2.2

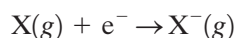
A main group element has the following first five successive ionization energies in  $\text{MJ}\cdot\text{mol}^{-1}$ : 0.58, 1.82, 2.75, 11.58, and 14.84. Which group contains this element?

#### Answer

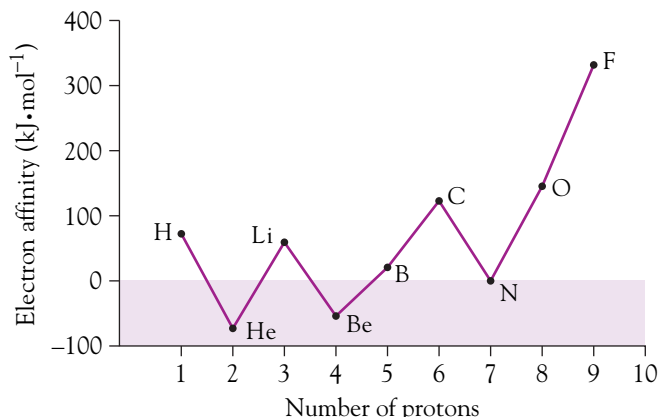
The element has three comparatively low ionization energies. These values must correspond to the ionization of valence electrons. Therefore, the main group element must be a member of Group 13. ■

## 2.7 Periodic Properties: Electron Affinity

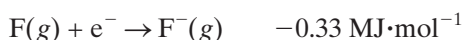
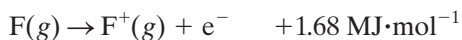
Just as ionization energy represents the loss of an electron by an atom, so electron affinity represents the gain of an electron. *Electron affinity* is defined as the energy change when an electron is added to the lowest energy unoccupied orbital of a free atom:



**FIGURE 2.18** First electron affinities ( $\text{kJ}\cdot\text{mol}^{-1}$ ) for the elements in Periods 1 and 2.

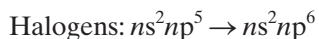


It is important to note that whereas the ionization process requires energy, for most elements, addition of an electron releases energy. This can be illustrated by a comparison of the two processes for fluorine:



### Period Trends in Electron Affinities

There are conflicting sets of values for experimental electron affinities, but the trends are always consistent, and it is the trends that are important to inorganic chemists. A typical data set is shown in Figure 2.18. There are the three noticeable “spikes” which can be explained in terms of the addition of an electron resulting in the completion, or half-completion, of the valence levels as follows:



F
0.33
Cl
0.35
Br
0.33
I
0.30
At
0.27

**FIGURE 2.19** First electron affinities ( $\text{MJ}\cdot\text{mol}^{-1}$ ) for the elements in Group 17.

### WORKED EXAMPLE 2.3

Nitrogen has a zero electron affinity. Suggest a possible reason.

#### Answer

The nitrogen atom has an electron configuration of  $1s^22s^22p^3$ .

As it already possesses a half-full p orbital set, addition of an electron would be less energetically favorable than for other electron configurations. ■

### Group Trends in Electron Affinities

Down a group, as the atoms become larger, so the electron affinities decrease. The trend is illustrated in Figure 2.19 for the halogens. As is often the case, fluorine does not fit the trend. An accepted explanation is that the fluorine atom is so small that an inter-electron repulsion factor reduces the attraction for an additional electron.

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## KEY IDEAS

- There are a variety of forms of the periodic table, all of which are arranged in order of increasing atomic number.
- Nucleons fill shells analogous to electron shells, with filled nucleon shells (“magic numbers”) conferring additional stability to the nuclei.
- Elements can be classified as gas/liquid/solid according to phase at room temperature or as metals/weak metals/metalloids/nonmetals.
- Atomic (covalent/van der Waals/metallic) radius is defined by the effective nuclear charge on the outermost electrons.
- Trends in ionization energy and electron affinity can be explained in terms of electron energies.
- Many chemical elements are essential in biochemical processes.

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## EXERCISES

- 2.1** Define the following terms: (a) rare earth metals; (b) van der Waals radius; (c) effective nuclear charge.
- 2.2** Define the following terms: (a) second ionization energy; (b) electron affinity; (c) Bertrand’s rule.
- 2.3** Explain the two reasons why the discovery of argon posed problems for the original Mendeleev periodic table.
- 2.4** Explain why the atomic mass of cobalt is greater than that of nickel even though the atomic number of cobalt is less than that of nickel.
- 2.5** Give one advantage and one disadvantage of the long form of the periodic table.
- 2.6** Suggest why the Group 11 elements are sometimes called the coinage metals.
- 2.7** Suggest why it would be more logical to call element 2 “helon” rather than helium. Why is the *-ium* ending inappropriate?
- 2.8** Why were the names lanthanides and actinides inappropriate for those series of elements?
- 2.9** Why is iron the highest atomic number element formed in stellar processes?
- 2.10** Why must the heavy elements on this planet have been formed from the very early supernovas that exploded?
- 2.11** Identify
- (a) the highest atomic number element for which stable isotopes exist
  - (b) the only transition metal for which no stable isotopes are known
  - (c) the only liquid nonmetal at SATP.
- 2.12** Identify the only two radioactive elements to exist in significant quantities on Earth. Explain why they are still present.
- 2.13** Which element—sodium or magnesium—is likely to have only one stable isotope? Explain your reasoning.
- 2.14** Suggest the number of neutrons in the most common isotope of calcium.
- 2.15** Yttrium, element 39, exists in nature as only one isotope. Without consulting tables, deduce the number of neutrons in this isotope.
- 2.16** Suggest why polonium-210 and astatine-211 are the isotopes of those elements with the longest half-lives.
- 2.17** In the classification of elements into metals and nonmetals,
- (a) Why is a metallic luster a poor guide?
  - (b) Why can’t thermal conductivity be used?
  - (c) Why is it important to define electrical conductivity in three dimensions as the best criteria for metallic behavior?
- 2.18** On what basis are elements classified as metalloids?
- 2.19** Which atom should have the larger covalent radius, potassium or calcium? Give your reasoning.
- 2.20** Which atom should have the larger covalent radius, fluorine or chlorine? Give your reasoning.
- 2.21** Suggest a reason why the covalent radius of germanium (122 pm) is almost the same as that of silicon (117 pm), even though germanium has 18 more electrons than silicon.
- 2.22** Suggest a reason why the covalent radius of hafnium (144 pm) is less than that of zirconium (145 pm), the element above it in the periodic table.
- 2.23** In Table 2.1, we show the values of effective nuclear charge for the second period elements calculated by the sophisticated method of Clementi and Raimondi. For each of those elements, calculate the effective nuclear charge on each of the 1s, 2s, and 2p orbitals according to

Slater's rules. Compare them to the Clementi and Raimondi values and discuss whether the differences are really significant.

**2.24** Using Slater's rules, calculate the effective nuclear charge on an electron in each of the orbitals in an atom of potassium.

**2.25** Using Slater's rules, calculate the relative effective nuclear charge on one of the 3d electrons compared to that on one of the 4s electrons for an atom of manganese.

**2.26** Using Slater's rules, calculate the effective nuclear charge on a 3p electron in (a) aluminum and (b) chlorine. Explain how your results relate to

- (a) the relative atomic radii of the two atoms
- (b) the relative first ionization energies of the two atoms.

**2.27** Which element should have the higher ionization energy, silicon or phosphorus? Give your reasoning.

**2.28** Which element should have the higher ionization energy, arsenic or phosphorus? Give your reasoning.

**2.29** An element has the following first through fourth ionization energies in  $\text{MJ}\cdot\text{mol}^{-1}$ : 0.7, 1.5, 7.7, 10.5. Deduce to

which group in the periodic table it probably belongs. Give your reasoning.

**2.30** Which one, in each pair of elements—boron and carbon and carbon and nitrogen—will have the higher second ionization energy? Give your reasoning in each case.

**2.31** For the elements sodium and magnesium, which has the higher first ionization energy? Second ionization energy? Third ionization energy?

**2.32** Which element, sodium or magnesium, should have an electron affinity closer to zero? Give your reasoning.

**2.33** Would you expect the electron affinity of helium to be positive or negative in sign? Explain your reasoning.

**2.34** What part of the periodic table contains the elements that we need in large quantities? How does this correspond to the element abundances?

**2.35** Without consulting data tables or a periodic table, write the mass number for

- (a) the most common isotope of lead (element 82)
- (b) the only stable isotope of bismuth (element 83)
- (c) the longest-lived isotope of polonium (element 84).

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## BEYOND THE BASICS

**2.36** Contrary to the general trend, the first ionization energy of lead ( $715 \text{ kJ}\cdot\text{mol}^{-1}$ ) is higher than that of tin ( $708 \text{ kJ}\cdot\text{mol}^{-1}$ ). Suggest a reason for this.

**2.37** Why are elemental hydrogen and helium not present in any significant amounts in the Earth's atmosphere even though they are the two most abundant elements in the universe?

**2.38** For nutritional considerations, why is it wise for your food to come from a number of different geographical locations?

**2.39** When element 119 is synthesized, what would you expect qualitatively in terms of its physical and chemical properties?

**2.40** Research the claimed synthesis of elements 114, 115, 116, 117, and 118. What do you notice about most of the isotopes of these elements?

**2.41** Use an advanced inorganic chemistry or bioinorganic chemistry text to identify a role in human nutrition for as many of the ultratrace elements shown in the chapter opener figure as possible.

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



# COVALENT BONDING AND MOLECULAR SPECTROSCOPY

## CHAPTER 3

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

The covalent bond, the sharing of electrons between pairs of atoms, is one of the most crucial concepts in chemistry. The valence-shell electron-pair repulsion model works surprisingly well to predict molecular shapes, but bonding is explained best in terms of molecular orbitals. The physical properties of small covalently bonded molecules can be understood by the concept of intermolecular forces between neighboring molecules. Vibrational spectroscopy is a major tool in studying covalent molecules. However, we must keep in mind that there is no rigid divide between covalent and ionic bonding.

### Context: The Greenhouse Effect

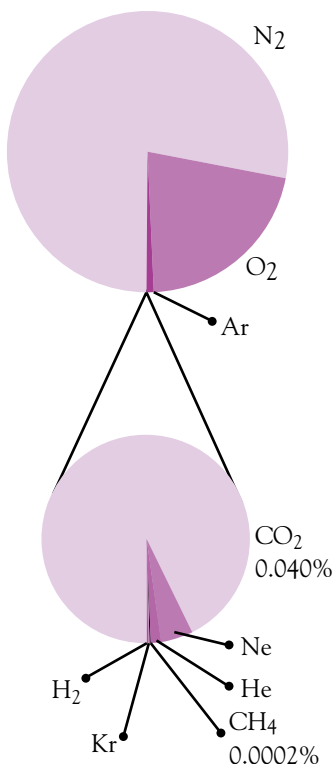
Most of us have heard of the so-called greenhouse effect, yet few people really understand the issues. The greenhouse effect—more correctly called *radiation trapping*—is nothing more than the large-scale application of principles of infrared vibrational spectroscopy, which we study in Section 3.13. The energy from the Sun reaches the Earth's surface as electromagnetic radiation, particularly centered around the visible region. This energy is absorbed by the Earth's surface and atmosphere. It is re-emitted mainly as infrared radiation ("heat" rays). If all the incoming energy were lost back into space as infrared radiation, the temperature of the Earth's surface would be between  $-20^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$ . Fortunately, molecules in the atmosphere with infrared vibrational frequencies absorb the energy corresponding to those frequencies. It is the re-radiation of the absorbed energy back to Earth and its conversion to molecular motion that results in the warming of the oceans, land, and air. As a result, the average temperature of the Earth's surface is about  $14^{\circ}\text{C}$ . In other words, the greenhouse effect makes this planet habitable.

As we explain in Section 3.13, it is only atmospheric gases containing more than two atoms which possess infrared-absorbing vibrations. The upper pie chart in the chapter opening figure shows the proportions of the atmospheric gases (apart from water vapor). These most abundant atmospheric gases: nitrogen (diatomic), oxygen (diatomic), and argon (monatomic), are not greenhouse gases. The lower pie chart in the same figure shows the most common "trace gases"—amounting

- 3.1** A Brief Review of Lewis Structures
- 3.2** Partial Bond Order
- 3.3** Formal Charge
- 3.4** Valence-Shell Electron-Pair Repulsion Rules
- 3.5** The Valence-Bond Concept
- 3.6** Introduction to Molecular Orbitals
- 3.7** Molecular Orbitals for Period 1 Diatomic Molecules
- 3.8** Molecular Orbitals for Period 2 Diatomic Molecules
- 3.9** Molecular Orbitals for Heteronuclear Diatomic Molecules
- 3.10** Network Covalent Substances
- 3.11** Intermolecular Forces
- 3.12** Molecular Symmetry
- 3.13** Symmetry and Vibrational Spectroscopy
- 3.14** The Bonding Continuum



The composition of the Earth's current atmosphere (without water vapor). The upper pie chart shows the major components while the lower pie chart shows the more common minor components. Of the species shown, only carbon dioxide and methane are infrared absorbing.



to just over 0.04% of the total. Of this very tiny proportion, carbon dioxide (triatomic) is the most common greenhouse gas, then methane (pentatomic)—although the greater number of the infrared absorptions of methane makes it a more considerable contributor than its concentration would indicate. There are additional greenhouse gases in even smaller, but significant, proportions, such as dinitrogen oxide (see Chapter 15, Section 15.8) and sulfur hexafluoride (see Chapter 16, Section 16.20).

By burning fossil fuels, we are injecting additional carbon dioxide into the atmosphere much faster than it can be removed by natural processes. This rapid increase in atmospheric carbon dioxide levels is causing concern among climatologists. Because carbon dioxide is an infrared absorber, logically, more carbon dioxide in the atmosphere will cause atmospheric warming. We also have to take into account contributions to global climate change from increases in atmospheric concentration of the other infrared-absorbing gases, in particular, methane.

### 3.1 A Brief Review of Lewis Structures

It was Gilbert N. Lewis, raised on a small farm in Nebraska, who in 1916 devised the concept of electron-sharing between atoms. As so often in science, his revolutionary idea was initially rejected by many other chemists at the time.

This simplistic bonding representation of Lewis—that atoms combine by sharing electron pairs—tells us nothing in detail about the bonds themselves.

Nevertheless, for complex molecules, constructing simple electron-dot representations is very useful. In particular, we can use such representations to deduce molecular shape.

The Lewis, or electron-dot, approach to covalent bond formation is covered extensively in high school and freshman chemistry; hence, only a brief review is provided here. The Lewis concept explains the driving force of bond formation as being the attainment by each atom in the molecule of an octet of electrons in its outer (valence) energy level (except hydrogen, where a duet is required). Completion of the octet is accomplished by a sharing of electron pairs between bonded atoms.

We can illustrate using two examples: hydrogen chloride and carbon monoxide. In hydrogen chloride, the sharing of an electron pair results in a single bond (Figure 3.1). The other electron pairs are lone pairs. To make up the octet around both carbon and oxygen in carbon monoxide, three bonding pairs are needed, resulting in a triple bond (Figure 3.2).



**FIGURE 3.1** Electron-dot diagram for hydrogen chloride.



**FIGURE 3.2** Electron-dot diagram for carbon monoxide.

### Constructing Lewis Structures

The most commonly used method for constructing Lewis structures involves the following steps:

1. Identify the central atom; usually the atom of lower electronegativity (although hydrogen is never central). Write the symbol of the central atom and place the symbols of the other atoms around the central atom.
2. Count the total number of valence electrons. If it is a charged ion and not a neutral molecule, add on the number of negative charges or subtract the number of positive charges.
3. Place an electron pair (single covalent bond) between the central atom and each of the surrounding atoms. Add lone pairs to the surrounding atoms. Then any excess electrons are added to the central atom.
4. If the number of electrons on the central atom is less than eight and there are “leftover” electrons, add lone pairs to the central atom. If the number of electrons shared with the central atom is less than eight and there are no more electrons, construct double and triple bonds using lone pairs from surrounding atoms.

#### WORKED EXAMPLE 3.1

Deduce the Lewis structure for nitrogen trifluoride.

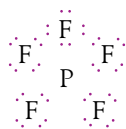
##### Answer

The lower electronegativity nitrogen atom will be surrounded by the three fluorine atoms.

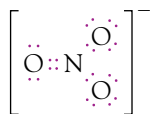
The total number of valence electrons is  $[(1 \times 5) + (3 \times 7)] = 26$ .

Six electrons will be used to form single covalent bonds. Eighteen electrons are needed to provide lone pairs to the fluorine atoms. The remaining electron pair will provide a lone pair on the nitrogen atom. ■

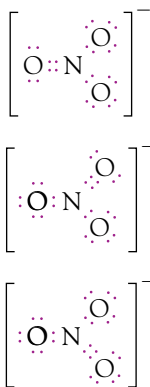




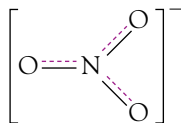
**FIGURE 3.3** Electron-dot diagram for phosphorus pentafluoride.



**FIGURE 3.4** Electron-dot diagram for the nitrate ion.



**FIGURE 3.5** The three resonance structures of the nitrate ion.



**FIGURE 3.6** Representation of the partial multiple bond character of the nitrate ion.

## Exceeding the Octet

In a few anomalous molecules, the central atom has fewer than eight electrons, and in a substantial number of molecules, the central atom has shares in more than eight bonding electrons. Lewis did not realize that the maximum of eight was generally applicable only to the Period 2 elements, for which the sum of the s and p electrons could not exceed eight. In reality, compounds of some of the higher period elements frequently have central atoms with 8, 10, or 12 bonding electrons. For example, phosphorus pentafluoride “pairs up” its 5 outer electrons with 1 electron of each of the fluorine atoms to attain an outer set of 10 electrons (Figure 3.3).

For elements in Period 3 and higher periods, traditionally, the use of d orbitals was invoked to make possible a theoretical maximum of 18 bonding electrons. From experimental studies, it is now established that d orbitals are rarely involved in main group bonding.

## 3.2 Partial Bond Order

In some cases, the only structure that can be drawn does not correlate with our measured bond information. The nitrate ion illustrates this situation. A conventional Lewis structure for the nitrate ion is shown in Figure 3.4. In this structure, one nitrogen-oxygen bond is a double bond, whereas the other two nitrogen-oxygen bonds are single bonds.

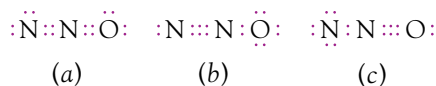
However, it has been shown that the nitrogen-oxygen bond lengths are all the same at 122 pm. This length is significantly less than the “true” (theoretical) nitrogen-oxygen single bond length of 141 pm. We explain this discrepancy by arguing that the double bond is shared between the three nitrogen-oxygen bond locations—a concept called *resonance*. The three alternatives could be represented by three different Lewis structures for the nitrate ion, each with the double bond in a different location (Figure 3.5).

A third approach is to use a structural formula with broken lines to represent a fractional bond order (Figure 3.6). In this case, because the double bond character is shared by three bonds, the average bond order would be 1. This representation is, in most ways, the best of the three. It indicates the equivalency of the three bonds and that they each have a bond order between 1 and 2.

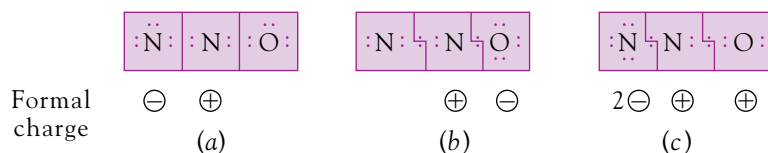
## 3.3 Formal Charge

In some cases, we can draw more than one feasible Lewis structure, with one such example being dinitrogen oxide. It is known that  $\text{N}_2\text{O}$  is an asymmetrical linear molecule with a central nitrogen atom, but there are a number of possible Lewis structures, with the three most feasible being shown in Figure 3.7.

To help decide which possibilities are unrealistic, we can use the concept of *formal charge*. To find the formal charge, we divide the bonding electrons equally among the constituent atoms and compare the number of assigned electrons for each atom with its original number of valence electrons. Any difference is identified by a charge sign (Figure 3.8). For example, in structure (a), the



**FIGURE 3.7** Three possible electron-dot diagrams for the dinitrogen oxide molecule.



**FIGURE 3.8** Assignment of formal charges to three electron-dot diagrams for the dinitrogen oxide molecule.

left-hand nitrogen atom is assigned six electrons; the free atom has five. Hence, its formal charge is  $(5 - 6) = -1$ . The central nitrogen atom has four assigned electrons and a formal charge of  $(5 - 4) = +1$ ; the oxygen atom has the same number of electrons as a free atom, that is  $(6 - 6) = 0$ .

According to the concept of formal charge, the lowest energy structure will be the one with the smallest formal charges on the atoms. In the case of dinitrogen oxide, structure (c) is eliminated, but both (a) and (b) have equal but different formal charge arrangements. The optimum representation, then, is likely to be a resonance mixture of these two possibilities. This resonance form can best be represented by partial bonds, as shown in Figure 3.9. If these two resonance forms contributed equally, there would be an NN bond order of  $2\frac{1}{2}$  and an NO bond order of  $1\frac{1}{2}$ , which is close to that estimated from measurement of bond lengths.



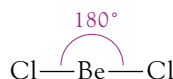
**FIGURE 3.9** Representation of the partial bond order in the dinitrogen oxide molecule.

### 3.4 Valence-Shell Electron-Pair Repulsion Rules

Lewis structures can be used to derive the probable molecular shape. To accomplish this, we can use a very simplistic set of rules that tells us nothing about the bonding but is surprisingly effective at predicting molecular shapes—the valence-shell electron-pair repulsion (VSEPR) rules; also called the electron domain (ED) model.

According to the VSEPR rules, repulsions between electron pairs in the outermost occupied energy levels on a central atom cause those electron pairs to be located as far from each other as is geometrically possible. For the purposes of this method, we must ignore the differences between the energies of the s, p, and d orbitals and simply regard them as degenerate. It is these outer electrons that are traditionally called the valence electrons. Although conceptually there are many flaws with the VSEPR approach; it is an effective tool for deducing molecular shape.

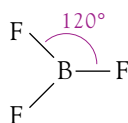
The VSEPR rules relate to the electron groupings around the central atom. An electron grouping can be an electron pair of a single bond, the two electron pairs in a double bond, the three electron pairs in a triple bond, a lone pair of electrons, or the rare case of a single electron. For simplicity, lone pairs are



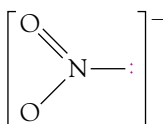
**FIGURE 3.10** Predicted and actual geometry for the gaseous beryllium chloride molecule.



**FIGURE 3.11** Predicted and actual geometry for the carbon dioxide molecule.



**FIGURE 3.12** Predicted and actual geometry for the boron trifluoride molecule.



**FIGURE 3.13** Predicted and actual geometry for the nitrite ion.

shown only for the central atom in diagrams of molecular geometry. In the following sections, we look at each of the common configurations in turn.

### Linear Geometry

All diatomic molecules and ions are, by definition, linear. However, our main interest is the few common examples of this simplest geometry with triatomic molecules and ions. The most often used example is beryllium chloride. This compound has a complex structure in the room-temperature solid phase, but when it is heated above its boiling point of 820°C, it forms simple triatomic molecules. The Lewis structure has the two outer electrons of beryllium pair with one electron of each chlorine atom and form two electron pairs around the central beryllium atom. Because there are only two electron groupings around the central atom, the bonds will be farthest apart when the angle between them is 180°. Hence, the molecule should be linear, and that is indeed what we find (Figure 3.10).

Another example of a molecule with two electron groupings is carbon dioxide. Although both carbon-oxygen bonds involve two electron pairs, each double bond represents only one electron grouping (Figure 3.11). Hence, the carbon dioxide molecule is linear.

### Trigonal Planar Geometry

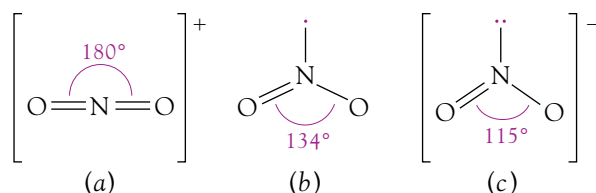
Boron trifluoride is the common example of trigonal planar geometry. The three outer electrons of the boron atom pair with one electron of each of the fluorine atoms to produce three electron pairs. The maximum separation of three electron pairs requires an angle of 120° between each pair, as shown in Figure 3.12.

The nitrite ion is a good example of a species containing a lone pair on the central atom. The electron-pair arrangement around the nitrogen atom is trigonal planar (Figure 3.13). However, we cannot detect lone pairs experimentally. The molecular shape we actually observe is V-shaped (also called angular or bent). According to the VSEPR rules, the lone pair must occupy that third site; otherwise the molecule would be linear. The names of the shapes for central atoms that have three electron groupings are given in Table 3.1.

Many molecules and ions containing lone pairs have bond angles that deviate from those of the theoretical geometrical figure. For example, we find that the O—N—O bond angle is “squashed” down to 115° from the anticipated 120° value. One suggested explanation is that the lone pairs of electrons occupy a greater volume of space than do the bonding pairs. We can use a series of ions and molecules to illustrate this concept. The nitronium ion,  $\text{NO}_2^+$ , with only two electron groupings, is linear (Figure 3.14a); the neutral nitrogen dioxide

**TABLE 3.1** Molecules and ions with trigonal planar geometry

Bonding pairs	Lone pairs	Shape
3	0	Trigonal planar
2	1	V



**FIGURE 3.14** Bond angles for the nitryl ion ( $\text{NO}_2^+$ ), the nitrogen dioxide molecule ( $\text{NO}_2$ ), and the nitrite ion ( $\text{NO}_2^-$ ).

molecule,  $\text{NO}_2$ , with three electron groupings (one an “odd” electron), has an  $\text{O—N—O}$  bond angle of  $134^\circ$  (Figure 3.14b); the nitrite ion,  $\text{NO}_2^-$ , which has a lone pair rather than a single electron, has an observed bond angle of  $115^\circ$  (Figure 3.14c). Thus, even though we cannot experimentally “see” lone pairs, they must play a major role in determining molecular shape.

### Tetrahedral Geometry

The most common of all molecular geometries is that of the tetrahedron. To place four electron pairs as far apart as possible, molecules adopt this particular three-dimensional geometry in which the bond angles are  $109.5^\circ$ . The simplest example is the organic compound methane,  $\text{CH}_4$ , shown in Figure 3.15. To represent the three-dimensional shape on two-dimensional paper, it is conventional to use a solid wedge to indicate a bond directed above the plane of the paper and a broken line to indicate a bond angled below the plane of the paper.

Ammonia provides the simplest example of a molecule where one of the four electron pairs on the central atom is a lone pair. The resulting molecular shape is trigonal pyramidal (Figure 3.16). Like the earlier example of the nitrite ion, the  $\text{H—N—H}$  bond angle of  $107^\circ$  is slightly less than the expected ( $109.5^\circ$ ).

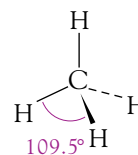
The most familiar molecule with two lone pairs is water (Figure 3.17). The  $\text{H—O—H}$  bond angle in this V-shaped molecule is reduced from the expected  $109.5^\circ$  to  $104.5^\circ$ . The names of the shapes for central atoms that have four electron groupings are given in Table 3.2.

### Trigonal Bipyramidal Geometry

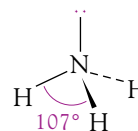
Atoms beyond Period 2 can possess more than four electron pairs when occupying the central position in a molecule. An example of five electron pairs around the central atom is provided by phosphorus pentafluoride in the gas phase (Figure 3.18). This is the only common molecular geometry in which the angles are not equal. Thus, three (equatorial) bonds lie in a single plane and are separated by angles of  $120^\circ$ ; the other two (axial) bonds extend above and below the plane and make an angle of  $90^\circ$  with it.

**TABLE 3.2** Molecules and ions with tetrahedral geometry

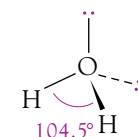
Bonding pairs	Lone pairs	Shape
4	0	Tetrahedral
3	1	Trigonal pyramidal
2	2	V



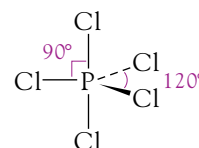
**FIGURE 3.15** Predicted and actual geometry for the methane molecule.



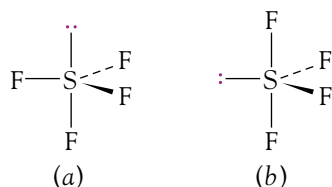
**FIGURE 3.16** Actual geometry for the ammonia molecule.



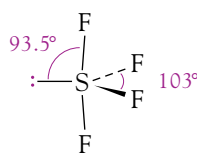
**FIGURE 3.17** Actual geometry for the water molecule.



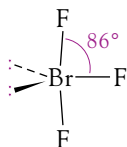
**FIGURE 3.18** Predicted and actual geometry for the gaseous phosphorus pentachloride molecule.



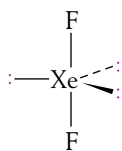
**FIGURE 3.19** Possible geometries for the sulfur tetrafluoride molecule (a) with the lone pair in the axial position and (b) with the lone pair in the equatorial position.



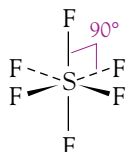
**FIGURE 3.20** Actual geometry for the sulfur tetrafluoride molecule.



**FIGURE 3.21** Actual geometry for the bromine trifluoride molecule.



**FIGURE 3.22** Predicted and actual geometry for the xenon difluoride molecule.



**FIGURE 3.23** Predicted and actual geometry for the sulfur hexafluoride molecule.

Sulfur tetrafluoride provides an example of a molecule that has a trigonal bipyramidal electron-pair arrangement with one lone pair. There are two possible locations for the lone pair: one of the two axial positions (Figure 3.19a) or one of the three equatorial positions (Figure 3.19b). In fact, we find that lone pairs are located so that, first, they are as far from each other as possible and, second, they are as far from the bonding pairs as possible. Sulfur tetrafluoride possesses one lone pair, so only the second guideline is applicable. If the lone pair were in an axial position, there would be three bonding pairs at  $90^\circ$  and one at  $180^\circ$ . However, if the lone pair were in an equatorial position, there would be only two bonding pairs at an angle of  $90^\circ$  and the other two at  $120^\circ$ . It is the second possibility, in which the atoms are arranged in the seesaw shape, that provides the optimum situation. This arrangement has been confirmed by bond angle measurements. In the measured angles, the axial fluorine atoms are bent away from the lone pair by  $93.5^\circ$  rather than by  $90^\circ$ . Much more striking is the compression of the F—S—F equatorial angle from  $120^\circ$  to  $103^\circ$ , presumably as a result of the influence of the lone pair (Figure 3.20).

The bromine trifluoride molecule provides an example of trigonal bipyramidal electron-pair arrangement with two lone pairs (Figure 3.21). The minimum electron repulsions occur with both lone pairs in the equatorial plane. Hence, the molecule is essentially T-shaped, but the axial fluorine atoms are bent away from the vertical to form an  $F_{\text{axial}}\text{—Br—}F_{\text{equatorial}}$  angle of only  $86^\circ$ .

There are a number of examples of molecules with trigonal bipyramidal electron-pair arrangements having three lone pairs. One of these is the xenon difluoride molecule (Figure 3.22). The third lone pair occupies the equatorial position as well, and so the observed molecular shape is linear. The names for the shapes of molecules and ions that have a trigonal bipyramidal geometry are given in Table 3.3.

### Octahedral Geometry

The most widely spaced possibility with six electron groupings results from bonds at equal angles of  $90^\circ$ , which is the octahedral arrangement. A common example of this molecular shape is sulfur hexafluoride (Figure 3.23).

Iodine pentafluoride provides an example of a molecule with five bonding electron pairs and one lone pair around the central atom. Because theoretically all the angles are equal, the lone pair can occupy any site (Figure 3.24), thus producing an apparent square-based pyramidal shape. However, experimental

**TABLE 3.3** Molecules and ions with trigonal bipyramidal geometry

Bonding pairs	Lone pairs	Shape
5	0	Trigonal bipyramidal
4	1	Seesaw
3	2	T
2	3	Linear



**TABLE 3.4** Molecules and ions with octahedral geometry

Bonding pairs	Lone pairs	Shape
6	0	Octahedral
5	1	Square-based pyramidal
4	2	Square planar

measurements show that the four equatorial fluorine atoms are slightly above the horizontal plane, thus giving a  $F_{\text{axial}}\text{—I—}F_{\text{equatorial}}$  angle of only  $82^\circ$ . Once again, this result indicates that the lone pair occupies a greater volume than do the bonding pairs.

Finally, xenon tetrafluoride proves to be an example of a molecule that has four bonding pairs and two lone pairs around the central xenon atom. The lone pairs occupy opposite sides of the molecule, thereby producing a square planar arrangement of fluorine atoms (Figure 3.25). The names for the shapes of molecules and ions that have an octahedral geometry are given in Table 3.4.

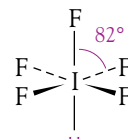
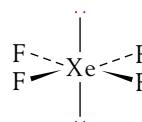
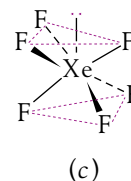
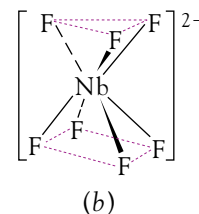
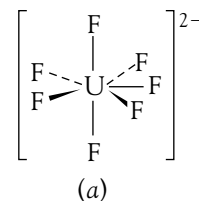
### Greater Than Six Bonding Directions

So far in this chapter, we have emphasized the existence of covalent bonds in compounds containing nonmetals and semimetals. Yet as we will see throughout this text, covalent bonding is also very important for compounds containing metals, such as metal-centered polyatomic ions. For example, the permanganate ion,  $\text{MnO}_4^-$ , contains manganese covalently bonded to four oxygen atoms. In the context of this section, it is covalently bonded metal-centered molecules and polyatomic ions which more commonly exceed six bonding directions.

To accommodate seven or more atoms around a central atom, the central atom/ion itself has to be quite large and the surrounding atoms and ions quite small. For example, the lanthanoid(III) ions (generic symbol  $\text{Ln}^{3+}$ ) are so large that nine water molecules can be fitted around the ion:  $[\text{Ln}(\text{OH}_2)_9]^{3+}$ .

The  $\text{MX}_7$  species are particularly interesting because they can assume three possible geometries: pentagonal bipyramid, capped trigonal prism, and capped octahedron. The pentagonal bipyramid resembles the trigonal bipyramid and octahedron except that it has five rather than three and four bonds, respectively, in the equatorial plane. The capped trigonal prism has three atoms in a triangular arrangement above the central atom and four atoms in a square plane below the central atom. The capped octahedron is simply an octahedral arrangement in which three of the bonds are opened up from the  $90^\circ$  angle and a seventh bond inserted between.

These three structures must be almost equally favored in terms of relative energy and atom spacing because all are found: the uranium(V) fluoride ion,  $\text{UF}_7^{2-}$ , adopts the pentagonal bipyramidal arrangement (Figure 3.26a), whereas the niobium(V) fluoride ion,  $\text{NbF}_7^{2-}$ , adopts the capped trigonal prismatic structure (Figure 3.26b), and it is believed that xenon hexafluoride,  $\text{XeF}_6$ , adopts the capped octahedral structure in the gas phase (Figure 3.26c).

**FIGURE 3.24** Actual geometry for the iodine pentafluoride molecule.**FIGURE 3.25** Predicted and actual geometry for the xenon tetrafluoride molecule.**FIGURE 3.26** (a) The pentagonal bipyramidal structure of uranium(V) fluoride; (b) the capped trigonal prismatic structure of niobium(V) fluoride; (c) the probable capped octahedral structure of xenon hexafluoride.



**WORKED EXAMPLE 3.2**

Predict the shape of  $\text{ICl}_2^-$ .

**Answer**

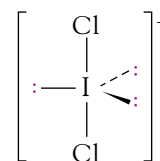
Iodine will be the central atom.

There are a total of 22 electrons: 7 from the iodine atom; 7 from each of the 2 chlorine atoms; and 1 from the negative ion charge.

An electron pair is needed for each of the two I—Cl bonds, and each chlorine atom will need three additional electron pairs. We are left with:  $[22 - (2 \times 2 + 2 \times 6)] = 6$  electrons.

The six electrons provides three lone pairs for the central iodine atom.

The geometry will be based on the trigonal bipyramid, with the lone pairs in the equatorial positions and the chlorine atoms in the axial positions. ■

**3.5 The Valence-Bond Concept**

The valence-bond concept builds on the Lewis proposal that bonding results from electron pairing between neighboring atoms. The Lewis approach was put into a quantum mechanical context and then the results (the valence-bond concept) were refined by Linus Pauling. This bonding explanation is used much less now than it used to be but is still employed by some chemists, particularly those in organic chemistry. We will see in Chapter 19, Section 19.6, that the valence-bond method can also be applied to the bonding in transition metal compounds.

The principles of the valence-bond method can be summarized in a series of statements:

1. A covalent bond results from the pairing of unpaired electrons in neighboring atoms.
2. The spins of the paired electrons must be antiparallel (one up and one down).
3. To provide enough unpaired electrons in each atom for the maximum bond formation, electrons can be excited to fill empty orbitals during bond formation.
4. The shape of the molecule results from the directions in which the orbitals of the central atom point.

**Orbital Hybridization**

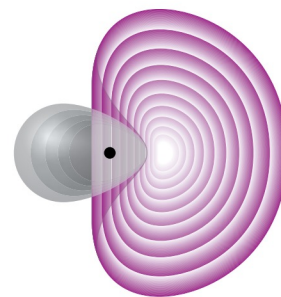
Solving the Schrödinger wave equation using the valence-bond method requires that the original atomic orbitals be combined into hybrid orbitals that better fit the known geometries. A good example is the ammonia molecule,  $\text{NH}_3$ .

Assuming the three unpaired 2p electrons on the central nitrogen atom are used, we see that statement 4 above tells us that the bonds to the hydrogen atoms should follow the axes of the bonding orbitals,  $2p_x$ ,  $2p_y$ , and  $2p_z$ . That is, the hydrogen atoms should be  $90^\circ$  apart. We now know from actual measurements that the bond angles in ammonia are  $107^\circ$ . To account for the substantial difference in theoretical versus actual bond angles for this and other covalent compounds, we invoke the modification known as *orbital hybridization*.

The orbital hybridization concept asserts that the wave functions of electrons in atomic orbitals of an atom (usually the central atom of a molecule) can mix together during bond formation to occupy hybrid atomic orbitals. According to this approach, electrons in these hybrid orbitals are still the property of the donor atom. If the wave functions of an s orbital and one or more p orbitals are combined, the possible hybrid orbitals produced are all similar to that shown in Figure 3.27. Such hybrid orbitals are given the symbols  $sp$ ,  $sp^2$ , and  $sp^3$  depending on whether the wave functions of one, two, or three p orbitals are “mixed in” with the s orbital wave function. These hybrid orbitals are oriented in a particular direction and should overlap more with the orbitals of another atom than do those of a spherical s orbital or of a two-lobed p orbital. A greater overlap means that the wave functions of the two atoms will mix better and form a stronger covalent bond.

The number of hybrid orbitals formed will equal the sum of the number of atomic orbitals that are involved in the mixing of wave functions. Like s and p orbitals, d orbitals can also be mixed in, although theoretical chemists now contend that d orbitals play a minimal role in covalent bonding. Nevertheless, for our simplistic bonding approach, it is often useful to propose d orbital involvement to account for the shapes of molecules where the central atom has more than four neighbors. The number of atomic orbitals used, the symbol for the hybrid orbital, and the geometry of the resulting molecule are all listed in Table 3.5.

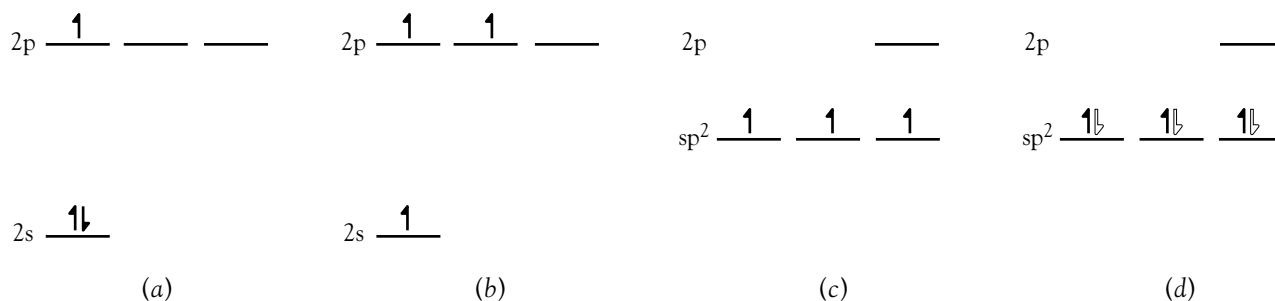
We can illustrate the concept of hybridization using boron trifluoride. Prior to compound formation, the boron atom has an electron configuration of  $[\text{He}]2s^22p^1$  (Figure 3.28a). Suppose that one of the 2s electrons moves to a 2p orbital (Figure 3.28b). The wave functions of the three orbitals, each



**FIGURE 3.27** The 90 percent probability surface of a hybrid orbital involving combinations of s and p orbitals. The black dot in the smaller lobe identifies the location of the nucleus.

**TABLE 3.5** Number of hybrid orbitals and type of hybridization for various molecular geometries

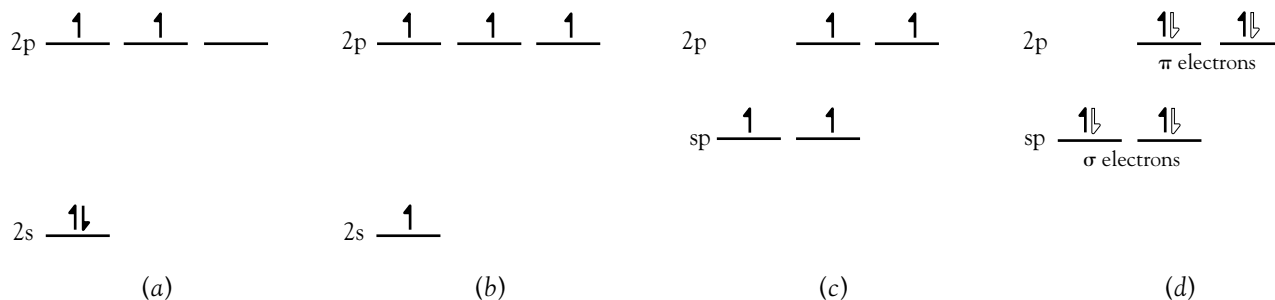
Orbitals			Type of hybridization	Number of hybrid orbitals	Resulting molecular geometry
s	p	d			
1	1	0	$sp$	2	Linear
1	2	0	$sp^2$	3	Trigonal planar
1	3	0	$sp^3$	4	Tetrahedral
1	3	1	$sp^3d$	5	Trigonal bipyramidal
1	3	2	$sp^3d^2$	6	Octahedral



**FIGURE 3.28** The concept of hybrid orbital formation applied to boron trifluoride. (a) The electron configuration of the free atom. (b) The shift of an electron from the 2s orbital to the 2p orbital. (c) The formation of three  $sp^2$  hybrid orbitals. (d) Pairing of boron electrons with three electrons (open half arrows) of the fluorine atoms.

containing a single electron, mix to provide three equivalent  $sp^2$  orbitals (Figure 3.28c). These orbitals, oriented at  $120^\circ$  to one another, overlap with the singly occupied 2p orbital on each fluorine atom to give three  $\sigma$  covalent bonds (Figure 3.28d). This explanation matches our experimental findings of equivalent boron-fluorine bonds, each forming  $120^\circ$  angles with the other two—the trigonal planar geometry.

Carbon dioxide provides an example of a molecule in which we assume that not all of the occupied orbitals are hybridized. We assume that the  $[\text{He}]2s^22p^2$  configuration of the carbon atom (Figure 3.29a) is altered to  $[\text{He}]2s^12p^3$  (Figure 3.29b). The s orbital and one of the p orbitals hybridize (Figure 3.29c). The resulting sp hybrid orbitals are  $180^\circ$  apart, and they overlap with one 2p orbital on each oxygen atom to provide a single  $\sigma$  bond and a linear structure. This leaves single electrons in the other two 2p orbitals of the carbon atom. Each p orbital overlaps side-to-side with a singly occupied 2p orbital on an oxygen atom to form a  $\pi$  bond with each of the two oxygen atoms (Figure 3.29d). Thus, the concept of hybridization can be used to explain the linear nature of the carbon dioxide molecule and the presence of two carbon-oxygen double bonds.



**FIGURE 3.29** The concept of hybrid orbital formation applied to carbon dioxide. (a) The electron configuration of the free carbon atom. (b) The shift of an electron from the 2s orbital to the 2p orbital. (c) The formation of two sp hybrid orbitals. (d) Pairing of the carbon electrons with four oxygen electrons (open half arrows).

### Limitation of the Hybridization Concept

To review, the formation of hybrid orbitals can be used successfully to account for a particular molecular shape. However, hybridization is simply a mathematical manipulation of wave functions, and we have no evidence that it actually happens. Furthermore, the hybridization concept is not a predictive tool: we can only use it when the molecular structure has actually been established.

## 3.6 Introduction to Molecular Orbitals

In Chapter 1, we saw that the quantum mechanical model of the atom provides the best means of understanding the properties and trends among the elements. For example, the underlying structure of the periodic table could be explained by means of the occupancy of the s, p, d, and f orbitals. The trends in such properties as ionization energy also become understandable using the probability model and such concepts as shielding.

Just as the properties of atoms can best be interpreted in terms of atomic orbitals, so the properties of covalent compounds can best be explained in terms of molecular orbitals. An electron in a molecular orbital is the property of the whole molecule, not of an individual atom. The construction of molecular orbital energy levels enables us to explain aspects of chemical bonding that are difficult to comprehend in terms of the simple Lewis structure representations that are taught in general chemistry.

### The Oxygen Molecule

Interestingly, it is one of the simplest molecules, dioxygen,  $O_2$ , which provides one of the greatest shortcomings of Lewis structures. In 1845, Michael Faraday showed that oxygen gas was the only common gas to be attracted into a magnetic field; that is, dioxygen is paramagnetic, so it must possess unpaired electrons (two, as we now know). Later, bond strength studies showed that the dioxygen molecule has a double bond. Thus, any acceptable electron-dot diagram should possess these two properties. In fact, we cannot devise a reasonable electron-dot diagram that will combine both attributes. We can draw a diagram with a double bond (Figure 3.30)—but that has no unpaired electrons. Alternatively, we can draw a diagram with two unpaired electrons (Figure 3.31)—but that has a single bond. However, the ground-state molecular orbital diagram for dioxygen, as we will see, corresponds correctly to a double bond and two unpaired electrons.



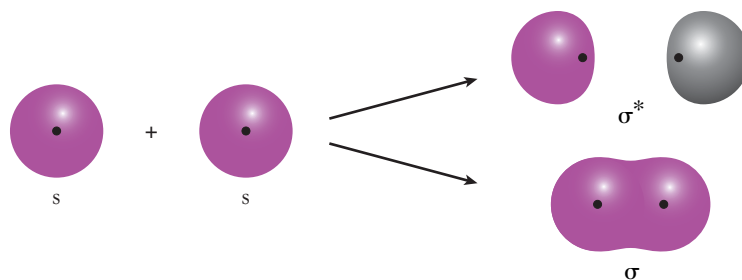
**FIGURE 3.30** Electron-dot diagram for dioxygen with a double bond.



**FIGURE 3.31** Electron-dot diagram for dioxygen with two unpaired electrons.

### Sigma Orbitals

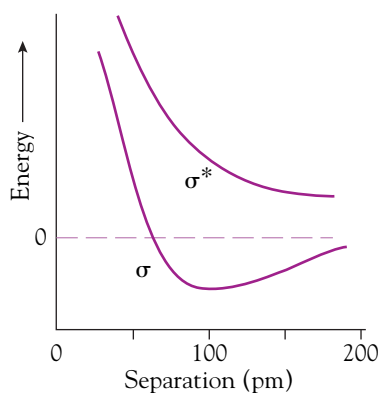
When two atoms approach each other, according to the molecular orbital concept, their atomic orbitals overlap. The electrons no longer belong to one atom but to the molecule as a whole. To represent this process, we can combine the two atomic wave functions to give two molecular orbitals. This realistic representation of the bonding in covalent compounds involves the linear combination of atomic orbitals and is thus called the *LCAO method*.



**FIGURE 3.32** The combination of two s atomic orbitals to form  $\sigma$  and  $\sigma^*$  molecular orbitals (computer-generated representations by Andrzej Okuniewski).

When the s orbitals mix, then the molecular orbitals formed are given the representation of  $\sigma$  and  $\sigma^*$  (pronounced “sigma” and “sigma star”). Figure 3.32 shows simplified electron density plots for the atomic orbitals and the resulting molecular orbitals.

For the  $\sigma$  orbital, the electron density between the two nuclei is increased relative to that between two independent atoms. There is an electrostatic attraction between the positive nuclei and this area of higher electron density, and the orbital is called a *bonding orbital*. Conversely, for the  $\sigma^*$  orbital, the electron density between the nuclei is decreased, and the partially exposed nuclei cause an electrostatic repulsion between the two atoms. Thus, the  $\sigma^*$  orbital is an *antibonding orbital*. Figure 3.33 illustrates the variation in the energies of these two molecular orbitals as the atoms are brought together.



**FIGURE 3.33** Molecular orbital energies as a function of atom separation for two hydrogen-like atoms.

When the atoms are an infinite distance apart, there is no attraction or repulsion, and so under those conditions they can be considered as having a zero energy state. As a result of electrostatic attraction between the electrons of one atom and the nuclear protons of the other, bringing together two atoms results in a decrease in energy. Figure 3.33 shows that the energy of the bonding orbital reaches a minimum at a certain internuclear separation. This point represents the normal bond length in the molecule. At that separation, the attractive force between the electron of one atom and the protons of the other atom is just balanced by the repulsions between the two nuclei. When the atoms are brought closer together, the repulsive force between the nuclei becomes greater, and the energy of the bonding orbital starts to rise.

For electrons in the antibonding orbital, there is no energy minimum. Electrostatic repulsion increases continuously as the partially exposed nuclei come closer and closer. Another way to picture the two types of molecular orbitals is to consider them as wave combinations. The overlap of electron wave functions of the constituent atoms in constructive interference corresponds to a bonding orbital. Destructive interference, however, corresponds to an antibonding orbital.

### Rules for Molecular Orbital Formation

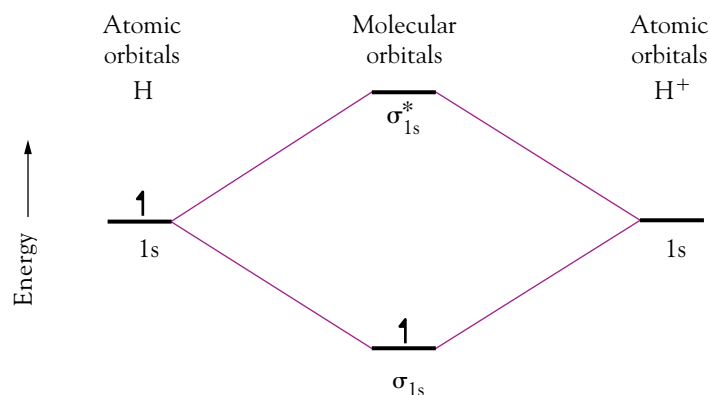
Several general statements can be made about molecular orbitals:

1. For orbitals to overlap, the signs on the overlapping lobes must be the same.
2. Whenever two atomic orbitals mix, two molecular orbitals are formed, one of which is bonding and the other antibonding. The bonding orbital is always lower in energy than the antibonding orbital.
3. For significant mixing to occur, the atomic orbitals must be of similar energy.
4. Each molecular orbital can hold a maximum of two electrons, one with spin  $+\frac{1}{2}$  the other  $-\frac{1}{2}$ .
5. The electron configuration of a molecule can be constructed by using the Aufbau principle by filling the lowest energy molecular orbitals in sequence.
6. When electrons are placed in different molecular orbitals of equal energy, the parallel arrangement (Hund's rule) will have the lowest energy.
7. The bond order in a diatomic molecule is defined as the number of bonding electron pairs minus the number of antibonding pairs.

In the next section, we see how the formation of molecular orbitals can be used to explain the properties of diatomic molecules of Period 1 and then, in the following section, look at the slightly more complex cases of Period 2 elements.

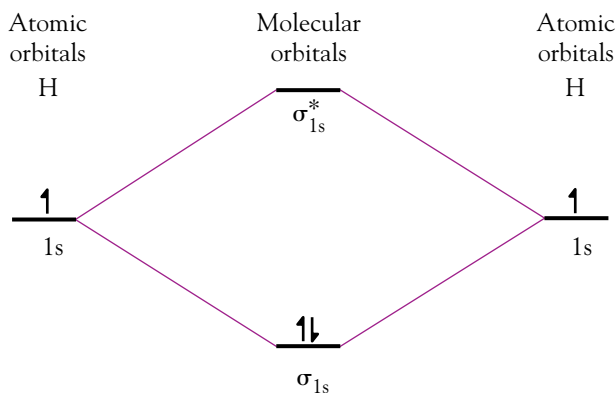
### 3.7 Molecular Orbitals for Period 1 Diatomic Molecules

The simplest diatomic species is that formed between a hydrogen atom and a hydrogen ion, the  $\text{H}_2^+$  molecular ion. Figure 3.34 is an energy-level diagram that depicts the occupancy of the atomic orbitals and the resulting molecular orbitals. Subscripts are used to indicate from which atomic orbitals the molecular orbitals are derived. Hence, the  $\sigma$  orbital arising from the mixing of two  $1s$  atomic orbitals is labeled as  $\sigma_{1s}$ . Notice that the energy of the electron is lower in the  $\sigma_{1s}$



**FIGURE 3.34** Molecular orbital diagram for the  $\text{H}_2^+$  molecular ion.

**FIGURE 3.35** Molecular orbital diagram for the  $\text{H}_2$  molecule.



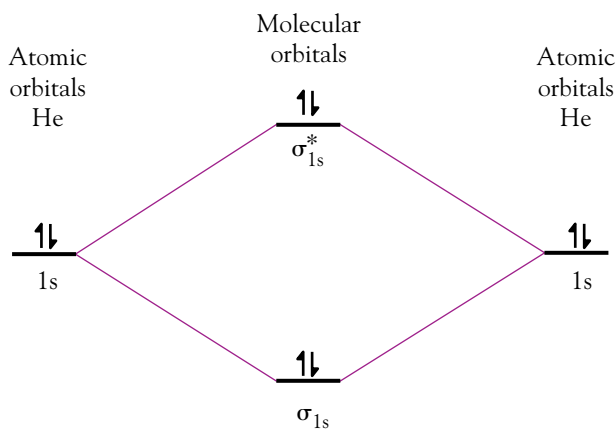
molecular orbital than it is in the  $1s$  atomic orbital. This is a result of the simultaneous attraction of the electron to two hydrogen nuclei. It is the net reduction in total electron energy that is the driving force in covalent bond formation.

The electron configuration of the dihydrogen cation is written as  $(\sigma_{1s})^1$ . A “normal” covalent bond consists of one pair of electrons. Because there is only one electron in the dihydrogen ion bonding orbital, the bond order is  $\frac{1}{2}$ . Experimental studies of this ion show that it has a bond length of 106 pm and a bond strength of  $255 \text{ kJ}\cdot\text{mol}^{-1}$ .

The energy-level diagram for the hydrogen molecule,  $\text{H}_2$ , is shown in Figure 3.35. With a second bonding electron, the bond order is 1. The greater the bond order, the greater the strength of the bond and the shorter the bond length. This correlation matches our experimental findings of a shorter bond length (74 pm) and a much stronger bond ( $436 \text{ kJ}\cdot\text{mol}^{-1}$ ) than that in the dihydrogen cation. The electron configuration is written as  $(\sigma_{1s})^2$ .

We can make up a molecular orbital diagram for the  $\text{He}_2$  molecule (Figure 3.36). Two electrons decrease in energy on formation of the molecular orbitals, while two electrons increase in energy by the same quantity. Thus, there is no net decrease in energy by bond formation. An alternative way of expressing the same point is that the net bond order will be zero. Thus, no covalent bonding would be expected to occur, and, indeed, helium is a monatomic gas.

**FIGURE 3.36** Molecular orbital diagram for the  $1s$  atomic orbitals of the (theoretical)  $\text{He}_2$  molecule.



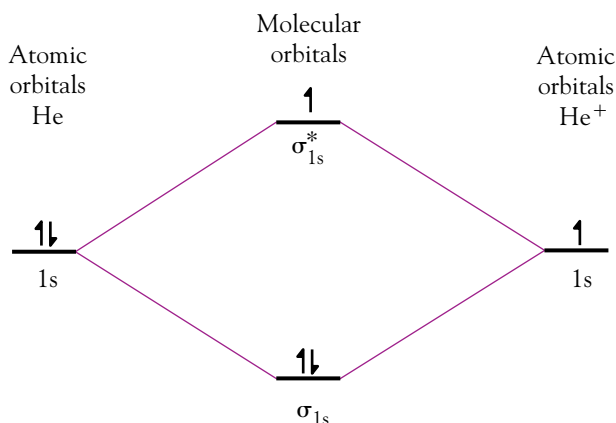
**WORKED EXAMPLE 3.3**

It is possible under extreme conditions to combine a helium atom and a helium ion to give the  $\text{He}_2^+$  molecular ion. Write the molecular electron configuration of the ion and deduce the bond order.

**Answer**

The helium atom will contribute two electrons to the molecular orbitals and the helium cation will contribute one electron.

Thus, two electrons will fill the  $\sigma$  orbital, with the third electron occupying the  $\sigma^*$  orbital.



The molecular ion has an electron configuration of  $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ .  
The bond order is  $(1 - \frac{1}{2})$ , or  $\frac{1}{2}$ . ■

### 3.8 Molecular Orbitals for Period 2 Diatomic Molecules

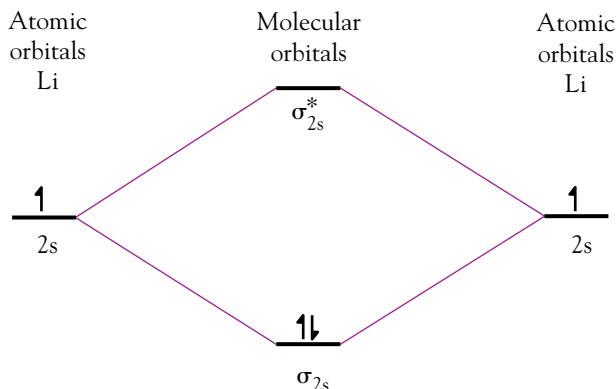
Whenever we start a new period, the inner (core) electrons become irrelevant to the bonding process. Hence, for the first two elements of Period 2, we need only construct a molecular orbital energy diagram corresponding to the 2s atomic orbitals. These outermost occupied orbitals, at the “edge” of the molecule, are often called the *frontier orbitals*, and they are always the crucial orbitals for bonding. Here we will focus on the highest occupied molecular orbitals (HOMOs), although for chemical reactions, the next levels, the lowest unoccupied molecular orbitals (LUMOs), are also important.

#### Molecular Orbital Diagrams for the Early Period 2 Elements

Lithium is the simplest of the Period 2 elements. In both solid and liquid phases, the bonding is metallic, a topic that we discuss in Chapter 4. In the gas phase, however, there is evidence for the existence of diatomic molecules. The two electrons from the 2s atomic orbitals occupy the  $\sigma_{2s}$  molecular orbital, thereby



**FIGURE 3.37** Molecular orbital diagram for the 2s atomic orbitals of the  $\text{Li}_2$  (gas-phase) molecule.



producing a bond order of 1 (Figure 3.37). Both the measured bond length and the bond energy are consistent with this value for the bond order. The occupancy of the frontier (valence) molecular orbitals is represented as  $(\sigma_{2s})^2$ .

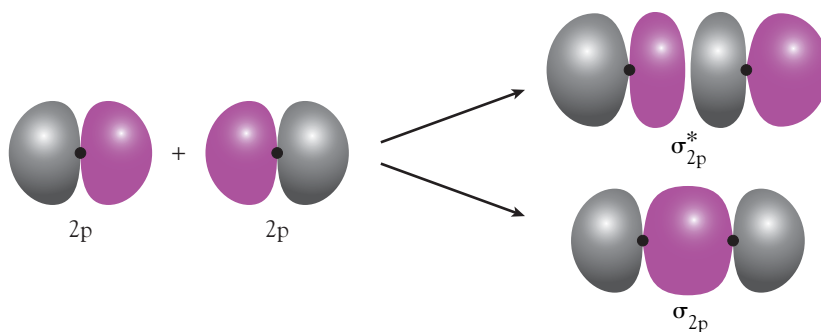
### Pi Orbitals

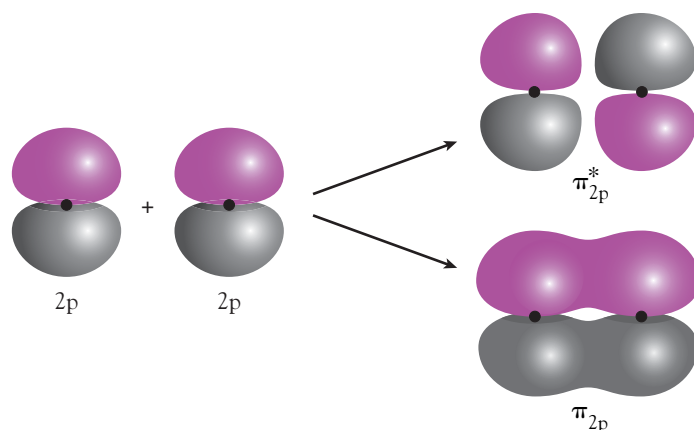
Before we consider the heavier Period 2 elements, we must examine the formation of molecular orbitals from 2p atomic orbitals. These orbitals can mix in two ways. First, they can mix end to end. When this orientation occurs, a pair of bonding and antibonding orbitals is formed and resembles those of the  $\sigma_{1s}$  orbitals. These orbitals are designated the  $\sigma_{2p}$  and  $\sigma_{2p}^*$  molecular orbitals (Figure 3.38). In fact, a  $\sigma$  bond is defined as one formed by atomic orbital overlap along the axis joining the two nuclear centers. As we mentioned earlier, orbitals can only overlap if the signs of the lobes are the same—in this case, we show positive to positive.

Alternatively, the 2p atomic orbitals can mix side to side. The bonding and antibonding molecular orbitals formed in this way are designated  $\pi$  orbitals (Figure 3.39). For  $\pi$  orbitals, the increased electron density in the bonding orbital is not between the two nuclei but above and below a plane containing the nuclei. Thus, in contrast to a  $\sigma$  bond, a  $\pi$  bond is formed by overlap of orbitals at right angles to the axis joining the two nuclear centers.

Because every atom has three 2p atomic orbitals, when two such atoms combine, there will be three bonding and three antibonding molecular orbitals produced in total from the 2p orbital set. If we assume the bonding direction to be along the  $z$ -axis, the orbitals formed in that direction will be  $\sigma_{2p}$  and  $\sigma_{2p}^*$ .

**FIGURE 3.38** The combination of two 2p atomic orbitals end-to-end to form  $\sigma_{2p}$  and  $\sigma_{2p}^*$  molecular orbitals (computer-generated representations by Andrzej Okuniewski).





**FIGURE 3.39** The combination of two 2p atomic orbitals side to side to form  $\pi_{2p}$  and  $\pi_{2p}^*$  molecular orbitals (computer-generated representations by Andrzej Okuniewski).

At right angles, the other two 2p atomic orbitals form two pairs of  $\pi_{2p}$  and  $\pi_{2p}^*$  molecular orbitals.

### Molecular Orbital Diagrams for the Later Period 2 Elements

It must be emphasized that bonding models are developed to explain experimental observations. We observe that the shorter the bond length and the higher the bond energy, the stronger the bond. For the Period 2 elements, bonds with energies of 200 to 300  $\text{kJ}\cdot\text{mol}^{-1}$  are typical for single bonds, those with energies of 500 to 600  $\text{kJ}\cdot\text{mol}^{-1}$  are defined as double bonds, and those with energies of 900–1000  $\text{kJ}\cdot\text{mol}^{-1}$  are defined as triple bonds. Thus, for dinitrogen, dioxygen, and difluorine, the molecular orbital model must conform to the bond orders deduced from the measured bond information shown in Table 3.6.

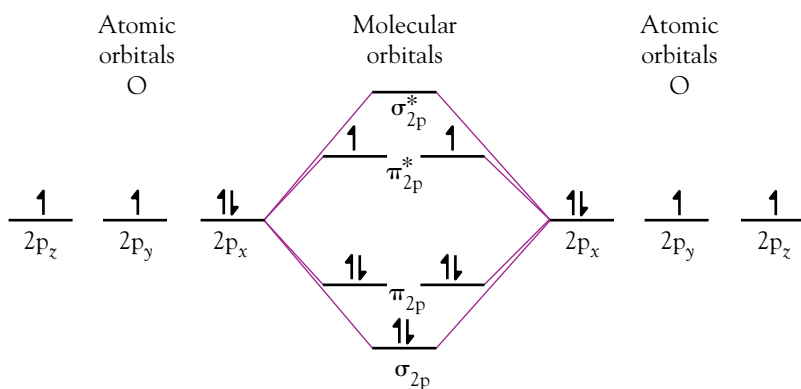
For all three of these diatomic molecules,  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{F}_2$  (and those of  $\text{B}_2$  and  $\text{C}_2$ ), the bonding and antibonding orbitals formed from both 1s and 2s atomic orbitals are filled, and so there will be no net bonding contribution from these orbitals. Hence, we need only consider the filling of the molecular orbitals derived from the 2p atomic orbitals.

For the Period 2 elements beyond dinitrogen, the  $\sigma_{2p}$  orbital is the lowest in energy, followed in order of increasing energy by  $\pi_{2p}$ ,  $\pi_{2p}^*$ , and  $\sigma_{2p}^*$ . When the molecular orbital diagram is completed for the dioxygen molecule (Figure 3.40), we see that, according to Hund's rule, there are indeed two unpaired electrons; this diagram is consistent with experimental measurements. Furthermore, the bond order of  $[(3) - (2 \times \frac{1}{2})] = 2$  net bonds is consistent with bond length and

**TABLE 3.6** Bond order information for the heavier Period 2 elements

Molecule	Bond length (pm)	Bond energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )	Assigned bond order
$\text{N}_2$	110	942	3
$\text{O}_2$	121	494	2
$\text{F}_2$	142	155	1

**FIGURE 3.40** Molecular orbital diagram for the 2p atomic orbitals of the  $O_2$  molecule.



bond energy measurements. Thus, the molecular orbital model explains our experimental observations perfectly.

In difluorine, two more electrons are placed in the antibonding orbital (Figure 3.41). Hence, the bond order of 1 represents the net bonding arising from three filled bonding orbitals and two filled antibonding orbitals. The valence electron configuration is represented as  $(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$ .

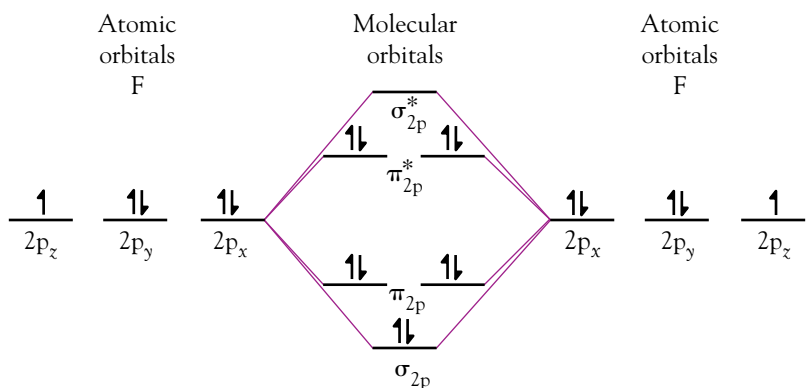
Neon is the last (heaviest) element in Period 2. If a molecular orbital diagram is constructed for the theoretical  $Ne_2$  molecule, all the bonding and antibonding orbitals derived from the 2p atomic orbitals are filled; as a result, the net bond order is 0. This prediction is consistent with the observation that neon exists as a monatomic gas.

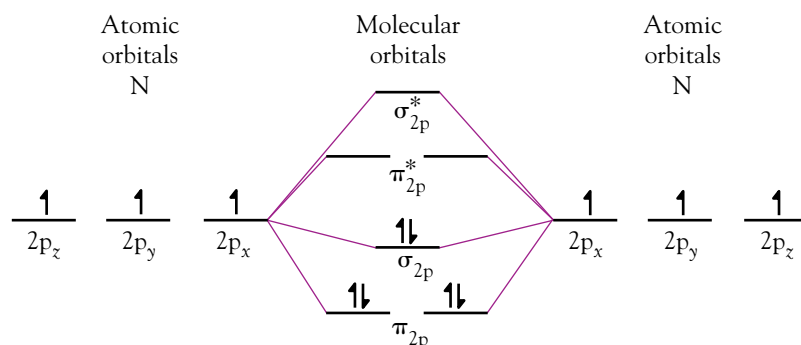
### Molecular Orbital Diagrams for the Middle Period 2 Elements

Until now, we have avoided discussion of the elements lying in the middle part of Period 2, particularly dinitrogen. The reason concerns the relative energies of the 2s and 2p orbitals. For fluorine, with a high  $Z_{\text{eff}}$ , the 2s atomic energy level is about  $2.5 \text{ MJ}\cdot\text{mol}^{-1}$  lower in energy than that of the 2p level. This difference results from the penetration of the s orbital close to the nucleus (as discussed in Chapter 2, Section 2.5); hence, an electron in an s orbital is more strongly influenced by the increasing nuclear charge.

However, at the beginning of the period, the levels differ in energy by only about  $0.2 \text{ MJ}\cdot\text{mol}^{-1}$ . In these circumstances, the wave functions for the 2s and

**FIGURE 3.41** Molecular orbital diagram for the 2p atomic orbitals of the  $F_2$  molecule.





**FIGURE 3.42** Molecular orbital diagram for the 2p atomic orbitals of the  $\text{N}_2$  molecule.

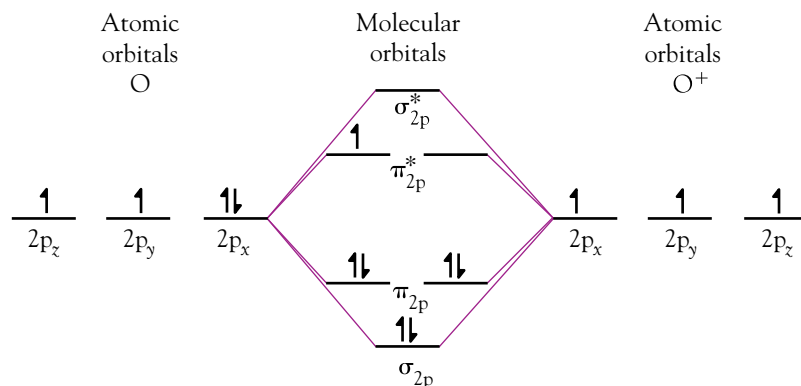
2p orbitals become mixed. One result of the mixing is an increase in energy of the  $\sigma_{2p}$  molecular orbital to the point where it has greater energy than the  $\pi_{2p}$  orbital. This ordering of orbitals applies to dinitrogen and the preceding elements in Period 2, the  $\sigma$ - $\pi$  crossover occurring between dinitrogen and dioxygen. When we use this modified molecular orbital diagram to fill the molecular orbitals from the 2p atomic orbitals for the dinitrogen molecule, a bonding order of 3 results (Figure 3.42). This calculation corresponds with the strong bond known to exist in the molecule. The valence electron configuration of dinitrogen is  $(\pi_{2p})^4(\sigma_{2p})^2$ .

### WORKED EXAMPLE 3.4

Determine the bond order and number of unpaired electrons for the  $\text{O}_2^+$  ion. Is the bond weaker or stronger than that in the dioxygen molecule?

#### Answer

For the oxygen atom, there are four 2p electrons and for the oxygen cation there are three 2p electrons. These will fill the molecular orbital diagram as shown.



This process gives a bond order of  $[(3) - (\frac{1}{2})] = 2\frac{1}{2}$ .

There is one unpaired electron.

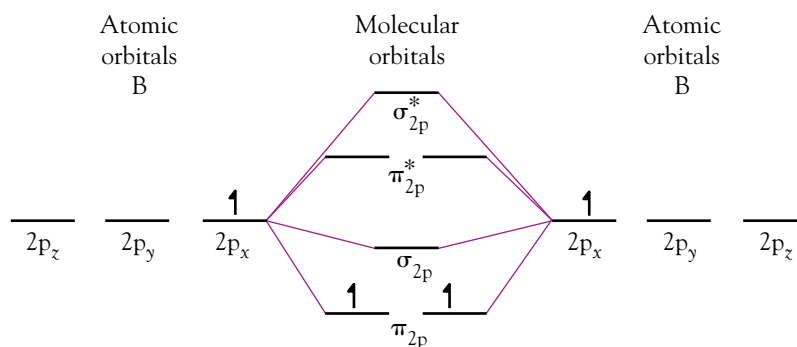
The covalent bond will be stronger for the  $\text{O}_2^+$  cation than the neutral  $\text{O}_2$  molecule. ■

**WORKED EXAMPLE 3.5**

When boron is heated strongly, it vaporizes to give diatomic molecules,  $B_2$ . These molecules are paramagnetic. Show that such an observation is consistent with the molecular orbital energy level diagram of Figure 3.42. How many unpaired electrons will this molecule possess? What is the bond order?

**Answer**

For the boron atom, there is one 2p electron. These will fill the molecular orbital diagram as shown.



There are two unpaired electrons.

This process gives a bond order of  $[2(\frac{1}{2})] = 1$ .

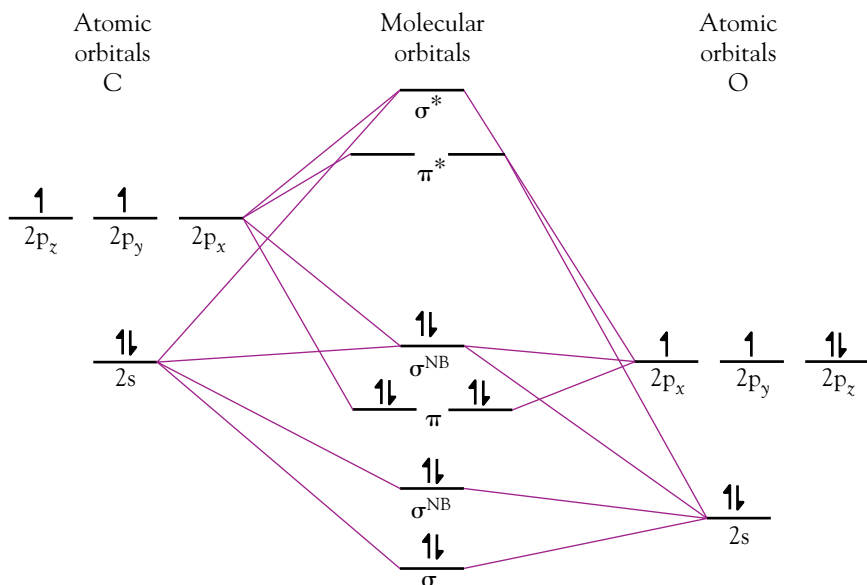
(This example supports the concept that, in the energy levels in the earlier Period 2 elements, the  $\sigma_{2p}$  orbital is higher in energy than the  $\pi_{2p}$  orbitals. If the orbitals followed the order in Figures 3.41 and 3.42, then the  $B_2$  molecule would be diamagnetic, with a pair of electrons in the  $\sigma_{2p}$  orbital.) ■

### 3.9 Molecular Orbitals for Heteronuclear Diatomic Molecules

When we combine atomic orbitals from different elements, we have to consider that the atomic orbitals will have different energies. For elements from the same period, we find that the higher the atomic number, the higher the  $Z_{\text{eff}}$  and hence the lower the orbital energies.

#### Molecular Orbital Diagram for Carbon Monoxide

We can use molecular orbital energy levels to visualize the bonding of carbon monoxide. A simplified diagram of the molecular orbitals derived from the 2s and 2p atomic orbitals is shown in Figure 3.43. The oxygen atomic orbitals are lower in energy than those of carbon as a result of the greater  $Z_{\text{eff}}$ , but they are close enough in energy that we can construct a molecular orbital diagram similar to that of the homonuclear diatomic molecules.



**FIGURE 3.43** Simplified molecular orbital diagram for the 2s and 2p atomic orbitals of the CO molecule.

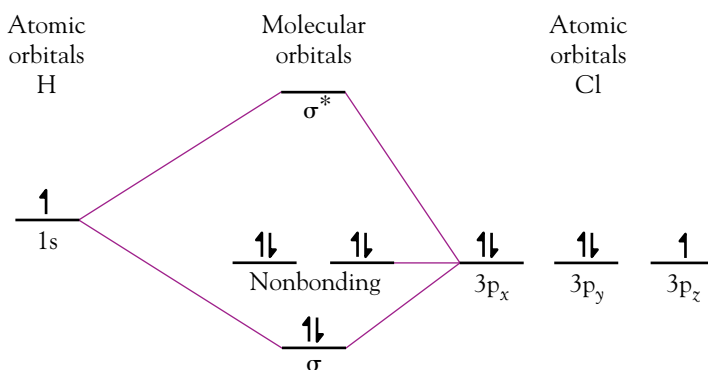
A major difference between homonuclear and heteronuclear diatomic molecules is that the molecular orbitals derived primarily from the 2s atomic orbitals of one element overlap significantly in energy with those derived from the 2p atomic orbitals of the other element. Thus, we must consider molecular orbitals derived from both these atomic orbitals in our diagram. Furthermore, because of the asymmetry of the orbital energies, the bonding molecular orbitals are derived mostly from the lower energy oxygen atomic orbitals, whereas the antibonding molecular orbitals are derived mostly from the higher energy carbon atomic orbitals. Finally, there are two molecular orbitals whose energies are between those of the contributing atomic orbitals. These orbitals,  $\sigma^{\text{NB}}$ , are defined as *nonbonding molecular orbitals*; that is, they do not contribute significantly to the bonding.

To determine the bond order of carbon monoxide, the number of antibonding pairs (0) is subtracted from the number of bonding pairs (3), a calculation leading to the prediction of a triple bond. The very high bond energy of  $1072 \text{ kJ}\cdot\text{mol}^{-1}$  supports this prediction. However, the molecular orbital diagram is much more meaningful because it provides us with a grasp of electron energies. The molecular orbital diagram also indicates that the triple bond is not made up of three equivalent bonds, as the electron-dot diagram suggests, but of a combination of one  $\sigma$  and two  $\pi$  bonds.

### Molecular Orbital Diagram for Hydrogen Chloride

The molecular orbital approach can be applied to diatomic molecules containing atoms of different periods. However, it is then necessary to identify the orbitals of similar energies on the two atoms, a task well beyond the scope of this descriptive inorganic chemistry course. It is instructive, however, to do one example and we have chosen the hydrogen chloride molecule (Figure 3.44).

**FIGURE 3.44** Molecular orbital diagram for the 1s atomic orbital of hydrogen and the 3p atomic orbitals of chlorine in the HCl molecule.



Calculations show that the 3p orbitals of chlorine have a slightly lower energy than that of the 1s orbital of hydrogen. The 1s orbital can only form a  $\sigma$  bond. Hence, we conclude that a  $\sigma$  bonding and  $\sigma$  antibonding pair of orbitals will be formed between the 1s(H) and the 3p(Cl) orbital that is aligned along the bonding axis (traditionally chosen as the  $p_z$  orbital). With each atom contributing one electron, the bonding molecular orbital will be filled. This configuration yields a single bond. The two other 3p orbitals are oriented in such a way that no net overlap (hence, no mixing) with the 1s orbital of hydrogen can occur. As a result, the electron pairs in these orbitals are considered to be nonbonding. That is, they have the same energy in the molecule as they did in the independent chlorine atom.

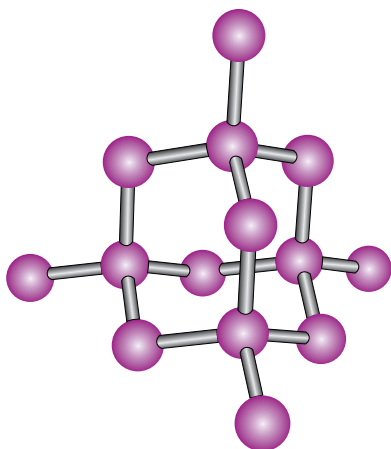
Molecular orbital diagrams can be constructed to develop bonding schemes for molecules containing more than two atoms. However, the energy diagrams and the orbital shapes become more and more complex. Thus these can be studied in a theoretical, or a more advanced, inorganic chemistry course.

### 3.10 Network Covalent Substances

Until now, we have been discussing elements and compounds that exist as small, individual molecules. However, there are some structures, such as diamond or quartz, in which all the atoms are held together by covalent bonds. Such linking by covalent bonds throughout a substance is known as *network covalent bonding*.

#### Network Covalent Crystals

In network covalent crystals, the whole crystal is one giant molecule. Diamond is a form of carbon in which each and every carbon atom is bonded in a tetrahedral arrangement to all its neighbors (Figure 3.45). The second common example of network covalent bonding is silica (mineral name, quartz), the common crystalline form of silicon dioxide,  $\text{SiO}_2$ . In this compound, each silicon atom is surrounded by a tetrahedron of oxygen atoms, and each oxygen atom is bonded to two silicon atoms.



**FIGURE 3.45** Arrangement of carbon atoms in diamond.

To melt a substance that contains network covalent bonds, the covalent bonds must be broken. As covalent bonds have energies in the range of hundreds of kilojoules per mole, very high temperatures are needed to accomplish this cleavage. So it is not surprising that diamond sublimates at about  $4000^{\circ}\text{C}$ , and silicon dioxide melts at  $2000^{\circ}\text{C}$ . For the same reason, network covalent substances are extremely hard: diamond is the hardest naturally occurring substance known. Furthermore, such substances are insoluble in all solvents.

### Amorphous Covalent Solids

Amorphous solids are materials in which the atoms are not arranged in a systematic repeating manner. One of the most interesting examples is *amorphous silicon* (a-Si). Amorphous silicon is 40 times more efficient at absorbing solar radiation than crystalline silicon; thus, a-Si is far superior for solar panels. In addition, a-Si can be deposited at temperatures as low as  $75^{\circ}\text{C}$ , allowing it to be deposited on organic polymer substrates.

*Crystalline silicon* (c-Si) also has the diamond lattice structure, with each silicon atom covalently bonded to four silicon atoms in a tetrahedral arrangement. However, in a-Si, the atoms are arranged more randomly and are often only bonded to three other silicon atoms, leaving what are referred to as *dangling bonds* (bond vacancies) at the fourth bonding site. It is the randomness of the structure, together with the dangling bonds, that gives a-Si its unique properties. On its own, a-Si is too insulating for use in electronic devices. The conductivity of the amorphous solid can be increased by condensing the silicon in the presence of small amounts of hydrogen. The hydrogen reacts with the dangling bonds of the silicon, forming silicon-hydrogen bonds and modifying the electrical conductivity of the amorphous silicon.

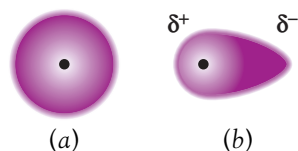
An even better electron mobility than a-Si is shown by *nanocrystalline silicon* (nc-Si). Nanocrystalline silicon has nanometer-size crystallites embedded



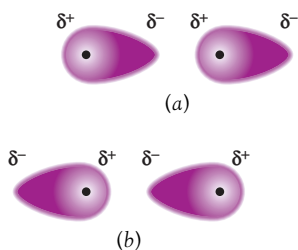
within an a-Si matrix. Another advantage of nc-Si over a-Si is that nc-Si has a higher stability. Thus, nc-Si is favored for the manufacture of thin film solar cells.

### 3.11 Intermolecular Forces

Network covalent substances are rare. Almost all covalently bonded substances consist of independent molecular units. If there were only intramolecular forces (the covalent bonds), there would be no attractions between neighboring molecules, and, consequently, all covalently bonded substances would be gases at all temperatures. We know this is not the case. Thus, there must be forces between molecules, or intermolecular forces. Indeed, there is one intermolecular force that operates between all molecules: induced dipole attractions, also called dispersion forces or London forces (after the scientist Fritz London, not the British capital). The other types of forces—dipole-dipole, ion-dipole, and hydrogen bonding—only occur in specific circumstances, which we discuss later in this chapter.



**FIGURE 3.46** (a) Average electron density for an atom. (b) Instantaneous electron density producing a temporary dipole.



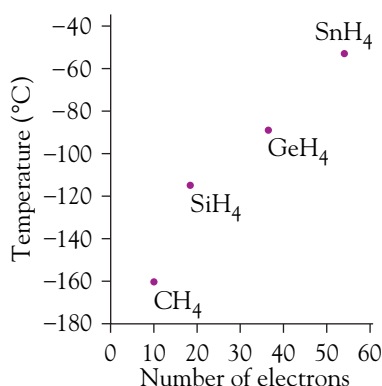
**FIGURE 3.47** (a) The instantaneous attraction between neighboring molecules. (b) The reversal of polarity in the next instant.

#### Dispersion (London) Forces

In the orbital representation of atoms and molecules, the probability distribution of the electrons (electron density) is a time-averaged value. It is the oscillations from this time-averaged value that lead to the attractions between neighboring molecules. The noble gas atoms provide the simplest example. On average, the electron density should be spherically symmetrical around the atomic nucleus (Figure 3.46a). However, most of the time, the electrons are asymmetrically distributed; consequently, one part of the atom has a higher electron density and another part has a lower electron density (Figure 3.46b). The end at which the nucleus is partially exposed will be slightly more positive ( $\delta^+$ ), and the end to which the electron density has shifted will be partially negative ( $\delta^-$ ). This separation of charge is called a *temporary dipole*.

The partially exposed nucleus of one atom will attract electron density from a neighboring atom (Figure 3.47a), and it is this induced dipole between molecules that represents the dispersion force between atoms and molecules. However, an instant later, the electron density will have shifted, and the partial charges involved in the attraction will be reversed (Figure 3.47b).

The strength of the *dispersion force* depends on a number of factors, and their discussion is more appropriate to an advanced physical chemistry course. However, a qualitative and predictive approach is to consider that the dispersion force relates to the number of electrons in the atom or molecule. On this basis, it is the number of electrons that determines how easily the electron density can be polarized, and the greater the polarization, the stronger the dispersion forces. In turn, the stronger the intermolecular forces, the higher will be both the melting and the boiling points. This relationship is illustrated by the graph in Figure 3.48, which shows the dependence of the boiling points of the Group 14 hydrides on the number of electrons in the molecule.



**FIGURE 3.48** Dependence of the boiling points of the Group 14 hydrides on the number of electrons.

Molecular shape is a secondary factor affecting the strength of dispersion forces. A compact molecule will allow only a small separation of charge, whereas an elongated molecule can allow a much greater charge gradient. A good comparison is provided by sulfur hexafluoride,  $\text{SF}_6$ , and decane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ . The former has 70 electrons and a melting point of  $-51^\circ\text{C}$ , whereas the latter has 72 electrons and a melting point of  $-30^\circ\text{C}$ . Hence, the dispersion forces are greater between the long decane molecules than between the near-spherical sulfur hexafluoride molecules.

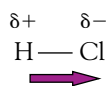
### The Pauling Electronegativity Scale

A very simple experiment shows the existence of two types of molecules. In this experiment, a positively charged rod is held near a stream of liquid. Many liquids (for example, carbon tetrachloride) are unaffected by the charged rod, whereas others (for example, water) are attracted by the rod. If the positively charged rod is replaced by a negatively charged rod, those liquids unaffected by the positive charge are also unaffected by the negative charge, whereas those attracted by the positive charge are also attracted by the negative charge. To explain these observations, we infer that the deflected liquids consist of molecules in which there is a permanent charge separation (a permanent dipole). Thus, the partially negative ends of the molecules are attracted toward the positively charged rod, and the partially positive ends are attracted toward the negatively charged rod. But why should some molecules have a permanent charge separation? For an explanation, we need to look at another concept of Linus Pauling's—*electronegativity*.

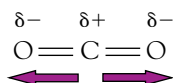
Pauling defined electronegativity as the power of an atom in a molecule to attract shared electrons to itself. This relative attraction for bonding electron pairs really reflects the comparative  $Z_{\text{eff}}$  of the two atoms on the shared electrons. Thus, the values increase from left to right across a period and decrease down a group in the same way as ionization energies do. Electronegativity is a relative concept, not a measurable function. The Pauling electronegativity scale is an arbitrary one, with the value for fluorine defined as 4.0. Some useful electronegativity values are shown in Figure 3.49.

<table border="1"> <tr> <td colspan="7">H 2.2</td></tr> </table>							H 2.2						
H 2.2													
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.4	F 4.0							
			Si 1.9	P 2.2	S 2.6	Cl 3.2							
						Br 3.0							
						I 2.7							

**FIGURE 3.49** Pauling's electronegativity values of various main group elements.



**FIGURE 3.50** Permanent dipole of the hydrogen chloride molecule.



**FIGURE 3.51** Because it has opposing bond dipoles, the carbon dioxide molecule is nonpolar.

Thus, in a molecule such as hydrogen chloride, the bonding electrons will not be shared equally between the two atoms. Instead, the higher  $Z_{\text{eff}}$  of chlorine will cause the bonding pair to be more closely associated with the chlorine atom than with the hydrogen atom. As a result, there will be a permanent dipole in the molecule. This dipole is depicted in Figure 3.50, using the  $\delta$  sign to indicate a partial permanent charge and an arrow to indicate the dipole direction.

Individual bond dipoles can act to “cancel” each other. A simple example is provided by carbon dioxide, where the bond dipoles are acting in opposite directions. Hence, the molecule does not possess a net dipole; in other words, the molecule is nonpolar (Figure 3.51).

### The Allred-Rochow Electronegativity Scale

Although Pauling’s scale is widely used, it does have the disadvantage of being very qualitative since Pauling adjusted the values to fit a nice linear sequence. A more quantitative scale, especially useful for our discussion here, is that devised by Allred and Rochow, based on effective nuclear charge values. Inorganic chemists frequently use the Allred-Rochow scale. The values for the main group elements are shown in Figure 3.52.

## The Origins of the Pauling Electronegativity Concept

Electronegativity is probably the most widely used concept in chemistry, yet its roots seem to have become forgotten. As a result, Pauling electronegativity values are sometimes imbued with a greater significance than was originally intended.

In his book *The Nature of the Chemical Bond*, Pauling made it clear that his development of the concept of electronegativity in the 1930s arose from studies of bond energies, for which he used the symbol  $\Delta$ . He considered two elements, A and B, and argued that, for a purely covalent bond, the AB bond energy should be the geometrical mean of the AA and BB bond energies.

However, he found this was often not the case. He defined this difference as  $\Delta'$ , where

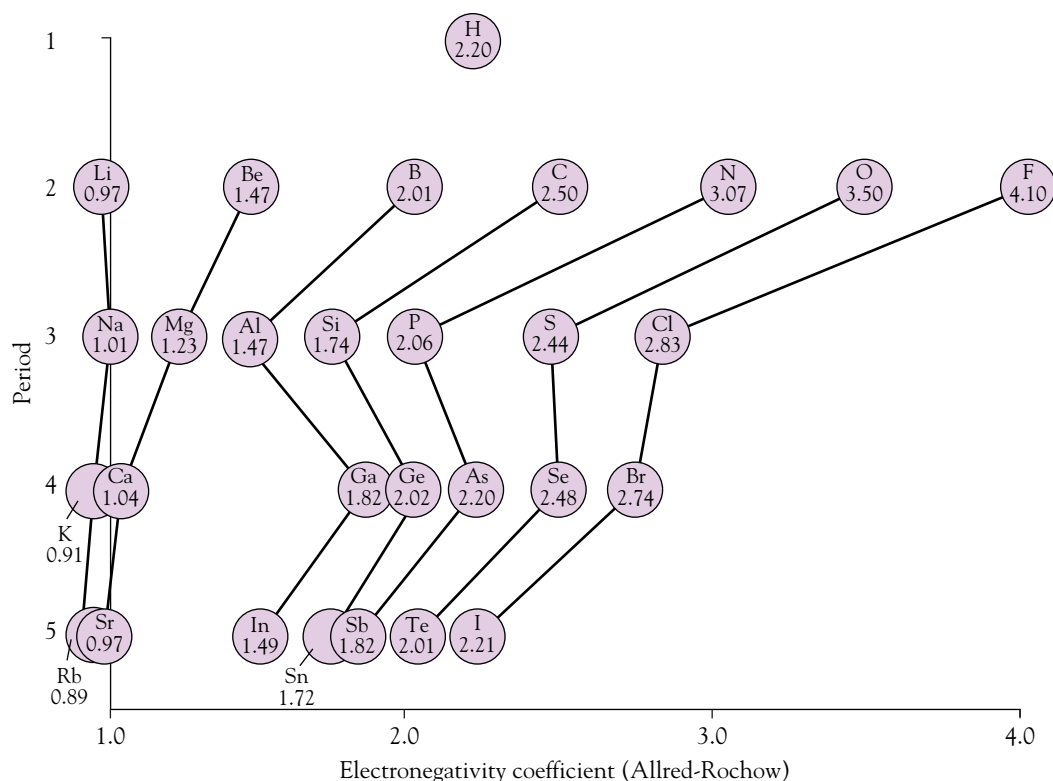
$$\Delta' = D(A - B) - \{D(A - A)(B - B)\}^{\frac{1}{2}}$$

For example, the Cl—Cl bond has an energy of  $242 \text{ kJ}\cdot\text{mol}^{-1}$  and that of the H—H bond is  $432 \text{ kJ}\cdot\text{mol}^{-1}$ . The geometrical mean is  $323 \text{ kJ}\cdot\text{mol}^{-1}$ , but the experimental value for the H—Cl bond energy is  $428 \text{ kJ}\cdot\text{mol}^{-1}$ . Thus,  $\Delta'(\text{H—Cl})$  is  $105 \text{ kJ}\cdot\text{mol}^{-1}$ . Pauling ascribed this

difference to an ionic contribution to the bonding, making the heterogeneous bond stronger than the mean of the two homogeneous bonds.

Pauling produced a table of data for combinations of 14 main group elements that expressed the “excess ionic energy” of heteronuclear covalent bonds; for example, that of C—H was 0.4, while that of H—F was 1.5. To provide a better fit, he adjusted some of the numbers; for example, he increased that of the H—F bond to 1.9. Taking the electronegativity of hydrogen as zero, Pauling assigned the balance of the ionic energy difference to the other element. Then he added 2.05 to all values to produce a simple numerical sequence across the second period elements.

Since Pauling published his first work on a scale of electronegativity, others have derived tables using alternative parameters. In particular, the Allred-Rochow electronegativity scale, widely used by inorganic chemists, employs the concept of effective nuclear charge to derive more quantitative electronegativity values.



**FIGURE 3.52** Allred-Rochow electronegativity values for some main group elements.

### Dipole-Dipole Forces

A permanent dipole results in an enhancement of the intermolecular forces. For example, carbon monoxide has higher melting and boiling points ( $-205^{\circ}\text{C}$  and  $-191^{\circ}\text{C}$ , respectively) than does dinitrogen ( $-210^{\circ}\text{C}$  and  $-196^{\circ}\text{C}$ ), even though the two compounds are isoelectronic.

It is important to realize that *dipole-dipole attractions* are often a secondary effect in addition to the induced dipole effect. This point is illustrated by comparing hydrogen chloride with hydrogen bromide. If the dipole-dipole effect were the more important, then the bigger electronegativity difference between hydrogen and chlorine atoms than between the atoms in hydrogen bromide (Table 3.7) would lead us to expect that the boiling point of hydrogen

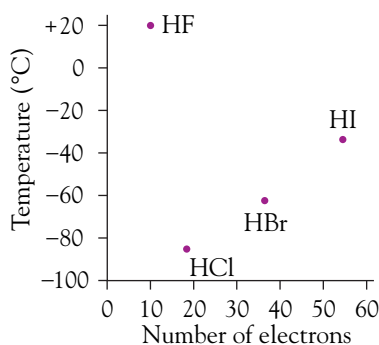
**TABLE 3.7** A comparison of hydrogen chloride and hydrogen bromide

	Hydrogen chloride	Hydrogen bromide
Boiling point ( $^{\circ}\text{C}$ )	-85	-67
H—X electronegativity difference (Allred-Rochow)	0.63	0.54
Number of electrons	18	36

chloride would be higher than that of hydrogen bromide. However, the converse is true, with hydrogen bromide having the higher boiling point. Therefore, induced dipole (dispersion) forces, which will be higher for the hydrogen bromide with its greater number of electrons, must be the predominant factor. In fact, complex calculations show that dispersion forces account for 83 percent of the attraction between neighboring hydrogen chloride molecules and 96 percent of the attraction between neighboring hydrogen bromide molecules.

### Hydrogen Bonding

If we look at the trend in boiling points of the Group 17 hydrides (Figure 3.53), we see that hydrogen fluoride has an anomalously high value. Similar plots for the Groups 15 and 16 hydrides show that the boiling points of ammonia and water also are anomalous. The elements involved have high electronegativities; thus, it is argued that the much stronger intermolecular forces are a result of exceptionally strong dipole-dipole forces. These forces are given the special name of *hydrogen bonds*. In chemistry, the hydrogen bonding of the water molecule is particularly important, as we will see in Chapter 10.



**FIGURE 3.53** Boiling points of the Group 17 hydrides.

Hydrogen bonding, then, is by far the strongest intermolecular force; indeed, it can represent 5 to 20 percent of the strength of a covalent bond. The strength of the hydrogen bond between molecules also depends on the identity of the non-hydrogen element. Thus, hydrogen bond strength decreases in the order  $\text{H}-\text{F} > \text{H}-\text{O} > \text{H}-\text{N}$ , and this order parallels the decrease in electronegativity differences. However, this factor cannot be the whole answer, because the  $\text{H}-\text{Cl}$  bond is only slightly less polar than the  $\text{H}-\text{N}$  bond (using Allred-Rochow values), yet hydrogen chloride molecules do not exhibit very strong intermolecular attractions.

Because the distances between two molecules sharing a hydrogen bond are significantly less than the sum of the van der Waals radii, it is contended that electron density is shared across a hydrogen bond. In this approach, a hydrogen bond is less of an intermolecular force and more of a weak covalent bond.

## 3.12 Molecular Symmetry

In synthesis of inorganic compounds (such as in a lab component of this course), we need to deduce the structure, the atomic arrangement, of the product molecule. One of the simplest means is through the study of the vibrational spectra of the compound, the topic of the next section. However, in order to interpret the spectra, it is first necessary to understand the basic principles of symmetry, the topic of this section.

Symmetry permeates the natural world: Flower petals are arranged symmetrically. Most creatures, like ourselves, have bilateral symmetry; that is, one

side of us is almost exactly the mirror reflection of the other. Rotational symmetry, such as that found in the letters *S* and *Z*, is also part of our everyday experience. The chemical world is based on symmetrical principles; in fact, the symmetry of a molecule determines some of the properties of that molecule. In our day-to-day lives, we use qualitative judgments on whether something “looks symmetrical,” but in science we have a set of mathematical rules to define precisely the symmetry of an object.

## Symmetry Operations

Molecular symmetry is deduced from a set of *symmetry operations*. A symmetry operation is a procedure performed on a molecule that leaves it in a conformation indistinguishable from, and superimposable on, the original conformation. A symmetry operation is performed with respect to a *symmetry element*: a point, an axis, or a plane. There are five symmetry operations:

1. Identity
2. Proper rotation: rotation about an  $n$ -fold axis of symmetry
3. Reflection through a plane of symmetry
4. Inversion through a center of symmetry
5. Improper rotation: rotation about an axis followed by a reflection (real or imagined) perpendicular to that axis

## Identity

The identity operator,  $E$ , leaves the molecule unchanged. Thus, all molecules possess  $E$ . This may seem a senseless activity, but the symmetry of molecules is linked to the mathematics of group theory. Group theory requires the existence of the identity operator.

## Proper Rotation

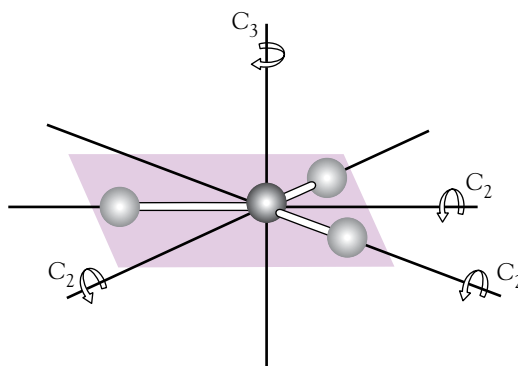
The rotation operation, symbol  $C_n^x$ , involves rotating the molecule by  $360/n$  degrees about an axis, symbol  $C_n$ , through the molecule. The value of  $n$  represents the number of times the molecule can be rotated during a complete  $360^\circ$  rotation while matching the original conformation after each rotation.

For example, rotating the planar boron trifluoride molecule about an axis (line) perpendicular to the plane and passing through the boron atom results in a conformation identical to the original position at angles of  $120^\circ$ ,  $240^\circ$ , and  $360^\circ$ . In this case,  $n$  has a value of 3: three rotations are required to return the molecule to its original position. Alternatively, we can define  $n$  as  $360^\circ$  divided by the first angle at which matching occurs, in this case

$$n = \frac{360^\circ}{120^\circ} = 3$$

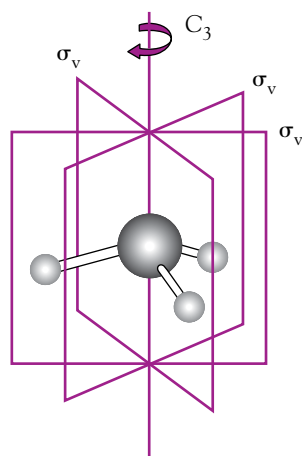
The axis about which the three operations of rotation were performed is called a  $C_3$  (threefold) rotation axis. The three individual rotations are designated as  $C_3^1$ ,  $C_3^2$ , and  $C_3^3$ , respectively.

**FIGURE 3.54** The rotation axes of the boron trifluoride molecule. [Adapted from C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry* (London: Prentice Hall, 2004).]



In addition, if we look along each B—F bond axis, there is a replication of the molecule following a  $180^\circ$  rotation about a line perpendicular to the  $C_3$ -axis. That is, the molecule also possesses three  $C_2$  (twofold) axes. The rotation axes of boron trifluoride are shown in Figure 3.54.

For molecules with more than one axis of symmetry, the axis with the highest value of  $n$  is called the *principal axis*, and that axis is said to be the axis of *highest molecular symmetry*. For linear molecules, a rotation through any angle about the molecular axis will match the original position. The presence of infinitely many rotational operations is indicated by the symbol  $C_\infty$ .



**FIGURE 3.55** The vertical mirror planes of the boron trifluoride molecule. The horizontal mirror plane is at right angles to the  $C_3$ -axis, bisecting all of the atoms. [Adapted from C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry* (London: Prentice Hall, 2004).]

### Reflection through a Plane of Symmetry (Mirror Plane)

If a plane is constructed through a molecule and the atoms on one side of the plane reflect perfectly onto the locations of the atoms on the other side of the plane, the molecule is said to have a *mirror plane*, represented by the symbol  $\sigma$ . We further define the mirror plane with reference to the location of the principal axis, which is, by convention, considered as defining the vertical direction. For example, in the case of the boron trifluoride molecule, we can “slice” the molecule through all of its atoms perpendicular to the principal axis,  $C_3$ . This plane, following the convention, is called a horizontal mirror plane, symbol  $\sigma_h$ .

In addition, we can “slice” the molecule with a plane through one BF bond and bisect the angle between other two BF bonds. This plane contains the principal axis and is called the vertical mirror plane,  $\sigma_v$ . The boron trifluoride molecule has three vertical mirror planes, as shown in Figure 3.55.

The dihedral mirror plane,  $\sigma_d$ , is a third type of mirror plane. Dihedral mirror planes are vertical mirror planes that are between two vertical mirror planes or between two rotation axes.

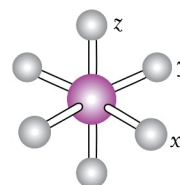
### Inversion through a Center of Symmetry

If inversion of all parts of the molecule through the center produces an indistinguishable configuration, the molecule is said to possess a *center of symmetry*,



also called a *center of inversion*, and given the symbol  $i$ . For example, boron trifluoride does not possess a center of inversion. However, any molecule with an even-numbered rotation axis, for example,  $C_2$ ,  $C_4$ , or  $C_6$ , and a mirror plane perpendicular to that axis does have a center of symmetry. Inversion can be considered as the combination of a  $C_2$  and a  $\sigma_h$ .

There is an alternative way of identifying a center of symmetry. Consider the example of the sulfur hexafluoride molecule (Figure 3.56): if the sulfur atom is said to be at the center of a three-dimensional grid (point 0, 0, 0), then three of the fluorine atoms would be at a distance  $r$  along the  $x$ -,  $y$ -, and  $z$ -axes. For each fluorine atom, there is a matching atom along the same axis at distance  $-r$  from the sulfur (that is, on the opposite side of the sulfur atom).



**FIGURE 3.56** The sulfur hexafluoride molecule has a center of symmetry.

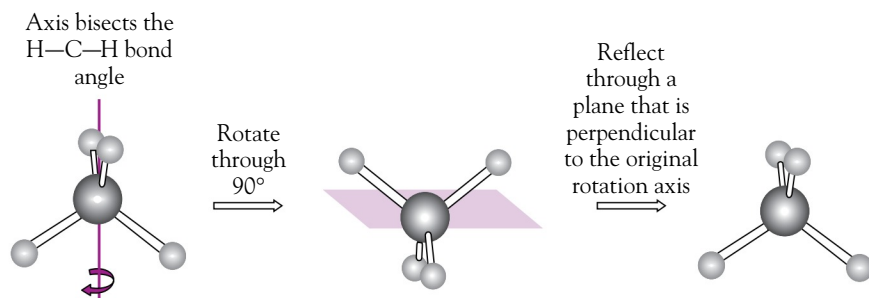
### Improper Rotation

A so-called improper axis of rotation is the combination of a rotation operation and a reflection through a plane perpendicular to the axis of rotation. An improper axis of rotation is denoted by the symbol  $S_n$ .

To provide an example of an improper rotation, we choose a tetrahedral molecule, such as methane,  $\text{CH}_4$ . Methane contains four  $C_3$ -axes, one along each C—H bond. In addition, and harder to see, is a  $C_2$ -axis bisecting each H—C—H bond angle, giving a total of three  $C_2$ -axes. Figure 3.57 shows how the rotation by  $90^\circ$  about one of the  $C_2$ -axes followed by reflection through a plane at right angles (an imaginary  $\sigma_h$  plane) results in a conformation matching that of the original position. This transformation represents an  $S_4$ -axis. An  $S_4$ -axis corresponds to each of the  $C_2$ -axes, and so methane possesses three  $S_4$  improper rotation axes. Thus, it is possible to have a molecular shape with an improper rotation axis with a higher value of  $n$  than the highest value of  $n$  for a proper rotation.

### Point Groups

Any particular molecular shape can possess only certain combinations of symmetry elements. For example, the tetrahedral shape of methane possesses four



**FIGURE 3.57** The improper rotation of the methane molecule. The rotation through  $90^\circ$  followed by a reflection provides a fourfold improper rotation axis, designated  $S_4$ . [Adapted from C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry* (London: Prentice Hall, 2004).]



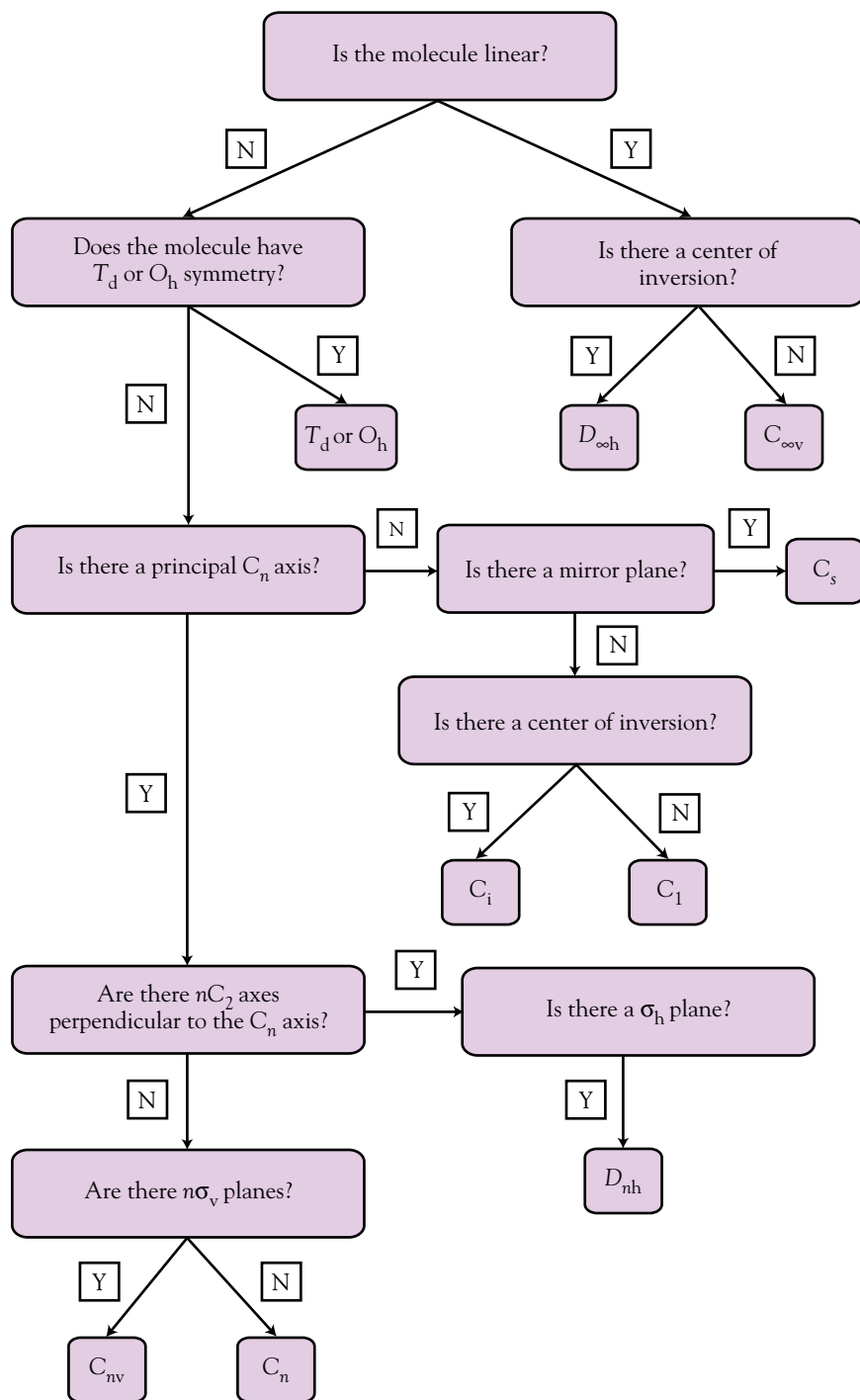
$C_3$ -axes, three  $C_2$ -axes, six  $\sigma_v$  planes, three  $S_4$  improper rotation axes, and the ubiquitous  $E$ . The collection (a group) of symmetry elements all of which coincide at the center of a molecule (a point) is called a *point group*. In the case of methane, the point group is called  $T_d$ .

To determine a point group, it is often sufficient to identify the number and type of proper rotation axes, the number of vertical and horizontal planes, and whether the molecular shape possesses a center of symmetry. Table 3.8

**TABLE 3.8** The common point groups: corresponding rotation axes and vertical and horizontal reflection planes, structure, and common examples

Point group	$C_n$ , $\sigma_h$ , and $\sigma_v$ symmetry elements	Structure	Example
$C_1$	None	—	CHFCIBr
$C_i$	Center of inversion	—	—
$C_s$	One plane	—	SOCl <sub>2</sub>
$C_2$	One $C_2$ axis	—	H <sub>2</sub> O <sub>2</sub>
$C_{2v}$	One $C_2$ axis	AB <sub>2</sub> bent	H <sub>2</sub> O
	Two $\sigma_v$ planes	or XAB <sub>2</sub> planar	BFCI <sub>2</sub>
$C_{3v}$	One $C_3$ axis	AB <sub>3</sub> trigonal pyramidal	NH <sub>3</sub>
	Three $\sigma_v$ planes		
$C_{4v}$	One $C_4$ axis	AB <sub>4</sub> square-based pyramid	BrF <sub>5</sub>
	Two $\sigma_v$ planes		
$C_{\infty v}$	One $C_{\infty}$ axis	ABC linear	HCN
	$\infty$ $\sigma_v$ planes		
$D_{2h}$	Three $C_2$ axes		
	One $\sigma_h$ , two $\sigma_v$ planes	Planar	N <sub>2</sub> O <sub>4</sub>
	Center of symmetry		
$D_{3h}$	One $C_3$ , three $C_2$ axes	AB <sub>3</sub> trigonal planar	BF <sub>3</sub>
	One $\sigma_h$ , three $\sigma_v$ planes		
$D_{4h}$	One $C_4$ , four $C_2$ axes	AB <sub>4</sub> square planar	XeF <sub>4</sub>
	One $\sigma_h$ , four $\sigma_v$ planes		
	Center of symmetry		
$D_{\infty h}$	One $C_{\infty}$ , $\infty$ $C_2$ axes	AB <sub>2</sub> linear	CO <sub>2</sub>
	$\infty$ $\sigma_v$ , one $\sigma_h$ planes		
	Center of symmetry		
$T_d$	Four $C_3$ , three $C_2$ axes	AB <sub>4</sub> tetrahedral	CH <sub>4</sub>
	Six $\sigma_v$ planes		
$O_h$	Three $C_4$ , four $C_3$ , six $C_2$ axes	AB <sub>6</sub> octahedral	SF <sub>6</sub>
	Nine $\sigma_v$ planes		
	Center of symmetry		

lists the common point groups, their basic symmetry elements (proper rotation axes,  $\sigma_v$  and  $\sigma_h$  reflection planes, center of symmetry), corresponding molecular shape, and examples. A flowchart for identifying the common space groups is shown in Figure 3.58.



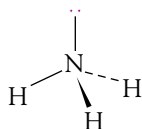
**FIGURE 3.58** Scheme for assigning common point groups of molecules. The rare  $D_{nd}$  groups are excluded. [Adapted from C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry* (London: Prentice Hall, 2004).]

**WORKED EXAMPLE 3.6**

Determine the point group of the ammonia molecule.

**Answer**

Having a lone pair in addition to three bonding pairs around the central nitrogen atom, the ammonia molecule is pyramidal in shape.



We can proceed through the flowchart in question-and-answer format:

Is the molecule linear? No.

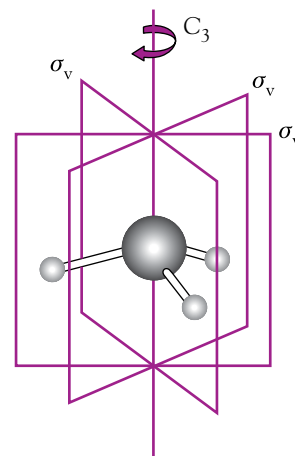
Does the molecule have  $T_d$  or  $O_h$  symmetry? No.

Is there a principal  $C_n$ -axis? Yes, a  $C_3$ -axis.

Are there  $nC_2$ -axes perpendicular to the  $C_3$ -axis? No.

Are there three  $\sigma_v$  planes? Yes.

Then the point group is  $C_{3v}$ . ■



The  $C_3$ -axis and the three  $\sigma_v$  planes of the ammonia molecule are shown later in the chapter.

### 3.13 Symmetry and Vibrational Spectroscopy

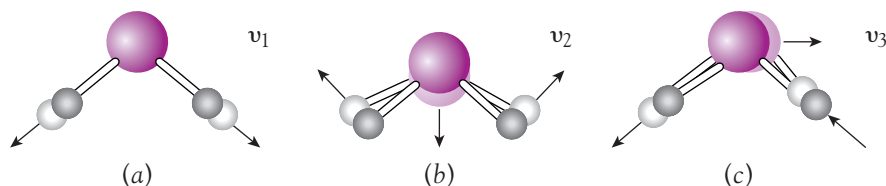
Symmetry plays an important role in molecular behavior. For example, in transition metal compounds, molecular symmetry is key in determining the number and energies of electronic excited states and the probability of an electron being excited into each of those states (see Chapter 19). These electronic excitations result in the color and color intensity of the compound.

Here we focus on the effects of symmetry on vibrational excitations (transitions). Atoms within molecules are in constant motion. For example, when we state that the water molecule has O—H bond lengths of 95.7 pm and a bond angle of 104.47°, these are mean values. The bonds are constantly undergoing lengthening and shortening while the scissoring results in the angle becoming larger and smaller. There are only a certain number of possible vibrations. For a molecule consisting of  $N$  atoms:

Nonlinear molecules have  $3N - 6$  possible vibrations

Linear molecules have  $3N - 5$  possible vibrations

The pattern of vibrations relates to the molecular symmetry. A molecule of a particular symmetry has a set of characteristic vibrations; for example, Figure 3.59 shows the three vibrations of the water molecule: symmetrical stretch, bending (scissoring), and asymmetrical stretch. From the pattern of vibrations, we can



**FIGURE 3.59** The three vibrational modes of the water molecule.

deduce the molecular shape. The energy of the vibrations of a molecule provides us with information about the strength of each bond within the molecule. We find that the stronger the bond, the higher the energy of the vibration. Because each molecule has a unique set of vibrational energies, we can use *vibrational spectroscopy* to identify an unknown substance, provided it contains covalent bonds.

There are two ways to study the vibrations of molecules: *infrared spectroscopy* and *Raman spectroscopy*. The former is the more common technique, but now that a low-cost Raman spectrophotometer has become available, the latter technique will become increasingly commonplace. In fact, the combination of the two techniques provides the most detailed information about the molecular symmetry and hence the molecular structure, and also the bond energies.

### Infrared Spectroscopy

Infrared spectroscopy involves the passing of a beam of infrared light through a substance. The molecules of that substance will selectively absorb the energies of infrared light corresponding to certain, and not necessarily all, molecular vibrations. For a bond vibration to absorb infrared radiation, the bond must be polar and there must be a change in dipole moment of the bond.

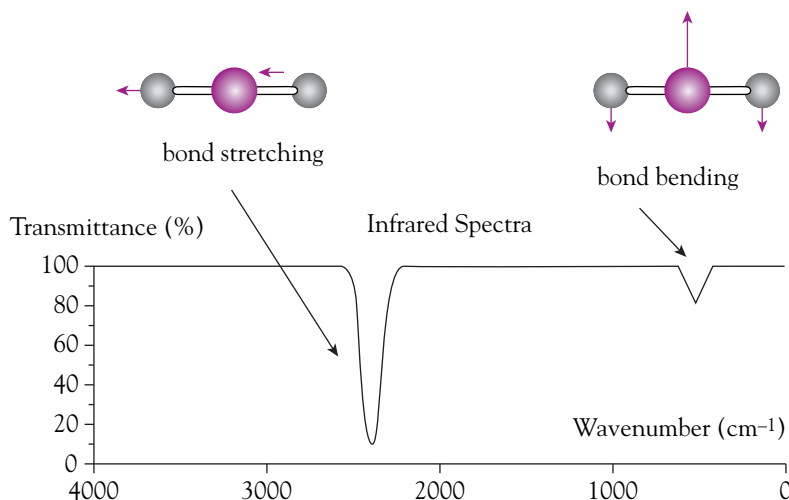
In the context of the atmosphere, the monatomic species, such as argon, Ar, cannot be infrared absorbing. For a homonuclear diatomic molecule, such as nitrogen, N<sub>2</sub>, and oxygen, O<sub>2</sub>, the only possible molecular vibration is a symmetrical stretching mode. This will not change the zero dipole moment of the bond. Thus, as we discussed in the opening Context of this chapter, neither the monatomic nor the diatomic gases contribute to radiation trapping (the “greenhouse effect.”)

On the other hand, water is a low-symmetry triatomic molecule and all three vibrations absorb infrared radiation. We usually report the absorption values in frequency units of reciprocal centimeters, cm<sup>-1</sup>, often called wave numbers. For water, the two stretching modes are at 3450 cm<sup>-1</sup> and 3615 cm<sup>-1</sup> and the bending absorption is at 1640 cm<sup>-1</sup>. All three modes, therefore, contribute to the greenhouse effect. For linear symmetrical carbon dioxide, the symmetrical stretch is not active in the infrared spectrum, so we observe only two absorptions for that molecule, the asymmetrical stretch and the bending modes (Figure 3.60). It is these two absorptions in the infrared part of the spectrum which result in carbon dioxide being a greenhouse gas.

### Raman Spectroscopy

Raman spectroscopy uses the passage of a beam of visible light. Molecules absorb and re-emit the light, but some of the energy is absorbed by the molecular vibrations. Thus, a very small proportion of the light is re-radiated at a frequency that differs from the original frequency by the vibrational energy. The rules that govern the Raman-active vibrations are different from those of the direct infrared absorption; that is, there must be a change in polarizability

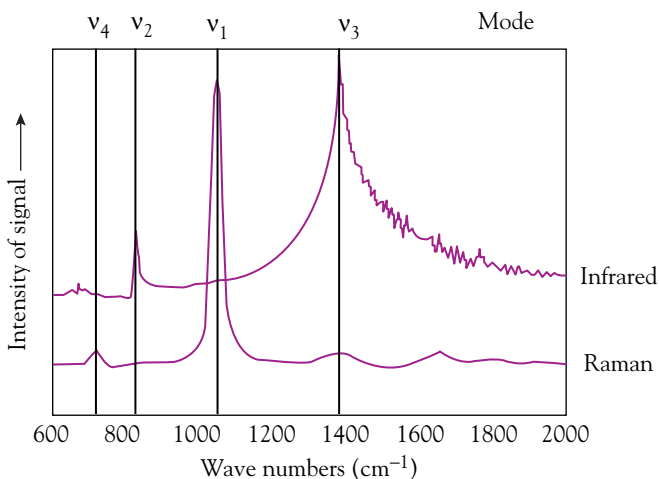
**FIGURE 3.60** The two infrared active vibrational modes of the carbon dioxide molecule and the corresponding infrared spectrum.



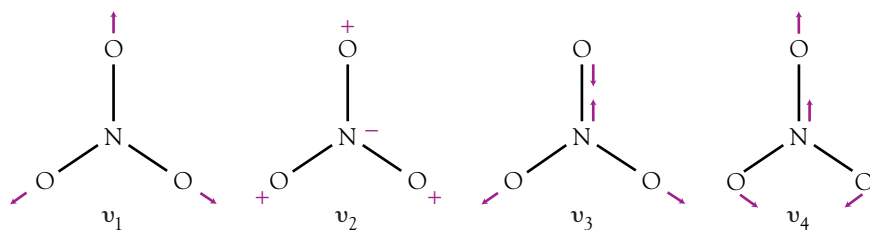
Raman spectroscopy is named after its discoverer, Indian chemist C. V. Raman.

of the molecule during the vibration. As a result, the vibrations that we observe in the Raman spectrum of a molecule are often quite different from those in the infrared. For example, Raman spectra can be collected for oxygen and nitrogen. The vibrations in the Raman spectrum are most often symmetrical modes such as symmetrical stretching. Absorptions also tend to be strong for nonpolar bonds, whereas such vibrations are weak in the infrared spectrum.

If a molecule has a center of inversion, there are no absorptions that are common between the infrared and Raman spectra. The Raman technique has one great practical advantage over infrared: Raman can be used with aqueous solutions, whereas it is difficult to measure infrared spectra of aqueous solutions due to the strong absorption of the radiation by water molecules. Figure 3.61 shows the pair of infrared and Raman spectra for the nitrate ion; Figure 3.62 shows the corresponding vibrational modes. The two stretching modes, the symmetrical ( $\nu_1$ , Raman active) and asymmetrical ( $\nu_3$ , infrared active), are particularly prominent.



**FIGURE 3.61** Matching pair of infrared and Raman spectra of the nitrate ion, showing the four active modes.  $\nu_1$  is the symmetrical stretching mode;  $\nu_3$  is the asymmetric stretching mode. [Courtesy of Delta Nu Division, CC Technology Inc., Laramie, WY.]



**FIGURE 3.62** The four vibrations of the nitrate ion corresponding to the infrared and Raman absorptions shown in Figure 3.61 (the plus and minus of the  $v_2$  vibration indicates the motion is above and below the plane of the molecule).

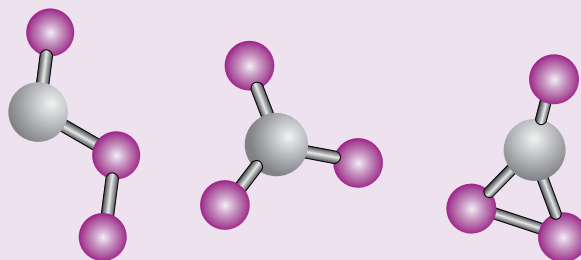
### Transient Species—A New Direction for Inorganic Chemistry

Traditionally, inorganic chemicals were stable substances found in bottles, but more and more, inorganic chemists are interested in transient species—those short-lived compounds only detectable and identifiable by spectroscopic means. In this text, we introduce several such compounds.

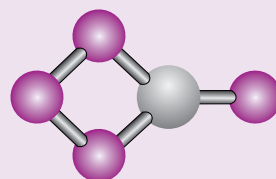
We now know that short-lived free-radical species (molecules with unpaired electrons) are particularly important in the chemistry of the atmosphere. Two molecules act as scavengers of atmospheric pollutants: the nitrate radical,  $\text{NO}_3$  (see Chapter 15, Section 15.8), at night, and the hydroxyl radical,  $\text{OH}$  (see Chapter 16, Section 16.10), in the daytime. In the upper atmosphere, the stratosphere, a key species is the chlorine monoxide radical,  $\text{ClO}$  (see Chapter 17, Section 17.8).

Some chemists are turning their attention to cosmochemistry to study species that may not exist on Earth but may be of importance under very different conditions. Everyone has heard of the two common oxides of carbon, carbon monoxide and carbon dioxide, and we also mention the intermediate in a reaction, dicarbon tetroxide,  $\text{C}_2\text{O}_4$  (see Chapter 14, Section 14.7). There are even more oxides of carbon, two of which may exist on the surfaces of comets and the moons of the outer planets: carbon trioxide,  $\text{CO}_3$ , and carbon tetroxide,  $\text{CO}_4$ . Chemists have proposed that such species are formed by the effect of ultraviolet radiation from the Sun on carbon dioxide. Replication of the conditions in the cold outer parts of the solar system showed that at 10 K, carbon monoxide molecules and excited oxygen atoms were formed on a solid carbon dioxide surface. Some of

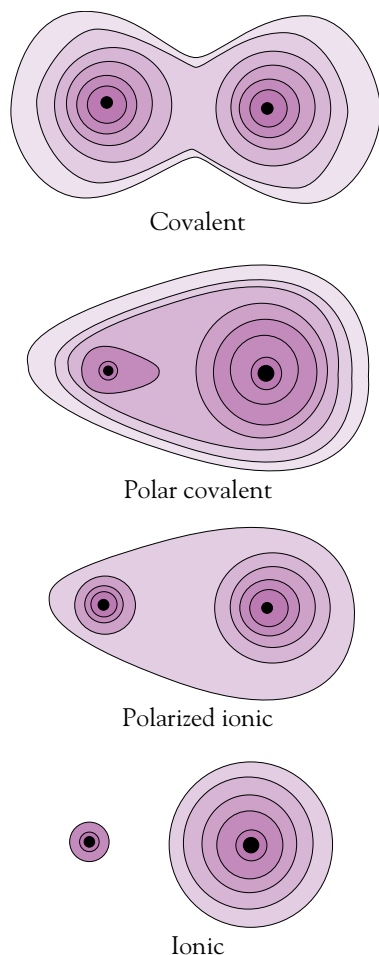
the excited oxygen atoms then combined with carbon dioxide to give carbon trioxide and a smaller proportion of carbon tetroxide. Three possible structures of carbon trioxide exist (Figure 3.63), and from the infrared spectra, the reaction produced the  $D_{3h}$  isomer, together with the  $C_{2v}$  isomer of carbon tetroxide (Figure 3.64). These molecules were not stable at higher temperatures but may exist transiently in the upper atmospheres of the inner planets.



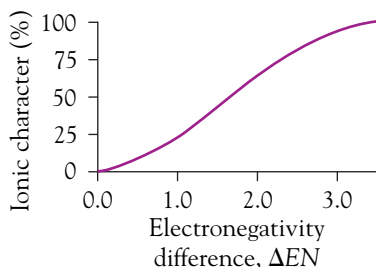
**FIGURE 3.63** The structures of three possible isomers of carbon trioxide. They are of  $C_s$ ,  $D_{3h}$ , and  $C_{2v}$  symmetry, respectively. Infrared spectra of known carbon trioxide shows it to be of  $D_{3h}$  symmetry.



**FIGURE 3.64** The structure of carbon tetroxide.



**FIGURE 3.65** Four examples of electron density profiles of diatomic species on the bonding continuum.



**FIGURE 3.66** Approximate relationship between electronegativity difference and ionic character in a bond.

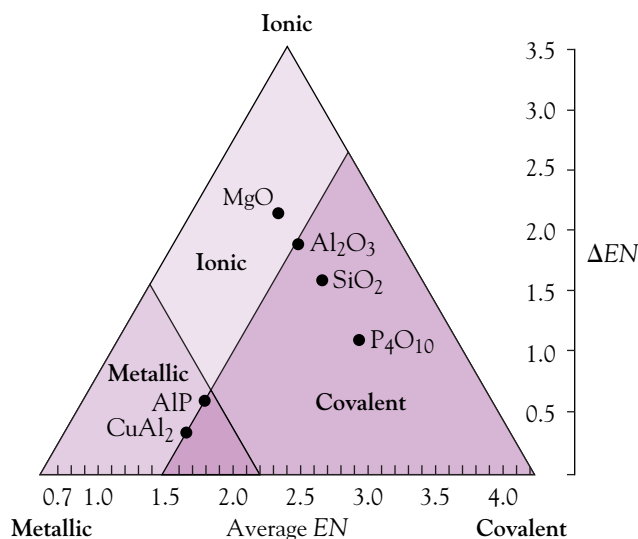
### 3.14 The Bonding Continuum

In general chemistry courses, the bonding between atoms is depicted as covalent or ionic. However, in reality, bonding is often a mixture of the two. Earlier, we saw how compounds of two nonmetals can have an ionic component to their bonding (polar covalency). Thus, inorganic chemists see not a rigid ionic-covalent divide but a *bonding continuum*. Figure 3.65 shows electron density profiles for four points on this continuum: the pure covalent, a polar covalent bond, a polarized ionic bond, and a pure ionic bond.

The ratio of ionic to covalent character can be defined as the difference in electronegativities,  $\Delta EN$ , between the pairs of atoms. Thus, pairs of atoms with  $\Delta EN$  close to zero will possess essentially pure covalent bonds with equally shared electrons, whereas those with  $\Delta EN > 3.0$  are regarded as purely ionic (Figure 3.66).

#### The Bond Triangle

The bonding continuum is not confined to two dimensions: metallic bonding provides a third component. This *bond triangle* (or more correctly, the Van Arkel–Ketelaar triangle) has a horizontal axis of electronegativity. The metallic-covalent limits of this axis correspond to the change in bonding from the delocalized bonding in the metallic structure to the overlap of orbitals in particular directions (covalent). Elements lie along this axis, from purely metallic (such as cesium) to purely covalent (such as fluorine). The  $\Delta EN$  becomes the vertical axis in this plot, the left side of the triangle representing the metallic to ionic transition and the right representing the covalent to ionic transition. Figure 3.67 shows the bond triangle, with a rough division into metallic, ionic, and covalent “zones.”



**FIGURE 3.67** The Van Arkel–Ketelaar bond triangle.

We can locate any binary compound on this triangle by plotting the average electronegativity of the two atoms against their electronegativity difference. To illustrate, we show the location of some compounds using the Allred-Rochow values of electronegativities. The series of oxides shows a nice trend from the ionic magnesium oxide to the covalent tetraphosphorus decaoxide. The location of aluminum oxide is appropriate since it is sometimes more useful to consider it as ionic and at other times as network covalent. The alloy  $\text{CuAl}_2$  fits in the metallic zone, whereas aluminum phosphide provides an example of a material whose bonding (and properties) is consistent with a hybrid of all three categories. Fortunately, as we discuss in later chapters, most elements and compounds appear to have properties that can be explained in terms of one bonding type or, at most, a combination of two bonding types.

### WORKED EXAMPLE 3.7

Predict whether the bonding in  $\text{BeO}$  is likely to be predominantly ionic or covalent. The Allred-Rochow electronegativity values are  $\text{Be} = 1.47$  and  $\text{O} = 3.50$ .

#### Answer

The value of  $\Delta EN = 3.50 - 1.47 = 2.03$ . The average  $EN = (3.50 + 1.47)/2 = 2.49$ . These two values place  $\text{BeO}$  in the covalent bonding region of the bonding triangle. ■

## KEY IDEAS

- Molecular orbitals provide chemists with the best understanding of the properties and behavior of molecules.
- The linear combination of atomic orbitals results in the formation of bonding and antibonding molecular orbitals.
- The combination of p (or d) orbitals gives sets of orbitals formed by end-on overlap ( $\sigma$ ) and side-to-side overlap ( $\pi$ ).
- For more complex molecules, valence-shell electron-pair repulsion (VSEPR) rules are usually adequate to provide an explanation for bond angles and comparative bond lengths.
- The valence-bond approach, involving the theoretical hybridization of atomic orbitals, can be used to rationalize molecular shapes.
- There are two classes of covalently bonded compounds: network covalent and small-molecule covalent.
- The properties of small-molecule covalent compounds are defined by their intermolecular forces (dispersion, dipole-dipole, hydrogen bonding).

## EXERCISES

- 3.1** Define the following terms: (a) LCAO; (b)  $\sigma$  orbital; (c) VSEPR; (d) hybridization; (e) principal axis.
- 3.2** Define the following terms: (a) network covalent molecules; (b) intramolecular forces; (c) electronegativity; (d) hydrogen bonding; (e) point group.
- 3.3** Use a molecular orbital diagram to determine the bond order of the  $\text{H}_2^-$  ion. Would the ion be diamagnetic or paramagnetic?
- 3.4** Would you expect  $\text{Be}_2$  to exist? Use a molecular orbital diagram to explain your reasoning.



**3.5** Use a molecular orbital diagram to determine the bond order in the  $\text{N}_2^+$  ion. Write a valence-electron configuration  $[(\sigma_{2s})^2]$  for this ion.

**3.6** Use a molecular orbital diagram to determine the bond order in the  $\text{O}_2^+$  ion. Write a valence-electron configuration  $[(\sigma_{2s})^2]$  for this ion.

**3.7** Assuming that it has similar molecular orbital energies to those of carbon monoxide, deduce the bond order of the  $\text{NO}^+$  ion.

**3.8** Assuming that it has similar molecular orbital energies to those of carbon monoxide, deduce the bond order of the  $\text{NO}^-$  ion.

**3.9** Construct a molecular orbital diagram for diboron,  $\text{B}_2$ . What would you predict for the bond order? Construct a similar diagram for diboron using the ordering for the heavier Period 2 elements and compare the two results. What experimental property could be used to confirm this different ordering?

**3.10** Construct a molecular orbital diagram and write the valence-electron configuration of the dicarbon anion and cation,  $\text{C}_2^-$  and  $\text{C}_2^+$ . Determine the bond order in each of these ions.

**3.11** Construct electron-dot diagrams for (a) oxygen difluoride; (b) phosphorus trichloride; (c) xenon difluoride; (d) the tetrachloroiodate ion,  $\text{ICl}_4^-$ .

**3.12** Construct electron-dot diagrams for (a) the ammonium ion; (b) carbon tetrachloride; (c) the hexafluorosilicate ion,  $\text{SiF}_6^{2-}$ ; (d) the pentafluorosulfate ion,  $\text{SF}_5^-$ .

**3.13** Construct an electron-dot diagram for the nitrite ion. Draw the structural formulas of the two resonance possibilities for the ion and estimate the average nitrogen-oxygen bond order. Draw a partial bond representation of the ion.

**3.14** Construct an electron-dot diagram for the carbonate ion. Draw the structural formulas of the three resonance possibilities for the ion and estimate the average carbon-oxygen bond order. Draw a partial bond representation of the ion.

**3.15** The thiocyanate ion,  $\text{NCS}^-$ , is linear, with a central carbon atom. Construct all feasible electron-dot diagrams for this ion; then use the concept of formal charge to identify the most probable contributing structures. Display the result using a partial bond representation.

**3.16** The boron trifluoride molecule is depicted as having three single bonds and an electron-deficient central boron atom. Use the concept of formal charge to suggest why a

structure involving a double bond to one fluorine, which would provide an octet to the boron, is not favored.

**3.17** For each of the molecules and polyatomic ions in Exercise 3.11, determine the electron-pair arrangement and the molecular shape according to VSEPR rules.

**3.18** For each of the molecules and polyatomic ions in Exercise 3.12, determine the electron-pair arrangement and the molecular shape according to VSEPR rules.

**3.19** Which of the following triatomic molecules would you expect to be linear and which would you expect to be V-shaped? For those V-shaped, suggest approximate bond angles. (a) carbon disulfide,  $\text{CS}_2$ ; (b) chlorine dioxide,  $\text{ClO}_2$ ; (c) gaseous tin(II) chloride,  $\text{SnCl}_2$ ; (d) nitrosyl chloride,  $\text{NOCl}$  (nitrogen is the central atom); (e) xenon difluoride,  $\text{XeF}_2$ .

**3.20** Which of the following triatomic ions would you expect to be linear and which would you expect to be V-shaped? For those V-shaped, suggest approximate bond angles. (a)  $\text{BrF}_2^+$ ; (b)  $\text{BrF}_2^-$ ; (c)  $\text{CN}_2^{2-}$ .

**3.21** For each of the molecules and polyatomic ions in Exercise 3.11, identify in which cases distortion from the regular geometric angles will occur due to the presence of one or more lone pairs.

**3.22** For each of the molecules and polyatomic ions in Exercise 3.12, identify in which cases distortion from the regular geometric angles will occur due to the presence of one or more lone pairs.

**3.23** For each of the electron-pair arrangements determined in Exercise 3.11, identify the hybridization that would correspond to the shape.

**3.24** For each of the electron-pair arrangements determined in Exercise 3.12, identify the hybridization that would correspond to the shape.

**3.25** Using Figure 3.32 as a model, show how the concept of hybrid orbitals can be used to explain the shape of the gaseous beryllium chloride molecule.

**3.26** Using Figure 3.32 as a model, show how the concept of hybrid orbitals can be used to explain the shape of the methane molecule.

**3.27** Which would you expect to have the higher boiling point, hydrogen sulfide,  $\text{H}_2\text{S}$ , or hydrogen selenide,  $\text{H}_2\text{Se}$ ? Explain your reasoning clearly.

**3.28** Which would you expect to have the higher melting point, dibromine,  $\text{Br}_2$ , or iodine monochloride,  $\text{ICl}$ ? Explain your reasoning clearly.

**3.29** For each of the molecules and polyatomic ions in Exercise 3.11, determine whether they are polar or nonpolar.

**3.30** For each of the molecules and polyatomic ions in Exercise 3.12, determine whether they are polar or nonpolar.

**3.31** Which would you expect to have the higher boiling point, ammonia,  $\text{NH}_3$ , or phosphine,  $\text{PH}_3$ ? Explain your reasoning clearly.

**3.32** Which would you expect to have the higher boiling point, phosphine,  $\text{PH}_3$ , or arsine,  $\text{AsH}_3$ ? Explain your reasoning clearly.

**3.33** For each of the following covalent compounds, deduce its molecular shape and the possible hybridization of the central atom: (a) indium(I) iodide,  $\text{InI}$ ; (b) tin(II) bromide,  $\text{SnBr}_2$ ; (c) antimony tribromide,  $\text{SbBr}_3$ ; (d) tellurium tetrachloride,  $\text{TeCl}_4$ ; (e) iodine pentafluoride,  $\text{IF}_5$ .

**3.34** Arsenic trifluoride and arsenic trichloride have bond angles of  $96.2^\circ$  and  $98.5^\circ$ , respectively. Suggest reasons for the difference in angles.

**3.35** How many vibrational modes will the methane molecule possess?

**3.36** In what way do infrared and Raman spectroscopy differ?

**3.37** Determine the symmetry elements (rotation axes, mirror planes, and improper axes) and hence identify the space group for (a) phosphorus pentachloride (see Figure 3.18);

(b) iodine pentafluoride (see Figure 3.24); (c) xenon tetrafluoride (see Figure 3.25).

**3.38** Determine the symmetry elements (rotation axes, mirror planes, and improper axes) and hence identify the space group for the two different possible geometrical forms of the sulfur tetrafluoride molecule (see Figure 3.19).

**3.39** Use VSEPR rules to determine the shapes of each of the following species. Then establish their rotation axes and mirror planes and hence identify the point group to which they belong. *Hint:* Constructing a molecular model will help (a) phosphine,  $\text{PH}_3$ ; (b) the carbonate ion,  $\text{CO}_3^{2-}$ ; (c) the sulfate ion,  $\text{SO}_4^{2-}$ ; (d) the hexafluorophosphate ion,  $\text{PF}_6^-$ .

**3.40** Use VSEPR rules to determine the shapes of each of the following species. Then establish their rotation axes and mirror planes and hence identify the point group to which they belong. *Hint:* Constructing a molecular model will help (a) the thiocyanate ion,  $\text{SCN}^-$ ; (b) the ammonium ion,  $\text{NH}_4^+$ ; (c) carbon disulfide,  $\text{CS}_2$ ; (d) sulfur dioxide,  $\text{SO}_2$ .

**3.41** Using the bond triangle concept, state the probable combinations of bonding in (a)  $\text{CoZn}_3$ ; (b)  $\text{BF}_3$ .

**3.42** Using the bond triangle concept, state the probable combinations of bonding in (a)  $\text{K}_3\text{As}$ ; (b)  $\text{AsF}_3$ .

## BEYOND THE BASICS

**3.43** Research the molecular orbitals formed by the overlap of d orbitals with s and p orbitals. Draw diagrams to show how the d atomic orbitals overlap with the  $\sigma$  and  $\pi$  orbitals to form s and p molecular orbitals.

**3.44** The  $\text{CO}_2^-$  ion has been synthesized. What shape and approximate bond angles would you expect?

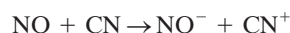
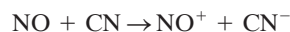
**3.45** The dinitrogen oxide molecule has the atomic order NNO rather than the symmetrical NON arrangement. Suggest a possible reason.

**3.46** The cyanate ion,  $\text{OCN}^-$ , forms many stable salts, while the salts of the isocyanate ion,  $\text{CNO}^-$ , are often explosive. Suggest a possible reason.

**3.47** Following from Exercise 3.38, a third possible arrangement would be  $\text{CON}^-$ . Explain why this order is unlikely to be a stable ion.

**3.48** Carbon forms similar free-radical species with hydrogen and fluorine:  $\text{CH}_3\cdot$  and  $\text{CF}_3\cdot$ ; yet one is planar whereas the other is pyramidal in shape. Which one adopts which geometry? Suggest an explanation.

**3.49** Using molecular orbital diagrams, predict which of the following free-radical gas-phase reactions is the more favored and give your reasoning.



**3.50** It is possible to synthesize the ion  $\text{C}(\text{CN})_3^-$ . Draw an electron-dot structure and deduce its most likely geometry. In fact, the ion is planar. Draw one of the resonance structures that would be compatible with this finding.

**3.51** Phosphorus pentafluoride has a higher boiling point ( $-84^\circ\text{C}$ ) than phosphorus trifluoride ( $-101^\circ\text{C}$ ), while

antimony pentachloride,  $\text{SbCl}_5$ , has a lower boiling point ( $140^\circ\text{C}$ ) than antimony trichloride,  $\text{SbCl}_3$  ( $283^\circ\text{C}$ ). Suggest why the two patterns are different.

**3.52** The pentafluoroxenate(IV) anion,  $\text{XeF}_5^-$ , has been prepared. The actual shape matches that predicted by VSEPR rules. What is that shape?

**3.53** Iodine heptafluoride has a pentagonal bipyramid shape (see Figure 3.30a). Identify the rotation axes and mirror planes of the molecule and hence identify its point group.

**3.54** The tetrachloroplatinate(II) ion,  $\text{PtCl}_4^{2-}$ , is square planar. How many vibrational modes will this ion exhibit?

What can you say about the infrared and Raman spectra of this ion?

**3.55** Why is trioxygen (ozone),  $\text{O}_3$ , a greenhouse gas, whereas dioxygen,  $\text{O}_2$ , is not?

**3.56** Contrast the structures of amorphous silicon, nanocrystalline silicon, and polycrystalline silicon. Research and identify an alternative name for nanocrystalline silicon.

**3.57** The planet Mars used to have a substantial and warm atmosphere. However, the small planet's core cooled and solidified. Why did this lead to a loss of atmosphere and atmospheric cooling?

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# METALLIC BONDING AND ALLOYS

## CHAPTER 4

The bonding in metals is explained best by the molecular orbital theory, which we have already discussed in the context of covalent bonding in Chapter 3. The arrangement of atoms in a metal crystal can be interpreted in terms of the packing of hard spheres. These packing arrangements are common to both metals and ionic compounds. Thus, a study of metallic bonding provides a link between covalent and ionic bonding.

### Context: Metal Matrix Composites

The quest for new materials is never-ending. For our increasingly complex world, be it architecture or microelectronics, we want materials with ever-specialized properties. In the nineteenth century, it was the discovery of new metallic elements which was important; in the twentieth century, metal alloys; now, in the twenty-first century, it is more sophisticated alloys and metal composites which are the research frontiers.

The use of composite building materials actually dates back to the earliest days of civilization: the use of mud and straw to make buildings, then, about 2000 years ago, concrete. Both the mud/straw and concrete materials employ a matrix (mud or cement) together with a reinforcing phase (straw or stones). Although the materials themselves have changed, the principle of matrix and reinforcing material are still the basis for composites.

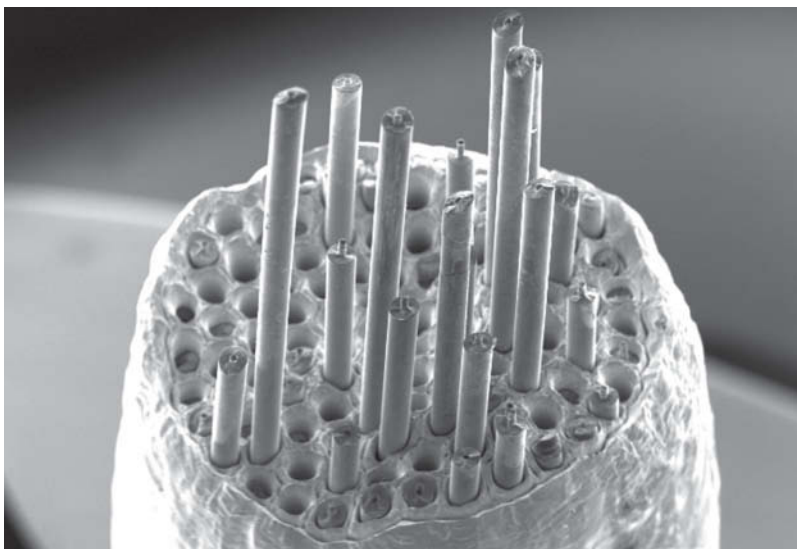
There are two types of metal-containing composites: cermets (see Chapter 5) and metal-matrix composites (MMCs). A MMC, as its name implies, involves a metal in which a different material is embedded, usually in the form of fibers (see the chapter opening illustration). It is the physical properties of MMCs that make them so attractive for a range of applications. In particular, the fibers strengthen the metal so it is less prone to cracking or similar catastrophic failure. It can also be used to modify other properties of the metal, such as wear resistance, friction coefficient, or thermal conductivity.

Metal-matrix composites are often used in applications where lightness, strength, and durability are important. For this reason, low-density metals are chosen, typically aluminum ( $2.7 \text{ g}\cdot\text{cm}^3$ ), magnesium ( $1.7 \text{ g}\cdot\text{cm}^3$ ), or titanium ( $4.5 \text{ g}\cdot\text{cm}^3$ ). These densities are much

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 4.1 Metallic Bonding
- 4.2 Bonding Models
- 4.3 Structure of Metals
- 4.4 Unit Cells
- 4.5 Alloys
- 4.6 Nanometal Particles
- 4.7 Magnetic Properties of Metals

A metal matrix composite wire of copper with embedded fibers of silicon carbide. This composite has been developed as a heat conductor from nuclear fusion reactors.



less than such metals as iron ( $7.9 \text{ g}\cdot\text{cm}^3$ ) or lead ( $11.4 \text{ g}\cdot\text{cm}^3$ ). For high-temperature applications, high melting point (m.p.) is more important than density, and for these applications, cobalt (m.p.  $1495^\circ\text{C}$ ), or cobalt-nickel alloy form the matrix. To strengthen the metal in a particular direction, long continuous fibers of boron or carbon are sometimes embedded in the metal. One method of producing such materials is to spray molten metal onto a continuous length of fibers. If it is desired to have overall strength, then short fibers, typically of aluminum oxide or silicon carbide, are stirred into the molten metal.

Metal-matrix composites are expensive to produce. For this reason, the most important applications are in the aerospace industry where the materials' low density, tailored thermal expansion, stiffness, and strength are more important than cost. The automotive industry also uses MMCs. For example, a composite of short aluminum or silicon fibers in an aluminum matrix is used to make diesel piston crowns which are lighter, more abrasion resistant, and cheaper than the nickel piston crowns that used to be used. Metal-matrix composites are used in many other contexts, such as high-performance mountain bikes and for heat sinks in computer systems. But to understand MMCs, we have to understand the nature of metals themselves, the subject of this chapter.

## 4.1 Metallic Bonding

In our discussions on the classification of elements (see Chapter 2, Section 2.4), we noted that high three-dimensional electrical conductivity at standard ambient temperature and pressure (SATP) was the one key characteristic of

metallic bonding. We can relate this property to the bonding in metals. Unlike nonmetals, where electron sharing is almost always within discrete molecular units, metal atoms share outer (valence) electrons with all nearest neighboring atoms. It is the free movement of electrons throughout the metal structure that can be used to explain the high electrical and thermal conductivity of metals together with their high reflectivity.

The lack of directional bonding can be used to account for the high malleability and ductility of most metals since metal atoms can readily slide over one another to form new metallic bonds. The ease of formation of metal bonds accounts for our ability to sinter the harder metals; that is, we can produce solid metal shapes by filling a mold with metal powder and placing the powder under conditions of high temperature and pressure. In those circumstances, metal-metal bonds are formed across the powder grain boundaries without the metal actually bulk melting.

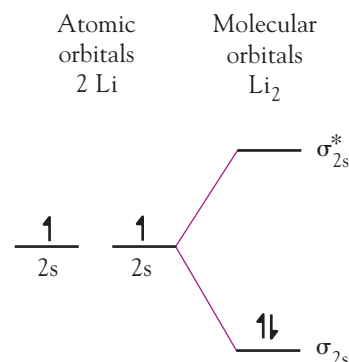
Whereas simple covalent molecules generally have low melting points and ionic compounds have high melting points, metals have melting points ranging from  $-39^{\circ}\text{C}$  for mercury to  $+3410^{\circ}\text{C}$  for tungsten. Metals continue to conduct heat and electricity in their molten state. (In fact, molten alkali metals are often used as heat transfer agents in nuclear power units.) This is evidence that metallic bonding is maintained in the liquid phase.

It is the boiling point that correlates most closely with the strength of the metallic bond. For example, mercury has a boiling point of  $357^{\circ}\text{C}$  and an enthalpy of atomization of  $61\text{ kJ}\cdot\text{mol}^{-1}$ , whereas the boiling point of tungsten is  $5660^{\circ}\text{C}$  and its enthalpy of atomization is  $837\text{ kJ}\cdot\text{mol}^{-1}$ . Thus, the metallic bond in mercury is as weak as some intermolecular forces, whereas that in tungsten is comparable in strength to a multiple covalent bond. In the gas phase, however, metallic elements like lithium exist as pairs,  $\text{Li}_2$ , or, like beryllium, as individual atoms and hence lose their bulk metallic properties. Metals in the gas phase do not even look metallic; for example, in the gas phase, potassium has a green color.

## 4.2 Bonding Models

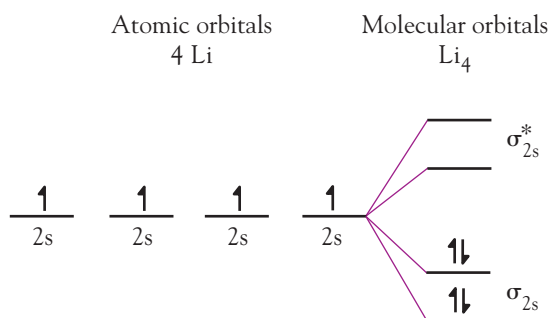
The simplest metallic bonding model is the electron-sea (or electron-gas) model. In this model, the valence electrons are free to move through the bulk metal structure (hence the term *electron sea*) and even leave the metal, thereby producing positive ions. It is valence electrons, then, that convey electric current, and it is the motion of the valence electrons that transfers heat through a metal. However, this model is more qualitative than quantitative.

Molecular orbital theory provides a more comprehensive model of metallic bonding. This extension of molecular orbital theory is sometimes called *band theory*, which we will illustrate by looking at the orbitals of lithium. In Chapter 3, Section 3.8, we saw that two lithium atoms combined in the gas phase to form the dilithium molecule. The molecular orbital diagram showing the mixing of two  $2s$  atomic orbitals is given in Figure 4.1. (Both sets of atomic orbitals are shown on the left.) Now suppose that the atomic orbitals of four lithium atoms

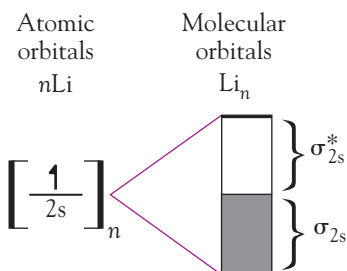


**FIGURE 4.1** Molecular orbital diagram for the dilithium (gas-phase) molecule.

**FIGURE 4.2** Molecular orbital diagram for the combination of four lithium atoms.



are mixed. Again, there must be the same number of  $\sigma_{2s}$  molecular orbitals as  $2s$  atomic orbitals, half of which are bonding and the other half antibonding. To avoid violating the quantum rules, the energies of the orbitals cannot be degenerate. That is, one  $\sigma_{2s}$  cannot have exactly the same energy as the other  $\sigma_{2s}$  orbital. Figure 4.2 shows the resulting orbital arrangement.



**FIGURE 4.3** Band derived from the  $2s$  atomic orbitals by the combination of  $n$  lithium atoms.

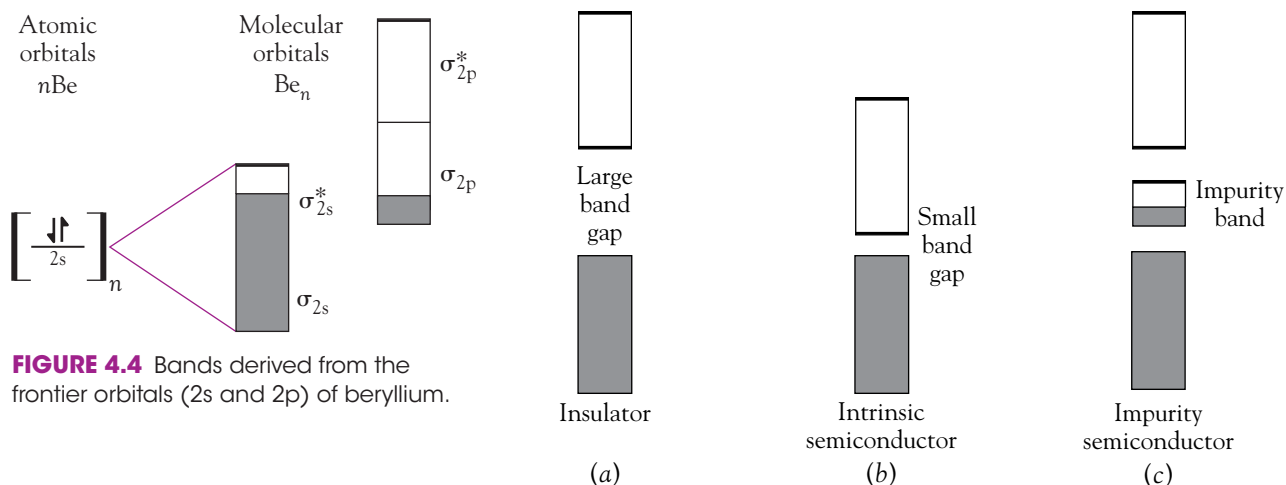
In a large metal crystal, the orbitals of  $n$  atoms, where  $n$  is some enormous number, are mixed. These orbitals interact throughout the three dimensions of the metal crystal, yet the same principles of bonding apply. There will be  $\frac{1}{2}n$   $\sigma_{2s}$  (bonding) molecular orbitals and  $\frac{1}{2}n$   $\sigma_{2s}^*$  (antibonding) molecular orbitals. With such a large number of energy levels, the spacing of levels becomes so close that they essentially constitute a continuum. This continuum is referred to as a band. For lithium, the band derived from the  $2s$  atomic orbitals will be half-filled. That is, the  $\sigma_{2s}$  part of the band will be filled and the  $\sigma_{2s}^*$  part will be empty (Figure 4.3).

We can visualize electrical conductivity simplistically as the gain by an electron of the infinitesimally small quantity of energy needed to raise it into the empty antibonding orbitals. It can then move freely through the metal structure as electric current. Similarly, the high thermal conductivity of metals can be visualized as “free” electrons transporting translational energy throughout the metal structure. It is important to remember, however, that the “real” explanation of these phenomena requires a more thorough study of band theory.

Light is absorbed when electrons move from a lower to a higher energy level. Conversely, light is emitted when electrons move from a higher to a lower energy level. For free gaseous atoms, the light emissions are observed as a line spectrum. With the multitudinous energy levels in a metal, there is an almost infinite number of possible energy-level transitions. As a result, the atoms on a metal surface can absorb any wavelength and then re-emit light at that same wavelength as the electrons release that same energy when returning to the ground state. Hence, band theory accounts for the luster of metals.

Beryllium also fits the band model. With an atomic configuration of  $[\text{He}]2s^2$ , both the  $\sigma_{2s}$  and  $\sigma_{2s}^*$  molecular orbitals will be fully occupied. That is, the band derived from overlap of the  $2s$  atomic orbitals will be completely filled. At first, the conclusion would be that beryllium could not exhibit metallic properties because there is no space in the band in which the electrons can “wander.” However, the empty  $2p$  band overlaps with the  $2s$  band, enabling the electrons to “roam” through the metal structure (Figure 4.4).





**FIGURE 4.4** Bands derived from the frontier orbitals (2s and 2p) of beryllium.

We can use band theory to explain why some substances are electrical conductors, some are not, and some are semiconductors. In the metals, bands overlap and allow a free movement of electrons. In nonmetals, bands are widely separated, so no electron movement can occur (Figure 4.5a). These elements are called *insulators*. In a few elements, the bands are close enough to allow only a small amount of electron excitation in an upper unoccupied band (Figure 4.5b). These elements are known as *intrinsic semiconductors*.

Our modern technology depends on the use of semiconducting materials, and it has become necessary to synthesize semiconductors with very specific properties. This can be done by taking an element with a wide band gap and “doping” it with some other element; that is, adding a trace impurity. The added element has an energy level between that of the filled and empty energy levels of the main component (Figure 4.5c). This impurity band can be accessed by the electrons in the filled band, enabling some conductivity to occur. By this means, the electrical properties of semiconductors can be adjusted to meet any requirements.

**FIGURE 4.5** Schematic of the band structure of (a) a nonmetal, (b) an intrinsic semiconductor, and (c) an impurity semiconductor.

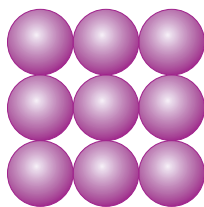
### 4.3 Structure of Metals

The way in which metal atoms pack together in a crystal is interesting in itself, but, of equal importance to an inorganic chemist, it also provides a basis from which to discuss the ion packing in an ionic compound (which we do in Chapter 5, Section 5.3). The concept of crystal packing assumes that the atoms are hard spheres. In a metal crystal, the atoms are arranged in a repeating array that is called a *crystal lattice*. The packing of metal atoms is really a problem in geometry. That is, we are concerned with the different ways in which spheres of equal size can be arranged.

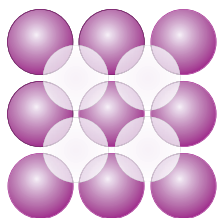
#### Cubic Packing

It is easiest to picture the atomic arrays by arranging one layer and then placing successive layers over it. The simplest possible arrangement is that in which

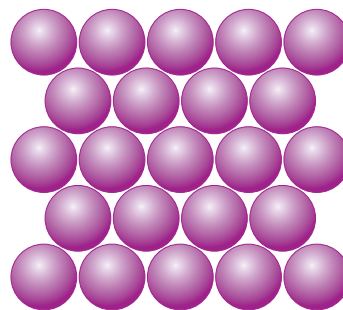




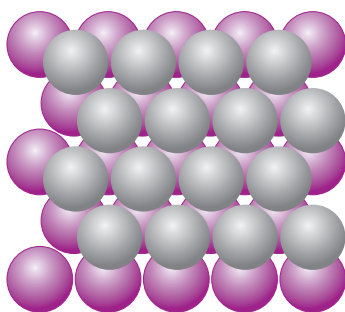
**FIGURE 4.6** Simple cubic packing. Successive layers are superimposed over the first array.



**FIGURE 4.7** Body-centered cubic packing. The second layer (gray) is placed over holes in the first layer and the third over the holes in the second.



**FIGURE 4.8** The first layer of the hexagonal arrangement.



**FIGURE 4.9** In hexagonal packing, the second layer (gray) fits over alternate holes in the first layer.

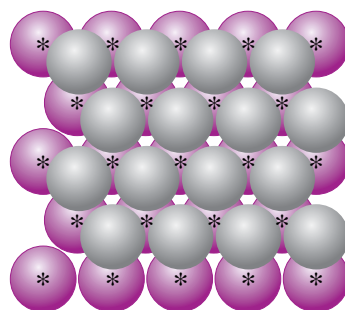
the atoms in the base are packed side-by-side. The successive layers of atoms are then placed directly over the layer below. This is known as *simple cubic packing* (sc) (Figure 4.6), or primitive cubic. Each atom is touched by four other atoms in its own plane plus one atom above and one below, a total of six neighboring atoms. As a result, it is said that each atom has a *coordination number* of six.

The simple cubic arrangement is not very compact and is known only for polonium in metal structures, although as we will see in Chapter 5, Section 5.3, it is found in some ionic compounds. An alternative cubic packing arrangement is to place the second layer of atoms over the holes in the first layer. The third layer then fits over the holes in the second layer—which happens to be exactly over the first layer. This more compact arrangement is called *body-centered cubic* (bcc) (Figure 4.7). Each atom is touched by four atoms above and four atoms below its plane. Thus, body-centered cubic results in a coordination number of eight.

### Hexagonal Packing

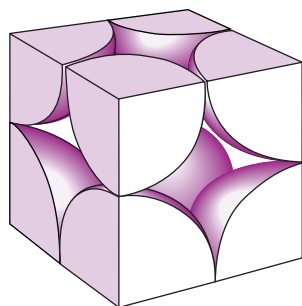
The other two possibilities are based on a hexagon arrangement for each layer; that is, each atom is surrounded by six neighbors in the plane. In the hexagonal arrangement, the holes between the atoms are much closer together than in the cubic array (Figure 4.8). When the second hexagonal layer is placed over the first, it is physically impossible to place atoms over all the holes in the first layer. In fact, only half the holes can be covered (Figure 4.9). If the third layer is placed over holes in the second layer so that it is superimposed over the first layer, then a *hexagonal close-packed* (hcp) arrangement is obtained (Figure 4.10). The fourth layer is then superimposed over the second layer. Hence, it is also known as an *abab* packing arrangement.

An alternative hexagonal packing arrangement involves placement of the third layer over the holes in the first and second layers (Figure 4.11). It is the fourth layer, then, that repeats the alignment of the first layer.

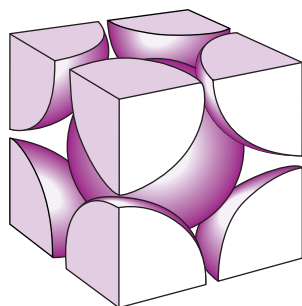


**FIGURE 4.10** The hexagonal close-packed arrangement involves placing the third layer over the top of the first layer (\*).

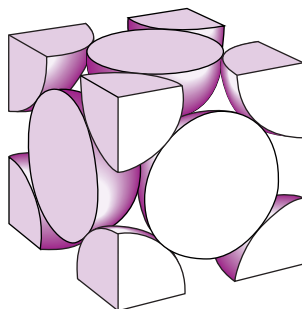




**FIGURE 4.13** The simple cubic unit cell.



**FIGURE 4.14** The body-centered cubic unit cell.



**FIGURE 4.15** The face-centered cubic unit cell.

## 4.4 Unit Cells

The simplest arrangement of spheres, which, when repeated, will reproduce the whole crystal structure, is called a *unit cell*. The cell is easiest to see in the simple cubic case (Figure 4.13). In the unit cell, we have cut a cube from the center of eight atoms. Inside the unit cell itself, there are eight segments, each one-eighth of an atom.

Because  $8(\frac{1}{8}) = 1$ , we can say that each unit cell contains one atom.

To obtain a unit cell for the bcc, we must take a larger cluster, one that shows the repeating three-layer structure. Cutting out a cube provides one central atom with eight one-eighth atoms at the corners. Hence, the unit cell contains  $[1 + 8(\frac{1}{8})]$ , which is equivalent to two atoms (Figure 4.14).

At first inspection, the ccp arrangement does not provide a simple unit cell. However, if a slice is taken through the corner of the fcc array, we can construct a face-centered cube in which there is an atom at each corner and an atom in the middle of each face (Figure 4.15). When we do this, the cube contains  $[6(\frac{1}{2}) + 8(\frac{1}{8})]$  segments, which is equivalent to four atoms.

### WORKED EXAMPLE 4.1

Demonstrate that the simple cubic structure has 52% of the space within it occupied.

#### Answer

If we look at Figure 4.13, we can see that the sc structure contains the equivalent of one atom. If the radius of the atom is  $r$ , then the atom volume is  $\pi r^3$ .

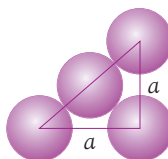
The length of the cell is  $2r$  as two spheres are in contact along a cell edge. Thus, the volume of the unit cell is:  $(2r)^3 = 8r^3$ . The fractional amount of space occupied is therefore  $\frac{4/3\pi r^3}{8r^3} \times 100\% = 52\%$ . ■

### WORKED EXAMPLE 4.2

Lead adopts the fcc structure. The radius of a lead atom is 175 pm. Calculate the length of the unit cell side.

#### Answer

In a fcc structure, the atoms are close-packed and, therefore, in contact with each other, along a face diagonal.



We can use Pythagoras' theorem to calculate the length of the unit cell side, labeled  $a$ . Pythagoras states that, in this example,  $a^2 + a^2 = (4r)^2$  so  $2a^2 = 16r^2$ . Rearranging the equation gives us  $r$ . Therefore, the length of the unit cell side for lead is  $\sqrt{8} \times 175 \text{ pm} = 495 \text{ pm}$ . ■

## 4.5 Alloys

A combination of two or more solid metals is called an *alloy*. The number of possible alloys is enormous. Alloys play a vital role in our lives, yet chemists rarely mention them. The atoms in alloys are held together by metallic bonds just like the component metallic elements. This bonding parallels the covalent bonding of nonmetals. Covalent bonds hold together molecules formed from pairs of different nonmetallic elements as well as from pairs of identical non-metallic elements. Similarly, the metallic bonds of an alloy hold together atoms of different metallic elements. There are two types of alloys: the solid solutions and the intermetallic compounds.

### Solid Solutions

In solid solutions, the molten metals blend to form a homogeneous mixture. To form a solid solution, the atoms of the two metals have to be about the same size, and the two metallic crystals must have the same structure. In addition, the metals must have similar chemical properties.

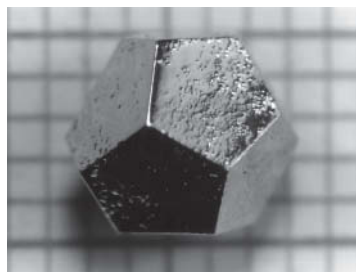
Gold and copper alloys are examples of solid solutions, forming a single phase all the way from 100 percent gold to 100 percent copper. These two metals have similar metallic radii (144 pm for gold and 128 pm for copper), and they both adopt ccp structures. Lead and tin have very similar metallic radii (175 pm and 162 pm, respectively), but lead forms a fcc structure and tin has a complex packing arrangement. Very little of one metal will crystallize with the other.

Brass, used in home decorative features and also sometimes in plumbing, is an alloy of copper (70 to 85 percent) and zinc (15 to 30 percent), which is harder than copper. Gold is also alloyed with other metals to make it harder and more durable. For example, 18-carat gold has a composition of gold (75 percent), silver (10 to 20 percent), and copper (5 to 15 percent).

### Intermetallic Compounds

Although similarly formed by mixing metals, intermetallic compounds have precise stoichiometries. Only certain compositions exist, but unlike ionic compounds, these atom ratios are not predictable. For example, copper and zinc form three alloy compounds:  $\text{CuZn}$ ,  $\text{Cu}_5\text{Zn}_8$ , and  $\text{CuZn}_{13}$ . Similarly, samarium and cobalt form alloy compounds  $\text{SmCo}_5$  or  $\text{Sm}_2\text{Co}_{17}$ , which are used as supermagnets. The first shape-memory alloy to be synthesized was the intermetallic compound, nitinol,  $\text{NiTi}$  (discussed in a later section: Memory Metal: The Shape of Things to Come).

The formation of an intermetallic compound is not always desired. In microelectronics, gold wire is sometimes bonded to an aluminum surface. The



**FIGURE 4.16** A dodecahedral quasicrystal of a holmium-magnesium-zinc alloy.

purple intermetallic compound,  $\text{AuAl}_2$ , sometimes called *purple plague*, can form at the interface and its low electrical conductivity causes the circuit to fail.

### Quasicrystals

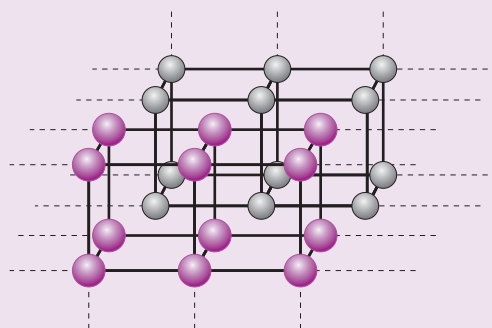
It was in 1982 that the world of crystal packing changed forever. Dan Shechtman of the U.S. National Bureau of Standards synthesized an alloy of aluminum and manganese. However, the structure did not match any of the simple packing arrangements. The atom-packing was ordered but not repeating. It is the repeating nature of the unit cell which defines the concept of a crystal. The term *quasicrystal* was invented to identify this type of solid, and Shechtman received the Nobel Prize for Chemistry in 2011 for the discovery.

Since the synthesis of the first quasicrystal alloy, literally hundreds of quasicrystals of different compositions have been produced (Figure 4.16). They are

### Memory Metal: The Shape of Things to Come

Although science is usually depicted as progressing through well thought-out advances, an amazing number of scientific discoveries are unexpected. One of the most interesting examples of chance's role in science is the discovery of memory metal. The story begins with attempts to develop a fatigue-resistant alloy for U.S. Navy missile nose cones. William J. Buehler, a metallurgist, discovered that an equimolar alloy of titanium and nickel had exactly the desired properties. He named the alloy *nitinol* (**N**ickel **T**itanium **N**aval **O**rdnance **L**aboratory). As a demonstration of nitinol's properties, he took long straight bands of the alloy and folded them into an accordion shape. He would show how the metal could be stretched repeatedly without breaking. The flexibility in itself was a very useful property. At one such demonstration, an attendee produced a lighter and idly heated the metal. Much to everyone's astonishment, the strip straightened out! The metal had "remembered" its original pre-accordion shape.

With an ordinary metal, bending it causes neighboring crystals to slide over one another. Nitinol has a very unusual crystal structure in that it consists of a simple cubic array of nickel atoms with a titanium atom at each nickel cube center, while the titanium atoms themselves are in simple cubic arrays with a nickel atom at each titanium cube center (Figure 4.17). This interlocking structure is what prevents neighboring crystals from moving relative to one another and imparts the superelastic properties of the material. At high temperatures, the symmetrical (austenite) phase is stable, but on cooling, the alloy undergoes a phase change to a distorted cubic (martensite) phase. In this phase, the martensite crystals



**FIGURE 4.17** The austenite phase of nitinol. Nickel atoms (gray) adopt a cubic arrangement with a titanium atom at each cube center. The titanium atoms (mauve) adopt an interlocking cubic arrangement with a nickel atom at each cube center.

are flexible enough that the bulk metal can be repeatedly bent without fracturing. Gentle warming will then cause the crystals to revert to their original shape. To impart a new shape, the metal must be heated above its phase transition temperature (which depends on the precise mole ratio of the two constituents).

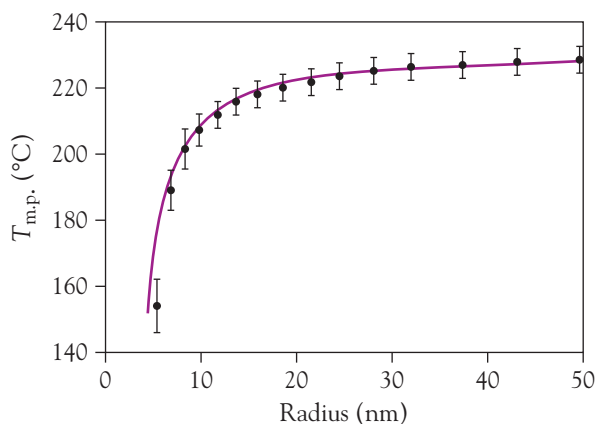
Nitinol has many uses, including in the manufacture of more comfortable and efficient orthodontic braces and unbreakable eyeglass frames. Automatic tweezers are another use. An ear specialist can bend open the tips of the tweezers, slide them into a patient's ear until the tip surrounds a foreign object, and apply a low current to the wire. The warming of the wire and the resulting return to the original atomic structure will cause the tips to close on the object so that it can be removed safely.

usually alloys of aluminum with two other metals. Such aluminum alloys come from all over the periodic table, such as aluminum-lithium-copper and aluminum-palladium-manganese. Some other quasicrystal combinations are even more unusual, such as indium-silver-ytterbium and palladium-uranium-silicon.

## 4.6 Nanometal Particles

Until now we have been discussing the properties of bulk metals. If the metal atoms are in very small clusters, then their properties, such as color and melting point, can be significantly different from those of a large crystal. Nanochemistry is not something new: it is our understanding of the phenomenon and the realization of applications that are new. As an example of its early use, in medieval Europe, the makers of the stained glass windows of cathedrals used nanochemistry: silver nanoparticles to give the glass a transparent yellow color and gold nanoparticles to provide a transparent red color.

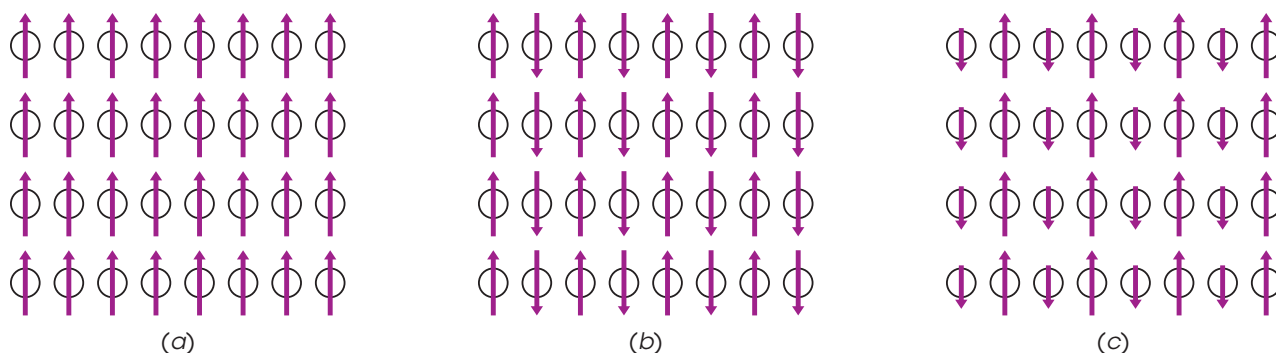
The dependence of melting point on particle size is the phenomenon that we will discuss here. Figure 4.18 shows the decrease in melting point of tin from its bulk value as the particle size is decreased. The decrease in melting point with decreasing particle size is a common feature of *nanometals*. The phenomenon can be explained in terms of metallic bonding. For bulk metals, the atoms are bonded to their nearest neighbors through the delocalized orbitals. In the case of nanometals, the particles are so small—always of the order of tens of nanometers—a high proportion of the atoms are on the particle surface and therefore are only bonded to the atoms beside or beneath them. Since atoms near the surface have fewer bonds, they require less energy to escape from the crystal lattice and the melting point will be lower.



**FIGURE 4.18** Plot of the melting point of tin against particle size.

## 4.7 Magnetic Properties of Metals

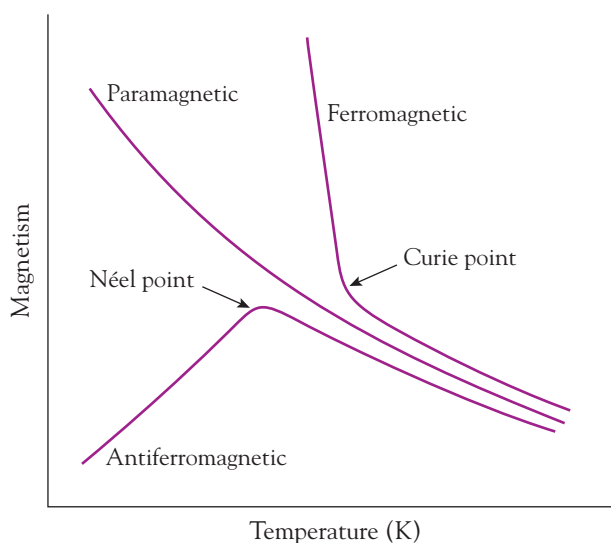
Diamagnetism and paramagnetism (discussed in Chapter 1, Section 1.5) occur within individual atoms. Here we introduce two types of bulk magnetic behavior: ferromagnetism and antiferromagnetism. In *ferromagnetic* materials, the



**FIGURE 4.19** Diagrammatic representations of (a) ferromagnetism, (b) antiferromagnetism, and (c) ferrimagnetism.

unpaired electrons are parallel-aligned with their neighbors even in the absence of a magnetic field. These groups of mutually aligned spins are known as *magnetic domains*. Application of a magnetic field causes all these domains to align with the magnetic field (Figure 4.19a). This alignment is much stronger than that of paramagnetism, and it can be permanent.

Ferromagnetism is found in metals that have unpaired electrons in their d or f orbitals. Electrons in these orbitals must weakly interact with those in neighboring atoms for the effect to occur. The phenomenon only occurs in the later 3d- and 4f-block elements. When a ferromagnetic material is heated, the atomic vibrations cause a breakdown of the magnetic domains until, at the *Curie point* (Figure 4.20), the material reverts to the weaker paramagnetic behavior. Only four metals exhibit ferromagnetism and have a Curie transition above 0°C: iron, cobalt, nickel, and gadolinium.



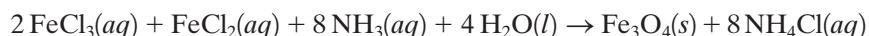
**FIGURE 4.20** Effect of temperature change on paramagnetic, ferromagnetic, and antiferromagnetic materials.



In addition to ferromagnetic metals, there are *antiferromagnetic* materials. Antiferromagnetism is similar to ferromagnetism except that the weak interactions between neighboring atoms result in an antiparallel alignment (Figure 4.19b). Thus, the attraction into a magnetic field is weaker than the paramagnetic effect would predict but only up to the *Néel temperature* (Figure 4.20), at which the antiferromagnetic material reverts to paramagnetic behavior. Antiferromagnetism is the rarer of the two bulk behaviors. It is found for chromium and in iron-manganese alloys.



In a special case of antiferromagnetism, the numbers of opposing spins do not balance, resulting in a net magnetization in one direction (Figure 4.19c). This is called *ferrimagnetism*. The most common ferrimagnetic material is  $\text{Fe}_3\text{O}_4$ , the mixed oxidation-state iron(II)–iron(III) oxide. This oxide is important as the magnetic component of *ferrofluids*—magnetic liquids. These liquids are attracted to magnetic fields; actually, the colloidal solid iron oxide particles within the bulk liquid are attracted into the magnetic field. A ferrofluid can be simply prepared by the reaction of iron(III) and iron(II) chlorides with aqueous ammonia in the presence of a surfactant (the surfactant prevents the oxide from coagulating and settling out):



## KEY IDEAS

- Metallic bonding is best described in terms of band theory derived from molecular orbital theory.
- Metal atoms can pack in only four ways.
- Each one of these packing arrangements has a characteristic simplest unit, the unit cell.
- Alloys, mixtures of two metals, can be solid solutions or alloy compounds.
- Nanometal particles can have significantly different properties from those of bulk metals.

## EXERCISES

- 4.1** Define the following terms: (a) electron-sea model of bonding; (b) unit cell; (c) alloy.
- 4.2** Explain the meanings of the following terms: (a) crystal lattice; (b) coordination number; (c) amalgam.
- 4.3** What are the three major characteristics of a metal?
- 4.4** What are the four most widely used metals?
- 4.5** Using a band diagram, explain how magnesium can exhibit metallic behavior when its 3s band is completely full.
- 4.6** Construct a band diagram for aluminum.
- 4.7** Explain why metallic behavior does not occur in the gas phase.
- 4.8** What is the likely formula of potassium in the gas phase? Draw a molecular orbital diagram to show your reasoning.
- 4.9** What are the two types of layer arrangements in metals? Which has the closer packing?
- 4.10** What is the difference in layer structure between cubic close-packed and hexagonal close-packed arrangements?
- 4.11** Draw the simple cubic unit cell and show how the number of atoms per unit cell is derived.
- 4.12** Draw the body-centered cubic unit cell and show how the number of atoms per unit cell is derived.
- 4.13** What conditions are necessary for the formation of a solid solution alloy?
- 4.14** Suggest two reasons why zinc and potassium are unlikely to form a solid solution alloy.



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## BEYOND THE BASICS

**4.15** Use geometry to show that about 48 percent of a simple cubic lattice is empty space.

**4.16** Use geometry to show that about 26 percent of a face-centered cubic lattice is empty space.

**4.17** In a face-centered cubic unit cell, the atoms usually touch across the diagonal of the face. If the atomic radius is  $r$ , calculate the length of each side of the unit cell.

**4.18** In a body-centered cubic unit cell, the atoms usually touch along the diagonal from one corner through the center of the cell to the opposite corner. If the atomic radius is  $r$ , calculate the length of each side of the unit cell.

**4.19** Chromium forms a body-centered cubic lattice in which the edge length of the unit cell is 288 pm. Calculate

(a) the metallic radius of a chromium atom and (b) the density of chromium metal.

**4.20** The atoms in barium metal are arranged in a body-centered cubic unit cell. Calculate the radius of a barium atom if the density of barium is  $3.50 \text{ g}\cdot\text{cm}^{-3}$ . *Hint:* Use your answer to Exercise 4.18.

**4.21** The atoms in silver metal are arranged in a face-centered cubic unit cell. Calculate the radius of a silver atom if the density of silver is  $10.50 \text{ g}\cdot\text{cm}^{-3}$ . *Hint:* Use your answer to Exercise 4.17.

**4.22** Suggest what might be a problem with placing two clean metal surfaces in contact in outer space.

**4.23** Research the properties of gold nanoparticles.

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# IONIC BONDING AND SOLID-STATE STRUCTURES

## CHAPTER 5

Chemical bonding can also occur through transfer of electrons and the subsequent electrostatic attraction between the charged particles. General chemistry courses usually imply that there is a rigid division between ionic and covalent bonding. In fact, there are few cases of “pure” ionic compounds, and chemical bonding is best regarded as a continuum between the extremes of covalent, ionic, and metallic bonding.

### Context: Superconductivity and Ionic Compounds

Magnetic resonance imaging (MRI) machines are now used widely in medicine. These instruments (and the equivalent scientific instrument, nuclear magnetic resonance (NMR) imaging) require the use of intense magnetic fields. To generate these fields, electromagnets with superconducting coils are essential. By “superconducting” we mean that a large electric current can pass through the magnet with almost zero resistance. If an ordinary electromagnet was used, the heat generated would cause the magnet to heat up and even, perhaps, become molten metal. To cool down a magnet so that it becomes superconducting is currently accomplished using liquid helium (boiling point 4.2 K). This liquid is very expensive and, as we shall see in Chapter 18, the world’s supplies of helium are dwindling. Thus, it is urgent that we try to synthesize materials that are superconducting at much higher temperatures—the ultimate goal being a material which will be superconducting at room temperature.

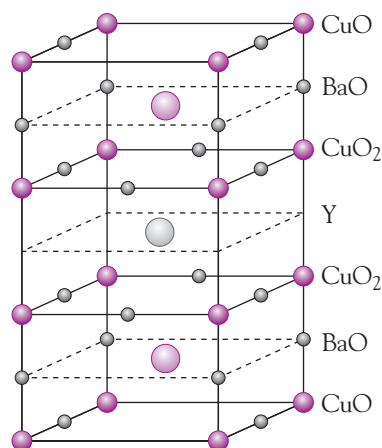
It was in 1911 that the property of superconductivity was first established by Kamerlingh Onnes. He found that below 4 K, mercury became superconducting. In 1962, superconducting alloys of niobium were identified. Today, nearly all hospital MRI machines use the intermetallic compound  $\text{Nb}_3\text{Sn}$  which becomes superconducting below 30 K. This is still a very low temperature, requiring liquid helium cooling.

The breakthrough came in Switzerland in 1985, when George Bedornz and K. Alex Müller prepared an oxide containing lanthanum, barium, and copper(II) ions. This compound becomes superconducting at 35 K, and Bedornz and Müller were awarded the Nobel Prize in Physics for their work. Since then, several families of superconducting complex ionic compounds have been synthesized. The highest superconducting compounds (superconducting as high as 133 K) so far have

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 5.1 The Ionic Model and the Size of Ions
- 5.2 Polarization and Covalency
- 5.3 Ionic Crystal Structures
- 5.4 Hydrated Salts
- 5.5 Isostructural Ionic Compounds
- 5.6 Perovskites
- 5.7 Spinel
- 5.8 Defects and Nonstoichiometry

three common features: their structures are related to the perovskite crystal lattice (see Section 5.6); they always contain slightly fewer oxygen atoms than the stoichiometry requires; and they usually contain copper as one of the metal ions. The figure below shows the ion lattice diagram of the superconducting compound  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , commonly abbreviated to YBCO. This compound was the first ever synthesized which exhibits superconductivity above the boiling point of liquid nitrogen. The most widely used copper-oxide superconductor is TBCCO-2223, composition  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ . Tens of kilometers of superconducting TBCCO-2223 electric cables are being used in the particle-accelerator called the Large Hadron Collider.



Ionic lattice diagram of the superconducting compound,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

## 5.1 The Ionic Model and the Size of Ions

Whereas covalent substances at room temperature can be solids, liquids, or gases, all conventional ionic compounds are solids and have the following properties:

1. Crystals of ionic compounds are hard and brittle.
2. Ionic compounds have high melting points.
3. When heated to the molten state (if they do not decompose), ionic compounds conduct electricity.
4. Many ionic compounds dissolve in high-polarity solvents (such as water), and, when they do, the solutions are electrically conducting.

According to the “pure” ionic model, some of the outermost electrons have been completely transferred from the element of lower electronegativity to the element of higher electronegativity. This model is surprisingly useful, although there is evidence for some small degree of covalency even when the electronegativity difference is very large. As we study the chemistry of the different groups, we will see many examples of covalent character in supposedly ionic compounds.

## A Comparison of Atomic and Ionic Radii

In Chapter 2, we saw that the size of atoms decreases from left to right in a period as a result of an increase in  $Z_{\text{eff}}$ . However, the conversion of many atoms to ions results in a significant change in size. The most noticeable examples are the main group metals, where cation formation usually involves the removal of all the outer (valence) electrons. The cation that remains possesses only the core electrons. Thus, the cation will be very much smaller than the parent atom. For example, the metallic radius of sodium is 186 pm, whereas its ionic radius is only 116 pm. In fact, the decrease in size is really more dramatic. The volume of a sphere is given by the formula  $V = \frac{4}{3}\pi r^3$ . Hence, the reduction of the radius of sodium on ionization actually means that the ion is one-fourth the volume of the atom!

For anions, the reverse situation is true: the negative ion is larger than the corresponding atom. For example, the covalent radius of the oxygen atom is 74 pm, whereas the radius of the oxide ion is 124 pm, resulting in a fivefold increase in volume. It can be argued that, with added electrons, the  $Z_{\text{eff}}$  on each individual outer electron will be less, resulting in a weaker nuclear attraction. There will also be additional inter-electron repulsions between the added electron and those present in the atom. Hence, the anion will be larger than the atom.

It should be noted that ionic radii cannot be measured directly and so the values are subject to error. For example, we can measure precisely the distance between the centers of a pair of sodium and chloride ions in a salt crystal, but this gives the sum of the two radii. The choice of how to apportion the distance between the two ions relies on an empirical formula rather than on a definitive measurement. In this text, we will use what are known as the Shannon-Prewitt values of ionic radii for consistency.

## Trends in Ionic Radii

The cation radii become even smaller if the ions have a multiple charge. We can see this from the set of isoelectronic ions in Table 5.1. Each of the ions has a total of 10 electrons ( $1s^2 2s^2 2p^6$ ). The only difference is the number of protons in the nucleus: the larger the proton number, the higher the effective nuclear charge,  $Z_{\text{eff}}$ , and hence the stronger the attraction between electrons and nucleus and the smaller the ion.

Table 5.2 shows that, for an isoelectronic series of anions, the smaller the nuclear charge, the larger the anion. These anions are isoelectronic with the cations in Table 5.1 and illustrate how much larger anions are than cations. It is *generally* true, then, that the metal cations are significantly smaller than the nonmetal anions.

**TABLE 5.1** Selected isoelectronic Period 3 cation radii

Ion	Radius (pm)
$\text{Na}^+$	116
$\text{Mg}^{2+}$	86
$\text{Al}^{3+}$	68

**TABLE 5.2** Selected isoelectronic Period 2 anion radii

Ion	Radius (pm)
$\text{N}^{3-}$	132
$\text{O}^{2-}$	124
$\text{F}^-$	117

**TABLE 5.3** Radii of the Group 17 anions

Ion	Radius (pm)
F <sup>-</sup>	119
Cl <sup>-</sup>	167
Br <sup>-</sup>	182
I <sup>-</sup>	206

**TABLE 5.4** Melting points of the potassium halides

Compound	Melting point (°C)
KF	857
KCl	772
KBr	735
KI	685

In Chapter 2, Section 2.5, we showed that atomic radius increases down each main group. It is also true that ions of the same charge, both anions and cations, increase in radius down a group. Values for the Group 17 anions are given in Table 5.3.

### Trends in Melting Points

The ionic bond is a result of the attraction of one ion to the ions of opposite charge that surround it in the crystal lattice. The melting process involves partially overcoming the strong ionic attractions and allowing the free movement of the ions in the liquid phase. The smaller the ion, the shorter the interionic distance; hence the stronger the electrostatic attraction and the higher the melting point. As shown in Table 5.3, the anion radii increase down the halogen group. This increase in radii corresponds to a decrease in melting points of the potassium halides (Table 5.4).

A second and usually more crucial factor in determining the value of melting points is ion charge: the higher the charge, the higher the melting point. Thus, magnesium oxide ( $\text{Mg}^{2+}\text{O}^{2-}$ ) has a melting point of 2800°C, whereas that of isoelectronic sodium fluoride ( $\text{Na}^+\text{F}^-$ ) is only 993°C.

## 5.2 Polarization and Covalency

Even though most combinations of metals and nonmetals have the characteristics of ionic compounds, there are a variety of exceptions. These exceptions arise when the outermost electrons of the anion are so strongly attracted to the cation that a significant degree of covalency is generated in the bond; that is, the electron density of the anion is distorted toward the cation. This distortion from the spherical shape of the ideal anion is referred to as *polarization*.

The chemist Kasimir Fajans developed the following rules summarizing the factors favoring polarization of ions and hence the increase in covalency:

1. A cation will be more polarizing if it is small and highly positively charged.
2. An anion will be more easily polarized if it is large and highly negatively charged.
3. Polarization is favored by cations that do not have a noble gas configuration.

A measure of the polarizing power of a cation is its *charge density*. The charge density is the ion charge (number of charge units times the proton charge in coulombs) divided by the ion volume. For example, the sodium ion has a charge of 1+ and an ionic radius of 116 pm (we use radii in millimeters to give an exponent-free charge density value). Hence,

$$\text{charge density} = \frac{1 \times (1.60 \times 10^{-19} \text{ C})}{\left(\frac{4}{3}\right) \times \pi \times (1.16 \times 10^{-7} \text{ mm})^3} = 24 \text{ C} \cdot \text{mm}^{-3}$$

Similarly, the charge density of the aluminum ion can be calculated as  $364 \text{ C} \cdot \text{mm}^{-3}$ . With a much greater charge density, the aluminum ion is much more polarizing than the sodium ion and so more likely to favor covalency in its bonding.

### Fajans' First Rule

Because the ionic radius is itself dependent on ion charge, we find that the value of the cation charge is often a good guide in determining the degree of covalency in a simple metal compound. As cation charge increases, the probability of covalent behavior increases.

One of the most obvious ways of distinguishing ionic behavior from covalent behavior is by observing melting points: those of ionic compounds (and network covalent compounds) tend to be high; those of small-molecule covalent compounds, low. This principle is illustrated by a comparison of two of the manganese oxides: manganese(II) oxide,  $\text{MnO}$ , and manganese(VII) oxide,  $\text{Mn}_2\text{O}_7$ . Studies have confirmed that high-melting manganese(II) oxide forms an ionic crystal lattice, whereas manganese(VII) oxide, a liquid at room temperature, consists of covalently bonded  $\text{Mn}_2\text{O}_7$  molecules. Table 5.5 shows that the ionic manganese(II) has a much lower charge density than the covalent manganese(VII).

### Fajans' Second Rule

To illustrate the effects of anion size, we can compare aluminum fluoride (m.p.  $1290^\circ\text{C}$ ) and aluminum iodide (m.p.  $190^\circ\text{C}$ ). The fluoride ion, with an ionic radius of 117 pm, is much smaller than the iodide ion, of radius 206 pm. In fact, the iodide ion has a volume more than five times greater than that of the fluoride ion. The fluoride ion cannot be polarized significantly by the aluminum ion. Hence, the bonding is essentially ionic. The electron density

**TABLE 5.5** A comparison of manganese(II) oxide and manganese(VII) oxide

Compound	Melting point ( $^\circ\text{C}$ )	Cation charge density ( $\text{C} \cdot \text{mm}^{-3}$ )	Bonding classification
$\text{MnO}$	1785	84	Ionic
$\text{Mn}_2\text{O}_7$	6	1238	Covalent

of the iodide ion, however, is distorted toward the high-charge-density aluminum ion to such an extent that covalently bonded aluminum iodide molecules are formed.

### Fajans' Third Rule

The third Fajans' rule relates to cations that do not have a noble gas electron configuration. Most common cations, such as calcium, have an electron configuration that is the same as that of the preceding noble gas (for calcium, [Ar]). However, some do not. The silver ion ( $\text{Ag}^+$ ), with an electron configuration of  $[\text{Kr}]4d^{10}$ , is a good example (among the others are  $\text{Cu}^+$ ,  $\text{Sn}^{2+}$ , and  $\text{Pb}^{2+}$ ). Since the ionic radius (and hence charge density) of the silver ion is close to that of the potassium ion, for the purely ionic model we might expect the melting points of silver salts to be close to those of the corresponding potassium salt. Table 5.6 shows that the melting point for silver chloride is considerably below that of potassium chloride.

We explain the comparatively low melting point of silver chloride as follows. In the solid phase, the silver ions and halide ions are arranged in a crystal lattice, like any other “ionic” compound. However, the overlap of electron density between each anion and cation is sufficiently high, it is argued, that we can consider the melting process to involve the formation of actual silver halide molecules. Apparently, the energy needed to change from a partial ionic solid to covalently bonded molecules is less than that needed for the normal melting process of an ionic compound.

Another indication of a difference in the bonding behaviors of the potassium ion and the silver ion is their different aqueous solubility. All of the potassium halides are highly water soluble, whereas the silver chloride, bromide, and iodide are essentially insoluble in water. The solution process, as we will see later, involves the interaction of polar water molecules with the charged ions. If the ionic charge is decreased by partial electron sharing (covalent bonding) between the anion and the cation, then the ion-water interaction will be weaker and the tendency to dissolve will be less. However, unlike the other silver halides, silver fluoride is soluble in water. This observation is consistent with Fajans' second rule, which predicts that silver fluoride should have the weakest polarization and the most ionic bonding of all the silver halides.

Often in chemistry, there is more than one way to explain an observed phenomenon. This is certainly true for the properties of ionic compounds. To illustrate this point, we can compare the oxides and sulfides of sodium and of

**TABLE 5.6** A comparison of potassium chloride and silver chloride

Compound	Melting point (°C)	Charge density ( $\text{C}\cdot\text{mm}^{-3}$ )	Bonding classification
KCl	770	11	Ionic
AgCl	455	15	Partially covalent

copper(I). Both these cations have about the same radius, yet sodium oxide and sodium sulfide behave as typical ionic compounds, reacting with water, whereas copper(I) oxide and copper(I) sulfide are almost completely insoluble in water. We can explain this in terms of the third rule of Fajans; that is, the non-noble gas configuration cation has a greater tendency toward covalency. Alternatively, we can use the Pauling concept of electronegativity and say that the electronegativity difference for sodium oxide of 2.5 would indicate predominantly ionic bonding, whereas that of copper(I) oxide (1.5) would indicate a major covalent character to the bonding.

### The Ionic-Covalent Boundary

Unfortunately, there is no firm predictable boundary between ionic and covalent behavior for solid compounds of metals and nonmetals as we first discussed in Chapter 3, Section 3.14. As predicted from Fajans' first rule, increasing theoretical cation charge results in increasing charge density, which will favor covalent behavior. However, as predicted by Fajans' second rule, the anion also plays a role: thus, as the metal oxidation state increases, the iodide is first likely to exhibit a low melting point, then the bromide, then the chloride, and finally the fluoride and oxide.

In aqueous solution, 1+ and 2+ hydrated cations are commonly found, the latter often as octahedral  $[\text{M}(\text{OH}_2)_6]^{2+}$  units. For 3+ ions,  $[\text{M}(\text{OH}_2)_6]^{3+}$ , such as aluminum (see Chapter 13, Section 13.6) and iron(III) (see Chapter 20, Section 20.6), the hydrated cations readily lose a hydrogen ion to give an acid solution and in this way reduce the charge of the "cluster":



With higher oxidation states, the free metal ions do not exist in solution. Instead, the metal ions sometimes reduce the charge by forming an oxo-cation. For example, vanadium(IV) in solution is found as the vanadyl ion,  $[\text{VO}]^{2+}$ , or more correctly,  $[\text{VO}(\text{OH}_2)_5]^{2+}$  (see Chapter 20, Section 20.5), while uranium(VI) occurs as the hydrated uranyl ion,  $[\text{UO}_2]^{2+}$  (see Chapter 24, Section 24.3). Guidelines for the type of bonding are given in Table 5.7.

**TABLE 5.7** Guidelines to bonding type for ionic compounds

Theoretical metal ion charge	Most predominant bonding type
+1	Ionic, except some lithium compounds
+2	Ionic, except some magnesium and beryllium compounds
+3	Covalent, except some oxides and fluorides of the heavier elements and hydrated cations
+4, +5	Covalent, except some oxides and fluorides of the heavier elements and oxo-cations
+6	Covalent, except some oxides and oxo-cations
+7, +8	Covalent



**WORKED EXAMPLE 5.1**

Thallium forms two series of compounds, one in which it has a charge of  $1+$ , and one in which it has a charge of  $3+$ . Write the formula of a compound of thallium with a halide ion which is most likely to be (a) ionic, (b) covalent.

**Answer**

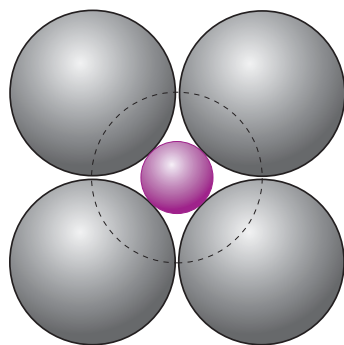
a) The metal ion should have the lower charge and it should be combined with the least-polarizable halide ion, fluoride. The answer is thallium(I) fluoride,  $\text{TlF}$ .

b) The metal ion should have the higher charge and it should be combined with the most-polarizable halide ion, iodide. The answer is thallium(III) iodide,  $\text{TlI}_3$ . ■

**5.3 Ionic Crystal Structures**

In Chapter 4, Section 4.3, we showed four different packing arrangements for metal atoms. The same packing arrangements are common among ionic compounds as well. Generally, the anions are much larger than the cations; thus, it is the anions that form the array and the smaller cations fit in holes (called *interstices*) between the anions. Before discussing the particular types of packing, however, we should consider general principles that apply to ionic lattices:

1. Ions are assumed to be charged, incompressible, nonpolarizable spheres. We have seen that there is usually some degree of covalency in all ionic compounds, yet the hard sphere model seems to work quite well for most of the compounds that we classify as ionic.
2. Ions try to surround themselves with as many ions of the opposite charge as possible and as closely as possible. This principle is of particular importance for the cation. Usually, in the packing arrangement adopted, the cation is just large enough to allow the anions to surround it without touching one another.
3. The cation-to-anion ratio must reflect the chemical composition of the compound. For example, the crystal structure of calcium chloride,  $\text{CaCl}_2$ , must consist of an array of chloride anions with only half that number of calcium cations fitting in the interstices in the crystal lattice.



**FIGURE 5.1** Representation of six anions surrounding a cation.

**Ion Packing and Radius Ratios**

As mentioned in point 2, the packing arrangement adopted by an ionic compound is usually determined by the comparative sizes of the ions. Figure 5.1 shows four solid circles representing the anions of part of a body-centered

**TABLE 5.8** The range of radius ratios corresponding to different ion arrangements

$r_+/r_-$ Values	Coordination number preferred	Name
0.732 to 0.999	8	Cubic
0.414 to 0.732	6	Octahedral
0.225 to 0.414	4	Tetrahedral

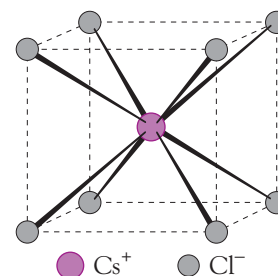
cubic anion array and a dashed circle representing the anions below and above the plane. To fit exactly in the space between these six anions, the cation has to be the size shown by the shaded circle. By using Pythagoras' theorem, we can calculate that the optimum ratio of cation radius to anion radius is 0.414. The numerical value,  $r_+/r_-$ , is called the *radius ratio*.

If the cation is larger than one giving the optimum 0.414 ratio, then the anions will be forced apart. In fact, this happens in most cases, and the increased anion-anion distance decreases the anion-anion electrostatic repulsion. However, when the radius ratio reaches 0.732, it becomes possible for eight anions to fit around the cation. Conversely, if the radius ratio is less than 0.414, the anions will be in close contact and the cations will be “rattling around” in the central cavity. Rather than allowing this to happen, the anions rearrange to give smaller cavities surrounded by only four anions. A summary of the radius ratios and packing arrangements is given in Table 5.8.

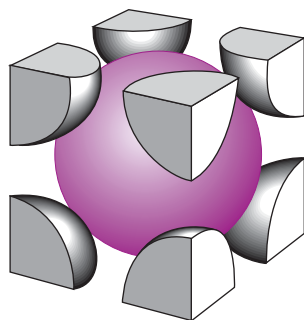
### The Cubic Case

The best way to picture the ionic lattice is to consider the anion arrangement first and then look at the coordination number of the interstices in the anion arrays. The packing arrangement of anions which can accept the largest cation is the simple cubic array. Considering the simple cubic unit cell, with spheres at each corner of a cube, the cation can then fit into the center of the cube.

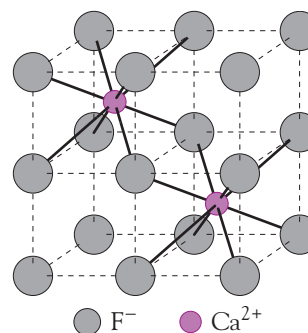
The classic example is *cesium chloride*, and this compound gives its name to the lattice arrangement. The chloride anions adopt a simple cubic packing arrangement, with each cation sitting at the center of a cube. In cesium chloride, the radius ratio of 0.934 indicates that the cations are sufficiently large to prevent the anions from contacting one another. To enhance our visualization of the various ion arrangements, we will display most of the ionic structures as *ionic lattice diagrams*. In these diagrams, the ionic spheres have been shrunk in size and solid lines have been inserted to represent points of ionic contact. Ionic lattice diagrams show the coordination numbers of the ions more clearly than the space-filling representation. But they give a false impression that the lattice is mostly empty space when, in reality, it consists of closely packed ions of very different ionic radii. The ionic lattice diagram for cesium chloride is shown in Figure 5.2.



**FIGURE 5.2** Ionic lattice diagram of cesium chloride. [Adapted from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed. (New York: Oxford University Press, 1984), p. 246.]



**FIGURE 5.3** Unit cell of cesium chloride. [Adapted from G. Rayner-Canham et al., *Chemistry: A Second Course* (Don Mills, ON, Canada: Addison-Wesley, 1989), p. 72.]



**FIGURE 5.4** Partial ionic lattice diagram of calcium fluoride.

In Chapter 4, Section 4.4, we saw that for metals, when the crystal packing arrangement and the density are known, the metallic radius of the element can be calculated. For ionic compounds adopting the cesium chloride structure, we can determine equally unit cell dimensions and the ionic radii of one or another of the ions.

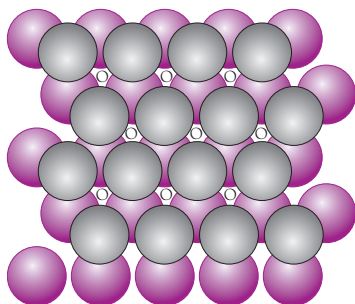
The cesium chloride unit cell is shown in Figure 5.3; it contains one cesium ion and  $8(\frac{1}{8})$  chloride ions. Hence, each unit cell contains, in total, one formula unit. The cesium cation separates the chloride anions, so the ions only make contact along a diagonal line that runs from one corner through the center of the unit cell to the opposite corner. This diagonal has a length equal to the sum of two anion radii and two cation radii.

If the cation-to-anion stoichiometry is not 1:1, then the less common ion occupies a certain proportion of the spaces. A good example is calcium fluoride,  $\text{CaF}_2$ , in which the cation-to-anion ratio is 1:2. This is called the *fluorite* structure, after the mineral name of calcium fluoride. Each calcium ion is surrounded by eight fluoride ions, similar to the cesium chloride structure. However, each alternate cation location (that is, every other space) in the lattice is empty, thus preserving the 1:2 cation-to-anion ratio (Figure 5.4).

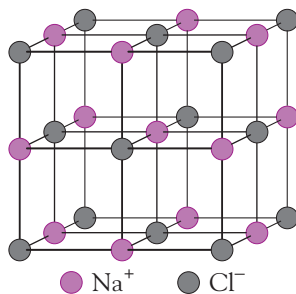
It is also possible to have cation-to-anion ratios of 2:1, as found for lithium oxide. The structure is again based on the cesium chloride lattice, but this time every alternate anion site is empty. Because the unoccupied lattice spaces in the lithium oxide structure are the opposite of those left unoccupied in the calcium fluoride (fluorite) structure, the name given to this arrangement is the *antifluorite* structure.

### The Octahedral Case

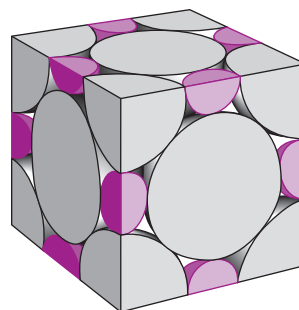
When the radius ratio falls below 0.732, the anions in the cesium chloride structure are no longer held apart by the cations. The potential repulsions between



**FIGURE 5.5** The first two layers of the cubic close-packed anion array, showing the octahedral holes (O) in which cations can fit.



**FIGURE 5.6** Ionic lattice diagram of sodium chloride. [Adapted from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed. (New York: Oxford University Press, 1984), p. 239.]



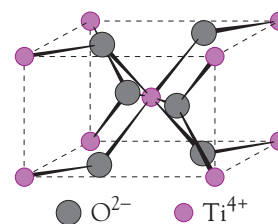
**FIGURE 5.7** Unit cell of sodium chloride. [Adapted from G. Rayner-Canham et al., *Chemistry: A Second Course* (Don Mills, ON, Canada: Addison-Wesley, 1989), p. 71.]

the anions cause the octahedral geometry to become the preferred arrangement. For this smaller radius ratio, six anions can fit around a cation without touching one another (see Figure 5.1). The actual anion arrangement is based on the cubic close-packed array in which there are octahedral holes and tetrahedral holes. Figure 5.5 shows the array with an O marking the location of the octahedral holes in which the cations can fit.

In the octahedral packing, all the octahedral holes are filled with cations and all of the tetrahedral holes are empty. *Sodium chloride* adopts this particular packing arrangement, and it gives its name to the structure. In the unit cell—the smallest repeating unit of the structure—the chloride anions form a face-centered cubic arrangement. Between each pair of anions is a cation. Because the cations are acting as separators of the anions, alternating cations and anions touch along the edge of the cube. The ionic lattice diagram shows that each sodium ion has six nearest-neighbor chloride ions and each chloride anion is surrounded by six sodium ions (Figure 5.6).

The sodium chloride unit cell (Figure 5.7) contains one central sodium ion plus  $12(\frac{1}{4})$  sodium ions along the edges. The centers of the faces hold  $6(\frac{1}{2})$  chloride ions, and the corners of the cube hold  $8(\frac{1}{8})$  more. As a result, the sodium chloride unit cell contains four formula units. The length of the side of the cube is the sum of two anion radii and two cation radii (note: the anions touch across the cell face only in the case of the limiting radius ratio).

It is also possible to have octahedral packing for compounds with stoichiometries other than 1:1. The classic example is that of titanium(IV) oxide,  $\text{TiO}_2$  (mineral name, *rutile*). For the crystal, it is easiest to picture the titanium(IV) ions as forming a distorted body-centered array (even though they are much smaller than the oxide anions), with the oxide ions fitting in between (Figure 5.8).



**FIGURE 5.8** Ionic lattice diagram of titanium(IV) oxide. [Adapted from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed. (New York: Oxford University Press, 1984), p. 247.]

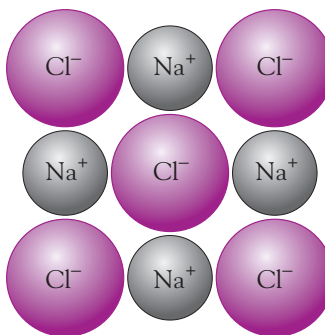
**WORKED EXAMPLE 5.2**

The length of the side of the sodium chloride unit cell is 566 pm. If the ionic radius of the sodium ion is 116 pm:

- What is the radius of the chloride ion.
- Show that, for sodium chloride, the chloride ions are not in contact across the diagonal.

**Answer**

- The ions are in contact along the edge of the unit cell as shown in the following figure.



So the length of a side =  $2r(\text{Na}^+) + 2r(\text{Cl}^-)$ .

$$566 \text{ pm} = 2(116 \text{ pm}) + 2r(\text{Cl}^-)$$

$$r(\text{Cl}^-) = 167 \text{ pm}$$

- The diagonal length can be found using Pythagoras' theorem:

$$d^2 = [a^2 + a^2]^{\frac{1}{2}} = [(566 \text{ pm})^2 + (566 \text{ pm})^2]^{\frac{1}{2}} = 800 \text{ pm}$$

The sum of four chloride ion radii =  $4 \times (167 \text{ pm}) = 668 \text{ pm}$ .

Therefore, the chloride ions do not touch across the diagonal. ■

**WORKED EXAMPLE 5.3**

The length of the side of the sodium chloride unit cell is 566 pm. Calculate the density of sodium chloride in  $\text{g}\cdot\text{cm}^{-3}$ .

**Answer**

The density of a solid is given by the equation,  $\rho = \text{mass}/\text{volume}$ .

The density of a unit cell will be the same as the density of the bulk NaCl, so we can use the mass and the volume of one unit cell.

One unit cell contains 4 atoms of Na and 4 atoms of Cl, so its mass is

$$\frac{(4 \times 22.99) + (4 \times 35.45)}{6.023 \times 10^{23}} = 2.35 \times 10^{-22} \text{ g.}$$

The length of the unit cell side is  $566 \times 10^{-10}$  cm giving a unit-cell volume of  $(566 \times 10^{-10})^3 = 1.81 \times 10^{-22}$  cm<sup>3</sup>.

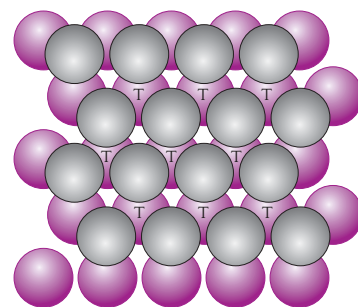
The density,

$$\rho = \frac{2.35 \times 10^{-22} \text{ g}}{1.81 \times 10^{-22} \text{ cm}^3} = 1.29 \text{ g} \cdot \text{cm}^{-3} \blacksquare$$

### The Tetrahedral Case

Ionic compounds in which the cations are very much smaller than the anions can be visualized as close-packed arrays of anions, with the cations fitting into the tetrahedral holes (the octahedral holes are always empty). Both hexagonal close-packed (*hcp*) and cubic close-packed (*ccp*) arrangements are possible, and usually a compound will adopt one or the other, although the reasons for particular preferences are not well understood. Figure 5.9 shows the *ccp* array; a T marks the location of the tetrahedral holes.

The prototype of this class is zinc sulfide, ZnS, which exists in nature in two crystal forms: the common mineral *sphalerite* (formerly called *zinc blende*), in which the sulfide ions form a *ccp* array; and *wurtzite*, in which the anion array is *hcp* (see Chapter 4). Both structures have twice as many tetrahedral holes as cations, so only alternate cation sites are filled (Figure 5.10).

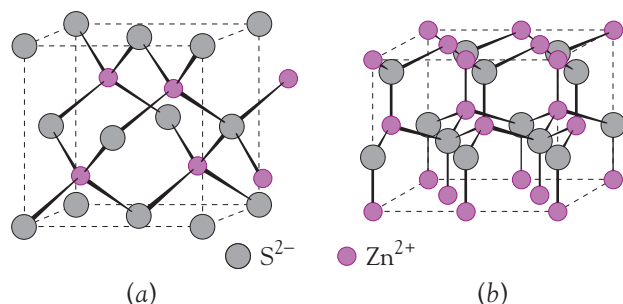


**FIGURE 5.9** The first two layers of the cubic close-packed anion array, showing the tetrahedral holes (T) in which cations can fit.

### Quantum Dots

The nanochemistry field of quantum dots relates to wurtzite and sphalerite structures, particularly the wurtzite structure of cadmium selenide, CdSe. Quantum dots are nanoparticles of tetrahedral-structure semiconductors (such as cadmium selenide) in a size range of 1 to 100 nm. Particles of these dimensions exhibit a property known as *quantum confinement*. Quantum confinement results when the electrons in a substance are restricted to a very small volume and the properties of the solid become dependent on particle size.

One particularly noticeable effect of quantum confinement is that particle size determines optical properties. For materials such as cadmium selenide,



**FIGURE 5.10** Ionic lattice diagrams of the two forms of zinc sulfide: (a) sphalerite; (b) wurtzite. [Adapted from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed. (New York: Oxford University Press, 1984), p. 121.]

which fluoresces under ultraviolet light, the larger the particle, the more the emission tends toward the red end of the spectrum, while a decrease in size shifts the emission to the blue end of the spectrum. As a result, very precise color emissions can be produced if the particle size range is carefully controlled.

Several semiconducting materials exhibit such properties, all of which have the wurtzite or sphalerite structures. These materials include the cadmium compounds with the heavier Group 16 elements: cadmium sulfide, CdS; cadmium selenide, CdSe; and cadmium telluride, CdTe. Quantum dots can also be produced by forming a monolayer of indium arsenide, InAs, over nanoparticles of indium phosphide, InP, or gallium arsenide, GaAs. It is the mismatch of ion sizes on the surface to that of the crystal lattice itself that results in the fluorescent behavior.

### Exceptions to the Packing Rules

Until now, we have discussed the different packing arrangements and their relationship to the radius ratio. However, the radius ratio is only a guide, and although many ionic compounds do adopt the predicted packing arrangement, there are many exceptions. In fact, the packing rules appear to predict the correct arrangement in about two-thirds of cases. Table 5.9 shows three of the exceptions.

Chemistry is not a simplistic subject, and to reduce the reasons for a specific packing arrangement to one single criterion, the radius ratio, is to disregard many factors. In particular, we discussed earlier that there is an appreciable degree of covalent bonding in most ionic compounds. Thus, the hard sphere model of ions is not considered valid for many compounds. For example, mercury(II) sulfide is likely to have such a high degree of covalency in its bonding that the compound might be equally well regarded as a network covalent substance, like diamond or silicon dioxide (see Chapter 3, Section 3.10). A high degree of covalency would specifically explain the preference of mercury(II) sulfide for the tetrahedral coordination of the ZnS structure, because in its covalent compounds, mercury(II) often forms four covalent bonds arranged at the tetrahedral angles.

Partial covalent behavior is also observed in lithium iodide. On the basis of standard values for ionic radii, its adoption of the octahedral coordination of the sodium chloride lattice makes no sense. The iodide anions would be in contact with one another, and the tiny lithium ions would “rattle around” in the octahedral holes. However, the bonding in this compound is believed to be about 30 percent covalent, and crystal structure studies show that the electron density of the lithium is not spherical but stretched out toward each of the six surrounding anions. Thus, lithium iodide, too, cannot be considered a “true” ionic compound.

**TABLE 5.9** Selected examples of exceptions to the packing predicted by the radius ratio rule

Compound	$r_+/r_-$	Expected packing	Actual packing
HgS	0.55	NaCl	ZnS
LiI	0.35	ZnS	NaCl
RbCl	0.84	CsCl	NaCl

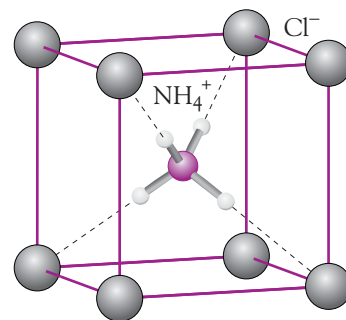


Furthermore, there is evidence that the energy differences between the different packing arrangements are often quite small. For example, rubidium chloride normally adopts the unexpected sodium chloride structure (see Table 5.9), but crystallization under pressure results in the cesium chloride structure. Thus, the energy difference in this case between the two packing arrangements must be very small.

Finally, we must keep in mind that the values of the ionic radii are not constant from one environment to another. For example, the cesium ion has a radius of 181 pm only when it is surrounded by six anion neighbors. With eight neighbors, such as we find in the cesium chloride lattice, it has a Shannon-Prewitt radius of 188 pm. This is not a major factor in most of our calculations, but with small ions there is a very significant difference. For lithium, the four-coordinated ion has a radius of 73 pm, whereas that of the crowded six-coordinated ion is 90 pm. For consistency in this text, all ionic radii quoted are for six-coordination, except for the Period 2 elements, for which four-coordination is much more common and realistic.

### Crystal Structures Involving Polyatomic Ions

Up to this point, we have discussed only binary ionic compounds, but ionic compounds containing polyatomic ions also crystallize to give specific structures. In these crystals, the polyatomic ion occupies the same site as a monatomic ion. For example, ammonium chloride forms a cesium chloride structure at room temperature (see Chapter 11, Section 11.13), with the ammonium ions occupying the cation sites (Figure 5.11).



**FIGURE 5.11** Ion lattice diagram of ammonium chloride.

#### WORKED EXAMPLE 5.4

Predict which structure is adopted by titanium(II) oxide. The ionic radii are:  $\text{Ti}^{2+}$  86 pm,  $\text{O}^{2-}$  140 pm.

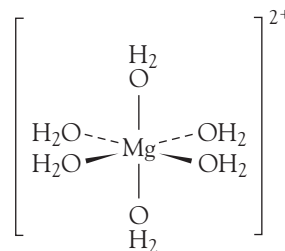
#### Answer

The structure can be predicted from the radius ratio,  $r_+/r_-$ , which for  $\text{TiO}$  is  $86/140 = 0.614$ . This indicates an octahedral arrangement and, as  $\text{TiO}$  has a 1:1 stoichiometry, we can predict that it adopts the sodium chloride structure. ■

## 5.4 Hydrated Salts

When an ionic compound crystallizes from an aqueous solution, water molecules often become incorporated in the solid crystal. These water-containing ionic compounds are known as *hydrates*. In some hydrates, the water molecules are simply sitting in holes in the crystal lattice, but in the majority of hydrates, the water molecules are associated closely with either the anion or the cation, usually the cation.

In the hydrated cation, the  $\delta^-$  oxygen atoms of the water molecules are electrostatically attracted toward the positively charged metal ions (see Figure 5.12). The hydrated cation is then closer in size to the anion. For example, magnesium nitrate only exists in the solid phase as the hexahydrate,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , where the



**FIGURE 5.12** Shape of the  $[\text{Mg}(\text{OH}_2)_6]^{2+}$  ion.



hydrated magnesium cation occupies the cation sites and the nitrate ion, the anion sites. The six water molecules are organized in an octahedral arrangement around the magnesium ion, with the oxygen atoms oriented toward the magnesium ion, and so, the solid compound is more accurately represented as:  $[\text{Mg}(\text{OH}_2)_6]^{2+}(\text{NO}_3^-)_2$  (the water molecule is written reversed to indicate that it is the  $\delta^-$  oxygen that forms an ion-dipole interaction with the positive magnesium ion).

The extent of hydration of ions in the solid phase usually correlates with the ion charge and size, in other words, the charge density. We can therefore account for the anhydrous nature of the simple binary alkali metal salts, such as sodium chloride, because both ions have low charge densities. Crystallization of an ion with a 3+ charge from aqueous solution always results in a hexahydrated ion in the crystal lattice. That is, the small, highly charged cation causes the ion-dipole interaction to be particularly strong.

The more highly charged oxyanions are almost always hydrated, with the  $\delta^+$  hydrogen atoms of the water molecules attracted toward the anions. Hydration of anions is usually less than that of the (smaller) cations. For example, many metal sulfates, including magnesium sulfate, are heptahydrates:  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . In these sulfates, six of the water molecules surround the metal ion, as for the nitrate, while the seventh water molecule is hydrogen-bonded to the sulfate ion through an interaction between the  $\delta^+$  of one hydrogen of the water with the  $\delta^-$  of one of the oxygen atoms of the sulfate ion, that is  $[\text{SO}_4(\text{HOH})]^{2-}$ .

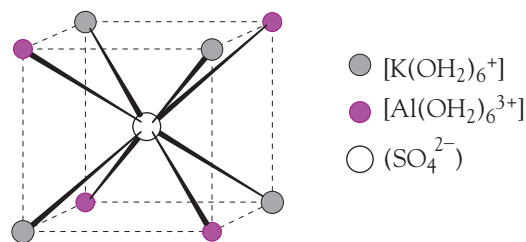
## 5.5 Isostructural Ionic Compounds

Isostructural ionic compounds are pairs or sets of compounds in which replacement of one ion by another leaves the crystal structure unchanged. That is, the ions are packed in the same way in the crystal lattice. Before chemists were able to determine the structure of crystals, different parallel compounds were studied according to the crystal shape. Thus, the former term for isostructural was *isomorphous* referring to crystals having the same shape. In this section, we will explore examples of isostructural compounds and describe the principles of isostructuralism.

### Alums

A good example of isostructural compounds is provided by the family of compounds called the *alums*, which have the generic formula  $\text{M}^+\text{M}^{3+}(\text{SO}_4^{2-})_2 \cdot 12\text{H}_2\text{O}$ . The possible monovalent cations,  $\text{M}^+$ , include potassium, rubidium, or ammonium, while the trivalent cation,  $\text{M}^{3+}$ , is most commonly aluminum, chromium(III), or iron(III).

The “parent” compound, potassium aluminum sulfate (commonly called alum), has the formula  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . As mentioned in Section 5.4, small high-charge cations are usually hydrated when crystals form from aqueous solution, and alum is no exception. In fact, the monovalent ions are also hexahydrated so the correct formulation is  $[\text{K}(\text{OH}_2)_6]^+[\text{Al}(\text{OH}_2)_6]^{3+}(\text{SO}_4^{2-})_2$ . The structure is essentially that of the cesium chloride lattice, but with the two hydrated cations,  $[\text{K}(\text{OH}_2)_6]^+$  and  $[\text{Al}(\text{OH}_2)_6]^{3+}$  occupying alternating sites at the corners of the cube and the sulfate ion in the center (Figure 5.13).



**FIGURE 5.13** Ion lattice diagram of an alum.

Large crystals can be grown simply by mixing equimolar mixtures of the monovalent sulfate and the trivalent sulfate. Thus, alums are favorite compounds for crystal-growing competitions. The name “alum” specifically pertains to the colorless aluminum-containing compound (see Chapter 13, Section 13.8), the others being named “chrome alum” (deep purple) and “ferric alum” (pale violet). The similarities in the sets of ionic radii can be seen in Table 5.10, although with the six molecules of water surrounding each ion, the “real” radius is significantly greater. Nevertheless, it can be seen that the monovalent and trivalent cations have to be within a certain range of radius. The lattice energy of alums is very high, accounting for the high stability of the compounds. In fact, alum is the most convenient water-soluble compound of aluminum, while ferric alum is a stable and convenient compound of iron(III).

### Principles of Isostructural Substitution

What determines the ability of an ion to substitute while maintaining the same crystal structure? There are two principles of isostructural substitution. The first principle states:

**One ion may substitute for another in a lattice if the two ions have identical charges and differ in radii by no more than 20 percent.**

This principle is really a restatement of the radius-ratio rules that were discussed in Section 5.3. A large difference in ionic radii precludes isostructuralism, but close values of ionic radii do not necessarily mean isostructuralism will occur.

In many cases, mixed structures can be formed. For example, pale purple crystals can be formed by crystallizing a mixture of alum and chrome alum, the crystals having the lattice sites of the 3+ ions randomly filled by aluminum and chromium(III) ions. Isostructuralism is of particular importance in mineral chemistry. For example, many precious gems involve isostructural substitution. Ruby is aluminum oxide containing some chromium(III) ion in place of the

**TABLE 5.10** A comparison of cation radii in alums

Monovalent ions		Trivalent ions	
K <sup>+</sup>	152 pm	Al <sup>3+</sup>	68 pm
Rb <sup>+</sup>	166 pm	Cr <sup>3+</sup>	75 pm
NH <sub>4</sub> <sup>+</sup>	151 pm	Fe <sup>3+</sup>	78 pm

**TABLE 5.11** Some comparative ion sizes

Ionic radii	+1 Charge	+2 Charge	+3 Charge	+4 Charge	+5 Charge
<b>Small</b>		Be <sup>2+</sup>	Al <sup>3+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup>	Si <sup>4+</sup>	P <sup>5+</sup>
<b>Medium</b>	Li <sup>+</sup>	Mg <sup>2+</sup> , Fe <sup>2+</sup>		Ti <sup>4+</sup>	W <sup>5+</sup>
<b>Large</b>	Na <sup>+</sup>	Ca <sup>2+</sup>	La <sup>3+</sup>		
<b>Very large</b>	K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	Ba <sup>2+</sup>			

aluminum ion. Thus, its formula is represented as  $(\text{Al}^{3+}, \text{Cr}^{3+})_2(\text{O}^{2-})_3$ . Likewise, sapphires contain titanium(III) in aluminum oxide:  $(\text{Al}^{3+}, \text{Ti}^{3+})_2(\text{O}^{2-})_3$ .

The composition of the natural gemstones reflects the composition of the molten rock from which the crystals formed. This is true of many minerals. As an example, olivine is a mixed magnesium/iron(II) silicate,  $(\text{Mg}^{2+}, \text{Fe}^{2+})_2(\text{SiO}_4^{4-})$ , where varying ratios of magnesium and iron(II) ions occupy the same lattice sites. The classic example of isostructural substitution is that of the lanthanoid phosphates,  $\text{MPO}_4$ , where  $\text{M}^{3+}$  is any of the lanthanoids. These ions are so similar in radii that the naturally occurring phosphate ore monazite usually contains a mixture of all the lanthanoids.

A second principle of isostructural substitution is applicable to compounds containing two different cations. This principle states:

**Isostructural substitution can occur by ions of different charges but the same radii as the ions they replace, provided the sum of the cation charges remains the same.**

Many examples are found in the important series of minerals called the *perovskites* (see Section 5.6 below). The parent compound is  $(\text{Ca}^{2+})(\text{Ti}^{4+})(\text{O}^{2-})_3$ , while one of the many other compounds adopting this structure is  $(\text{Na}^+)(\text{W}^{5+})(\text{O}^{2-})_3$ , where the monopositive sodium has replaced the similar-size dipositive calcium ion and the pentapositive tungsten ion has replaced the tetrapositive titanium ion. Some of the common substitution possibilities are shown in Table 5.11. (Note that drawing divisions in ionic radii is somewhat arbitrary; for example, an ion at the high end of the “small” category might well substitute for an ion at the low end of the “medium” category.)

## New Materials: Beyond the Limitations of Geochemistry

Most minerals are formed in the Earth under conditions of high temperature and pressure over millions of years. Now two chemists, Sandra Dann and Mark Weller, have produced minerals with novel compositions that never before existed. The minerals produced in geochemical processes reflect the abundances of the constituent elements in the Earth's crust. The two chemists have used the principles of isostructural substitution to manufacture minerals involving extremely rare elements. For example, they have synthesized an

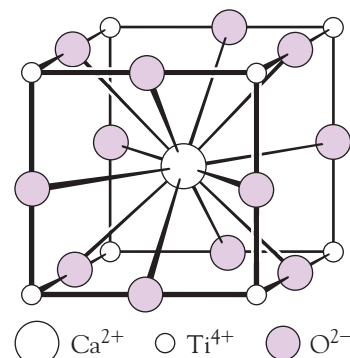
analog of sodalite,  $\text{Na}_8[\text{SiAlO}_4]\text{Cl}_2$ , in which each of the elements (except sodium) is replaced by the element one below it in the periodic table. The new compound,  $\text{Na}_8[\text{GeGaO}_4]\text{Br}_2$ , is unlikely to exist naturally anywhere in the universe since the abundances of the replacement elements are on the order of  $10^8$  less abundant than those in sodalite itself. Such novel compounds have potential as pigments, fluorescers, ferroelectrics, ion exchange materials, catalysts, and magnetic storage devices.

## 5.6 Perovskites

In this text, we will confine ourselves to ternary species containing one anion and two different cations. Actually, things are comparatively simple in that the large majority of ternary compounds are variations of two basic structures: the spinels and the perovskites. In this section, we will discuss the perovskites.

Perovskites have the general formula  $ABO_3$ , where A is usually a large dipositive metal ion and B is generally a small tetrapositive metal ion. It is important to distinguish these mixed-metal oxides from the oxyanion salts that we generally study in inorganic chemistry. The metal salts of oxyanions can have a formula parallel to that of a perovskite:  $AXO_3$ , involving a metal (A), a nonmetal (X), and oxygen. In these compounds, the  $XO_3$  consists of a covalently bonded polyatomic ion. For example, sodium nitrate consists of the  $Na^+$  and  $NO_3^-$  ions arrayed in a sodium chloride structure, in which each nitrate ion occupies the site equivalent to the chloride ion site. However, in perovskites, such as the parent compound calcium titanate,  $CaTiO_3$ , there is no such thing as a “titanate ion.” Instead, the crystal lattice consists of independent  $Ca^{2+}$ ,  $Ti^{4+}$ , and  $O^{2-}$  ions.

The ion arrangement in the perovskite structure is shown in the ion-lattice diagram in Figure 5.14. The large calcium ion occupies the center of the cube; it is surrounded by 12 oxide ions. Eight titanium(IV) ions are located at the cube corners; each has six oxide neighbors (three being in adjacent unit cells). Many perovskites are ferroelectric materials (although they contain no iron).



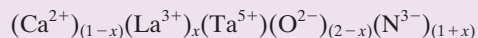
**FIGURE 5.14** Ion lattice diagram of the perovskite structure.

### New Pigments through Perovskites

Inorganic compounds are the mainstay of the pigment industry. Whenever permanent colors are required, inorganic compounds are preferred over organic ones for their long-term stability. Traditionally, lead(II) carbonate was used for white; yellow to red is provided by cadmium sulfide; green, by chromium(III) oxide; brown, by iron(III) oxide; and blue, by complex copper(II) compounds. A replacement for lead(II) carbonate has been titanium(IV) oxide. Cadmium sulfide has been particularly useful because the compound is very insoluble and extremely light-stable. By altering the particle size, it is possible to produce any color between yellow and red. However, a replacement for cadmium sulfide would remove one more toxic compound from the artist's palette and from the commercial paint industry.

To find a brilliant and pure color, it is necessary to find a compound in which there is a very sharp electronic transition. For gases, we can get very pure transitions, but the atoms and ions in solids usually give very “fuzzy”

absorptions; that is, because of the atomic vibrations in the solid, there is a range of ground and excited states. As a result, very broad absorption spectra are obtained. The solution has been found in a series of perovskites. This series has calcium ( $Ca^{2+}$ ) and lanthanum(III) ( $La^{3+}$ ) as the large low-charge cations, tantalum(V) ( $Ta^{5+}$ ) as the small cation, and oxide ( $O^{2-}$ ) and nitride ( $N^{3-}$ ) as the anions. The generic structure is



As the ratio of the 2+ calcium and the 3+ lanthanum changes, so the ratio of the 2- oxide and the 3- nitride must change in step to maintain electrical neutrality. By varying the proportion of the cations and anions, it is possible to synthesize pure colors ranging from a bright yellow, where  $x = 0.15$ , to an intense red, where  $x = 0.90$ . This is a great advance in color chemistry, for it is now possible to produce a very precise color just by adjusting the element ratio.

Such compounds can convert a mechanical pulse into an electrical signal (and vice versa), a property that is important for many electronic devices.

On this planet, the most important perovskite is the mixed magnesium iron silicate  $(\text{Mg,Fe})\text{SiO}_3$ . It is the major component of the lower mantle, the layer of the Earth between a depth of 670 and 2900 km. This compound consists of  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  ions alternating in the  $\text{M}^{2+}$  sites at the center of the unit cubes,  $\text{Si}^{4+}$  “ions” at the corners, and  $\text{O}^{2-}$  ions occupying the anion sites. (In the silicate perovskites, the silicon-oxygen bonds probably have significant covalent character.)

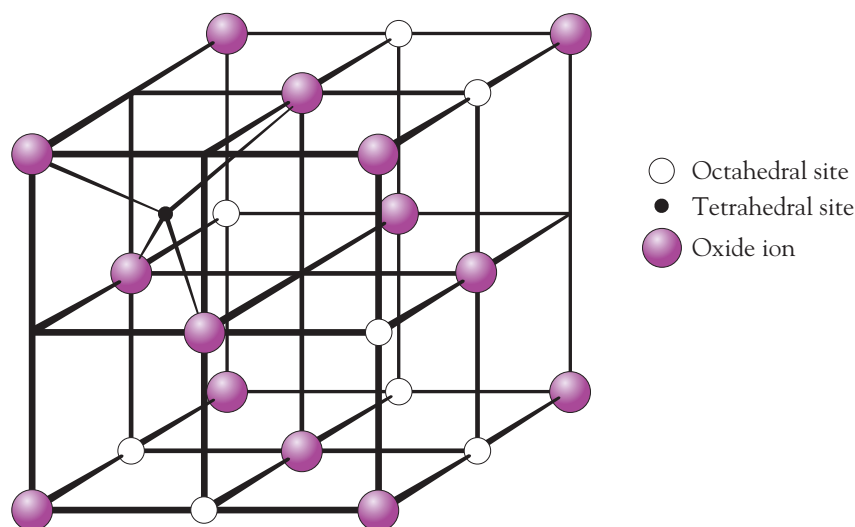
## 5.7 Spinel

Spinel itself is magnesium aluminum oxide,  $\text{MgAl}_2\text{O}_4$ , but of more importance are the enormous number of compounds that adopt the same crystal structure and are also called *spinel*s. Many of these compounds have unique properties that will make them important in the chemistry of the twenty-first century. The general formula of a spinel is  $\text{AB}_2\text{X}_4$ , where A is usually a dipositive metal ion; B, usually a tripositive metal ion; and X, a dinegative anion, usually oxygen.

The framework of the unit cell of a spinel consists of 32 oxide ions in an almost perfect ccp arrangement. Thus, the unit cell composition is actually  $\text{A}_8\text{B}_{16}\text{O}_{32}$ . Figure 5.15 shows one-eighth of the unit cell. The oxide ions form a *fcc* array, and there are octahedral sites at the center of the cube and in the middle of each cube edge and tetrahedral sites in the middle of each “cubelet.” In the normal spinel structure, the 8 A cations occupy one-eighth of the tetrahedral holes and the 16 B cations occupy one-half of the octahedral holes. Thus, the unit cell can be considered to consist of “cubelets” of zinc sulfide-type tetrahedral units interspersed among “cubelets” of sodium chloride-type octahedral units.

To indicate site occupancy, we can use the subscripts *t* and *o* to represent tetrahedral and octahedral cation sites; thus, spinel itself is  $(\text{Mg}^{2+})_t(2\text{Al}^{3+})_o(\text{O}^{2-})_4$ . There are some spinels in which the dipositive ions are located in the octahedral sites. Because there are twice as many available octahedral (B) sites as available tetrahedral (A) sites in the spinel structure, only half of the tripositive ions can be placed in tetrahedral sites; the remainder must occupy octahedral sites. Such compounds are called *inverse spinels*. The most common example is magnetite,  $\text{Fe}_3\text{O}_4$ , or more accurately,  $\text{Fe}^{2+}(\text{Fe}^{3+})_2(\text{O}^{2-})_4$ . The arrangement here is  $(\text{Fe}^{3+})_t(\text{Fe}^{2+}, \text{Fe}^{3+})_o(\text{O}^{2-})_4$ .

We might expect that all spinels would adopt the inverse structure, for the tetrahedral holes are smaller than the octahedral holes and the tripositive cations are smaller than the dipositive cations. However, in addition to size factors, we have to consider energy factors. Because lattice energy depends on the size of the ionic charge, it is the location of the 3+ ion that is responsible for the majority of the energy. Lattice energy will be higher when the 3+ ion is an octahedral site surrounded by six anions than when it occupies a



**FIGURE 5.15** Ion lattice diagram of the spinel structure.

tetrahedral site and is surrounded by only four anions. Nevertheless, the inverse spinel structure is preferred by many transition metal ions because the d-orbital occupancy affects the energy preferences, as we will see in Chapter 19, Section 19.8.

The interest in spinels derives from their unusual electrical and magnetic properties, particularly those in which the tripositive ion is  $\text{Fe}^{3+}$ . These compounds are known as *ferrites*. For example, it is possible to synthesize a series of compounds  $\text{MFe}_2\text{O}_4$ , where M is any combination of zinc ions and manganese ions, provided the formula  $\text{Zn}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$  is obeyed. By choosing the appropriate ratio, very specific magnetic properties can be obtained for these zinc ferrites.

Even more peculiar is sodium- $\beta$ -alumina,  $\text{NaAl}_{11}\text{O}_{17}$ . Although its formula does not look like that of a spinel, most of the ions fit the spinel lattice sites. The sodium ions, however, are free to roam throughout the structure. It is this property that makes the compound so interesting, because its electrical conductivity is very high, and it can act as a solid-phase electrolyte. This type of structure offers great potential for low-mass storage batteries.

## 5.8 Defects and Nonstoichiometry

In a perfect crystal, all ions would be in their regular locations, making a perfectly symmetrical crystal lattice. In reality, defects in crystal structures are very common and, in fact, they can impart unique and unusual properties to the compound. Such defects can cause spectacular color changes, in fact, the colors of many gemstones result from lattice defects. Also, defects can result in unusual physical properties, such as electrical conductivity. In this section, we

will focus on *point defects*, which result from an additional ion at a particular lattice site, or a vacancy where an ion should be.

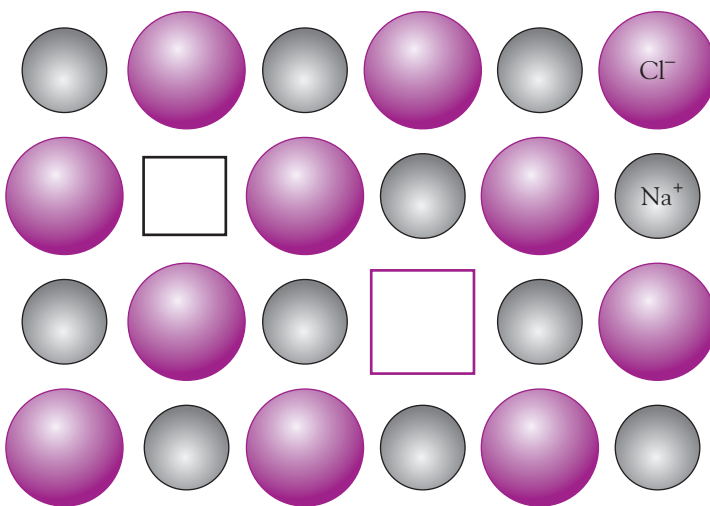
These point defects can themselves be categorized as *intrinsic point defects* or *extrinsic point defects*. Intrinsic defects do not change the overall composition of the lattice and, as a result, are also known as stoichiometric defects. Extrinsic defects result from the presence of an intruder ion into the structure.

### Intrinsic Defects

There are two categories of intrinsic defects: *Schottky defects* and *Frenkel defects*. Schottky defects occur when there are equal numbers of missing anions and cations in the structure (Figure 5.16). The lattice vacancy rate is very small, for example, in a typical sodium chloride crystal, about one in  $10^{15}$  ion sites are vacant. Schottky defects are most common in crystal lattices containing 1:1 ratios of anions and cations, such as sodium chloride, cesium chloride, and zinc sulfide (wurtzite).

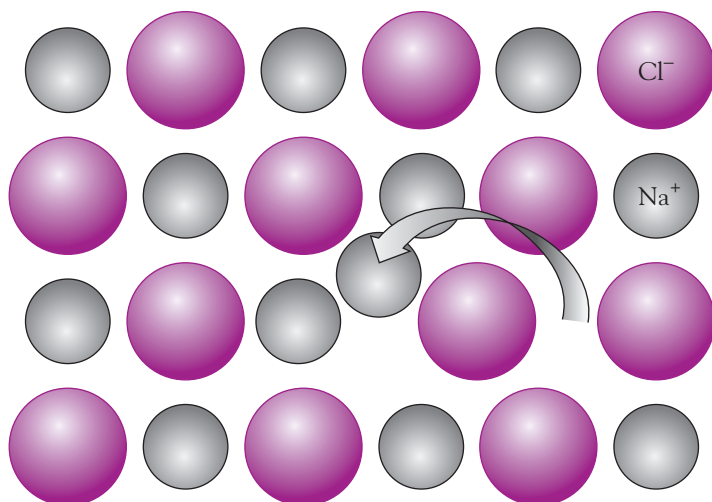
A Frenkel defect occurs when an ion is not in its regular lattice site, but is displaced into an abnormal location. Cation Frenkel defects, in which a cation is displaced, are more common, as cations tend to be significantly smaller than anions and therefore can be accommodated in small unoccupied sites in the lattice. A typical example is that of silver chloride. Figure 5.17 shows this type of defect as a two-dimensional array.

It is possible for electrons to be trapped in these anion vacancies (Figure 5.18). This process typically occurs by irradiation, either through natural processes or in a nuclear reactor. When this happens, the trapped electrons can be excited to different higher energy states within the lattice hole. Such energy transitions correspond to wavelengths in the visible region. As an example, the mineral fluorite, calcium fluoride is colorless. However, mineral



**FIGURE 5.16** A two-dimensional array in a sodium chloride crystal showing a Schottsky defect.



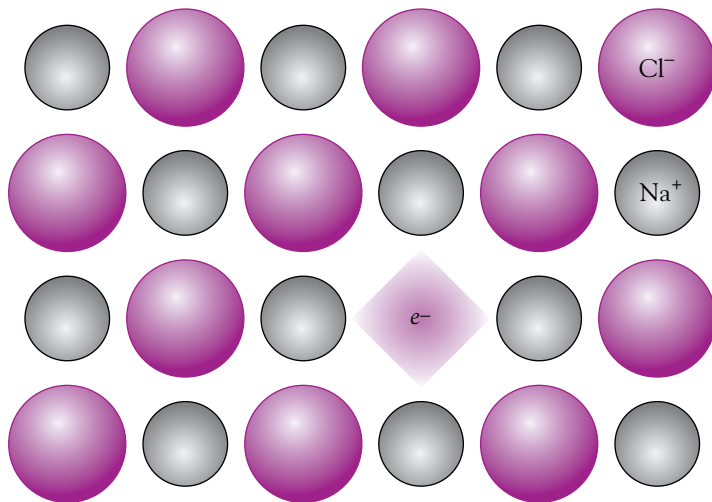


**FIGURE 5.17** A two-dimensional array in a silver chloride crystal showing a Frenkel defect.

deposits in northwest England, permeated with naturally occurring radioactive radon gas over geological time frames have turned the colorless mineral to an intensely colored material prized for making vases. Should the vase be heated strongly, the electrons escape and the worthless colorless mineral remains.

### Extrinsic Defects—Nonstoichiometric Compounds

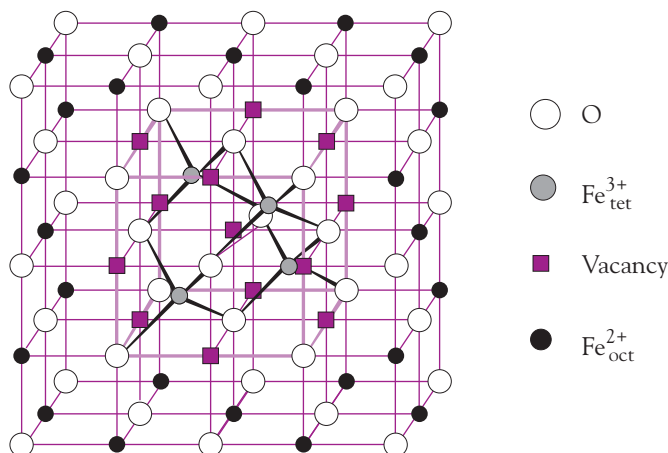
The concept that compounds consist of ions combined in precise ratios is a fundamental basis of chemistry. Yet the concept is not totally correct. In particular,



**FIGURE 5.18** A two-dimensional array in a sodium chloride crystal showing a trapped electron.



**FIGURE 5.19** An ion-lattice diagram of part of the structure of  $\text{Fe}_{0.95}\text{O}$  showing the tetrahedrally coordinated  $\text{Fe}^{3+}$  ions within the octahedrally coordinated  $\text{Fe}^{2+}\text{O}^{2-}$  structure.



transition, lanthanoid, and actinoid oxides can be nonstoichiometric. As this nonstoichiometry results from “intruder” ions, such defects are extrinsic.

The best-studied example of a nonstoichiometric oxide is iron(II) oxide which theoretically should have the formula  $\text{FeO}$ . In fact, its formula is  $\text{Fe}_x\text{O}$  where  $x$  is somewhere between 0.848 and 0.957, and typically about 0.95. This difference is explained in terms of some of the iron being present, not as the  $\text{Fe}^{2+}$  ion, but as the  $\text{Fe}^{3+}$  ion. To maintain charge balance, three  $\text{Fe}^{2+}$  ions are replaced by two  $\text{Fe}^{3+}$  ions, resulting in the stoichiometric imbalance, with fewer iron ions than oxygen ions. The iron(III) ions are not scattered randomly, but are found clustered together. Figure 5.19 shows a cluster of tetrahedrally coordinated iron(III) ions in among the octahedrally coordinated iron(II) ions. This particular structure is known as a *Koch-Cohen cluster*.

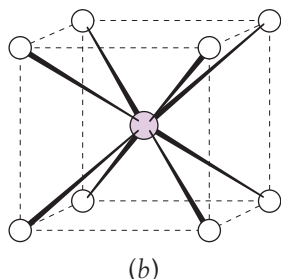
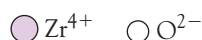
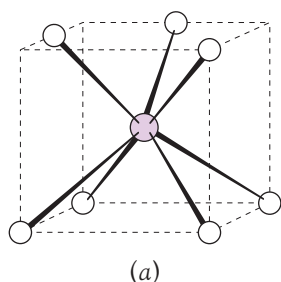
### Extrinsic Defects—Doping

It is possible to synthesize ionic compounds in which different ions are deliberately inserted into the crystal lattice of a pure compound. Such compounds, particularly doped oxides, have become vital to modern technology as solid-state oxide ion conductors in such products as:

- Oxygen sensors in the exhaust of motor vehicles to monitor clean burning.
- Membranes for oxygen separation to enable people with respiratory diseases to breath higher concentrations of oxygen.
- Solid oxide fuel cells (SOFCs) for producing electricity from hydrogen and air.

One common example of doping is that of zirconium(IV) oxide. The normal crystal lattice arrangement, found in the mineral baddeleyite, has seven oxide ions around each zirconium ion (Figure 5.20a). When heated above  $2300^\circ\text{C}$ , the lattice undergoes a rearrangement to give the eight-coordinate fluorite (Figure 5.20b).

The fluorite structure can be stabilized at room temperature by insertion of other ions of lower oxidation state, the two most common choices being yttrium(III) and calcium(II). These are known as yttria-stabilized zirconia (YSZ) and calcia-stabilized zirconia (CSZ), respectively. Taking the example of the calcium ion, for  $\text{Ca}^{2+}$  ion which replaces a  $\text{Zr}^{4+}$  ion, one corresponding



**FIGURE 5.20** The zirconium(IV) oxide ion arrangements in (a) baddeleyite and (b) cubic zirconia.

$\text{O}^{2-}$  anion must be removed for charge balance. As a result, the  $\text{Ca}^{2+}/\text{Zr}^{4+}$  fluorite structure has many vacant anion sites, enabling the oxide ions to move through the structure, from one site to another, and resulting in solid-state electrical conductivity. The best conductivity occurs when the doping ions are similar in size to those of zirconium, so that the fluorite lattice dimensions are altered as little as possible by the substitution.

## KEY IDEAS

- The strength of ionic bonding depends on an ion's charge and size.
- Many compounds of metals and nonmetals have properties consistent with significant covalent character in their bonding.
- Polarization, used to explain covalent character, can be estimated from the charge density of the ions.
- Many ions are hydrated even in the solid phase.
- In the solid phase, we can consider the anions to form a three-dimensional array, with the cations fitting in the intervening holes.
- The preferred packing arrangement in an ionic compound depends on the relative ionic radii of cation and anion.
- To account for the continuum of bonding types, we can use a bond triangle or tetrahedron.

## EXERCISES

- 5.1** Define the following terms: (a) polarization; (b) interstices; (c) bond triangle.
- 5.2** Define the following terms: (a) ion-dipole interactions; (b) radius ratio; (c) cubic arrangement.
- 5.3** What properties of a compound would lead you to expect that it contains ionic bonds?
- 5.4** Which would you expect to contain ionic bonds,  $\text{MgCl}_2$  or  $\text{SnCl}_2$ ? Explain your reasoning.
- 5.5** Which one of each of the following pairs will be smaller? Explain your reasoning in each case. (a)  $\text{K}$  or  $\text{K}^+$ ; (b)  $\text{K}^+$  or  $\text{Ca}^{2+}$ ; (c)  $\text{Br}^-$  or  $\text{Rb}^+$ .
- 5.6** Which one of each of the following pairs will be smaller? Explain your reasoning in each case. (a)  $\text{Se}^{2-}$  or  $\text{Br}^-$ ; (b)  $\text{O}^{2-}$  or  $\text{S}^{2-}$ .
- 5.7** Which one,  $\text{NaCl}$  or  $\text{NaI}$ , would be expected to have the higher melting point? Explain your reasoning.
- 5.8** Which one,  $\text{NaCl}$  or  $\text{KCl}$ , would be expected to have the higher melting point? Explain your reasoning.
- 5.9** Compare the charge density values of the three silver ions:  $\text{Ag}^+$ ,  $\text{Ag}^{2+}$ , and  $\text{Ag}^{3+}$  (see Appendix 2). Which is most likely to form compounds exhibiting ionic bonding?
- 5.10** Which would be more polarizable, the fluoride ion or the iodide ion? Give your reason.
- 5.11** Using data tables, find the melting points of uranium(III) fluoride, uranium(IV) fluoride, uranium(V) fluoride, and uranium(VI) fluoride.
- 5.12** Using data tables, find the melting points of manganese(II) oxide, manganese(III) oxide, manganese(IV) oxide, and manganese(VII) oxide. At what point does the bonding type appear to change?
- 5.13** Using data tables, find the melting points of tungsten(IV) fluoride, tungsten(VI) fluoride, tungsten(IV) oxide, and tungsten(VI) oxide. Comment on the difference between the fluoride pair and the oxide pair.
- 5.14** Titanium(IV) exists in aqueous solution, but not as the  $\text{Ti}^{4+}(\text{aq})$  ion. Suggest the identity of the species.
- 5.15** Explain the difference between the  $227^\circ\text{C}$  melting point of tin(II) chloride,  $\text{SnCl}_2$ , and the  $-33^\circ\text{C}$  melting point of tin(IV) chloride,  $\text{SnCl}_4$ .
- 5.16** Magnesium ion and copper(II) ion have almost the same ionic radius. Which would you expect to have the lower melting point, magnesium chloride,  $\text{MgCl}_2$ , or copper(II) chloride,  $\text{CuCl}_2$ ? Explain your reasoning.
- 5.17** Would you expect sodium chloride to dissolve in carbon tetrachloride,  $\text{CCl}_4$ ? Explain your reasoning.
- 5.18** Suggest a reason why calcium carbonate,  $\text{CaCO}_3$ , is insoluble in water.
- 5.19** Which of sodium chloride and magnesium chloride is more likely to be hydrated in the solid phase? Explain your reasoning.
- 5.20** Nickel(II) sulfate commonly exists as a hydrate. Predict the formula of the hydrate and explain your reasoning.

**5.21** Of lithium nitrate and sodium nitrate, which is more likely to exist as a hydrate in the solid phase? Explain your reasoning.

**5.22** What are the key assumptions in the ionic lattice concept?

**5.23** Explain the factor affecting the ion coordination number in an ionic compound.

**5.24** Why, in the study of an ionic lattice, is the anion packing considered to be the frame into which the cations fit?

**5.25** Although calcium fluoride adopts the fluorite structure, magnesium fluoride adopts the rutile structure. Suggest an explanation.

**5.26** Suggest the probable crystal structure of (a) barium fluoride; (b) potassium bromide; (c) magnesium sulfide. You can use comparisons or obtain ionic radii from data tables.

**5.27** Use Figure 5.4 as a model to draw a partial ionic lattice diagram for the antifluorite structure of lithium oxide.

## BEYOND THE BASICS

**5.28** The internuclear distance between sodium and chloride ions in the sodium chloride lattice,  $\text{NaCl(s)}$ , is 281 pm, while the bond distance in  $\text{NaCl(g)}$  from the vaporized lattice is 236 pm. Suggest why the gas-phase distance is much shorter.

**5.29** Which member of the following pairs has the higher melting point? Give your reasoning in each case. (a) copper(I) chloride,  $\text{CuCl}$ , or copper(II) chloride,  $\text{CuCl}_2$ ; (b) lead(II) chloride,  $\text{PbCl}_2$ , or lead(IV) chloride,  $\text{PbCl}_4$ .

**5.30** In a sodium chloride lattice, the ions usually touch along the edge of the unit cell. If the ionic radii are  $r_+$  and  $r_-$ , calculate the length of each side of the unit cell.

**5.31** In a cesium chloride lattice, the atoms usually touch along the diagonal from one corner through the center of the cell to the opposite corner. If the ionic radii are  $r_+$  and  $r_-$ , calculate the length of each side of the unit cell.

**5.32** Calculate the radius of a cesium ion in cesium chloride if the density of cesium chloride is  $3.97 \text{ g}\cdot\text{cm}^{-3}$  and it is assumed that the ions touch through the diagonal of the unit cell.

**5.33** Rubidium chloride adopts the sodium chloride structure. Calculate the radius of a rubidium ion if the density of rubidium chloride is  $2.76 \text{ g}\cdot\text{cm}^{-3}$  and it is assumed that the ions touch along the edges of the unit cell.

**5.34** Ammonium chloride crystallizes in the cesium chloride lattice. The cations and anions are in contact across the

body diagonal of the unit cell and the edge length is 386 pm. Determine a value for the radius of the ammonium ion.

**5.35** Sodium hexafluoroantimonate(V),  $\text{NaSbF}_6$ , density  $4.37 \text{ g}\cdot\text{cm}^{-3}$ , crystallizes in the sodium chloride lattice. The sodium cations and hexafluoroantimonate(V) anions are in contact along the edge of the unit cell. Determine a value for the radius of the hexafluoroantimonate(V) ion.

**5.36** The unit cell of a particular solid has tungsten atoms at the corners, oxygen atoms in the centers of each cube edge, and a sodium atom in the cube center. What is the empirical formula of the compound?

**5.37** Astatine, the lowest (and radioactive) member of the halogen series, can form the astatinide ion,  $\text{At}^-$ , which has an approximate ionic radius of 225 pm. What lattice type would be expected for each of the alkali metal compounds of the astatinide ion?

**5.38** Cerium(III) oxide,  $\text{Ce}_2\text{O}_3$ , can have a composition up to  $\text{Ce}_2\text{O}_{3.2}$ . What is likely to be the oxidation state of the cerium ions causing this stoichiometric imbalance?

**5.39** Zirconium(IV) oxide,  $\text{ZrO}_2$ , can have a composition down to  $\text{ZrO}_{1.7}$ . What is likely to be the oxidation state of the cerium ions causing this stoichiometric imbalance?

**5.40** Briefly explain why one of the best oxygen-ion conductors employs scandium ( $\text{Sc}^{3+}$ ) ion doped zirconium(IV) oxide.

## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# WHY COMPOUNDS EXIST—INORGANIC THERMODYNAMICS

## CHAPTER 6

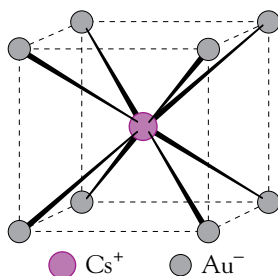
Descriptive inorganic chemistry is not simply a study of the chemical elements and the myriad compounds that they form. It also involves the need to explain why some compounds form and others do not. The explanation usually relates to the energy factors involved in the formation of compounds. This topic is a branch of thermodynamics, and in this chapter we present a simplified introduction to inorganic thermodynamics.

### Context: Against Convention: Ionic Compounds of Metal Anions

Many discoveries in chemistry are a result of simple curiosity. For example, what will happen if A is mixed with B? And sometimes the product overturns conventional ideas about chemistry.

Our story begins when, during a study of alloys, equal molar quantities of cesium and gold were melted and mixed. Instead of a metallic alloy, a clear, colorless liquid was produced! Upon cooling, a yellow, crystalline ionic solid was formed. How could two metals form an ionic compound? It became apparent that the ionic compound consisted of the cesium cation,  $\text{Cs}^+$ , and gold as the auride anion,  $\text{Au}^-$ , with the cesium cations in a simple cubic array, and the auride anions at the center of each unit cell (see figure below). A metal as an anion? But surely metals only form cations! As the old song says: “it ain’t necessarily so.”

A wide range of compounds is now known to contain the auride ion, including cesium oxide auride,  $\text{Cs}_3\text{AuO}$ , which has the true formulation



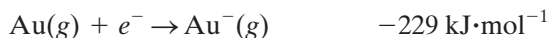
An ionic lattice diagram for cesium auride,  $\text{CsAu}$ .

25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 6.1 Thermodynamics of the Formation of Compounds
- 6.2 Formation of Ionic Compounds
- 6.3 Nonexistent Ionic Compounds
- 6.4 Thermodynamics of the Solution Process for Ionic Compounds
- 6.5 Lattice Energies and Comparative Ion Sizes and Charges
- 6.6 Formation of Covalent Compounds
- 6.7 Thermodynamic versus Kinetic Factors

of  $(\text{Cs}^+)_3(\text{Au}^-)(\text{O}^{2-})$ , and its rubidium and potassium analogs. Platinum, too, forms a platinide ion,  $\text{Pt}^{2-}$ , in such compounds as cesium platinide,  $\text{Cs}_2\text{Pt}$ . And compounds of alkali metal anions (the alkalides), such as  $\text{Na}^-$ , are known.

In this chapter, we will see that the existence, or non-existence, of a compound can be explained by considering its formation to occur in a series of theoretical steps, each of which is a measurable value (see Section 6.2). For the formation of compounds containing metal anions, a key component is considered to be a negative value for the electron affinity of the metal. For example, for gold:



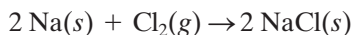
In addition, the large cesium cation plays a role by having a comparatively low ionization energy.



So why should gold have such a high electron affinity? An explanation can be found from the electron configurations. Gold has an electron configuration of  $[\text{Xe}]6s^14f^{14}5d^{10}$  (analogous to copper). By gaining an electron, the resulting  $\text{Au}^-$  ion will have the filled-orbital configuration of  $[\text{Xe}]6s^24f^{14}5d^{10}$ .

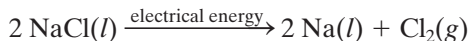
## 6.1 Thermodynamics of the Formation of Compounds

Compounds are produced from elements by chemical reactions. For example, common salt, sodium chloride, can be formed by the combination of the reactive metal sodium with a toxic green gas, chlorine:



Because this reaction occurs without need for external “help,” it is said to be a *spontaneous reaction* (although being spontaneous does not give any indication of how fast or slow the reaction may be).

The reverse reaction, the decomposition of sodium chloride, is a nonspontaneous process, which is just as well; we certainly would not want the salt on the dining table to start releasing clouds of poisonous chlorine gas! One way to obtain sodium metal and chlorine gas back again is to pass an electric current (an external energy source) through molten sodium chloride:



The thermodynamic feasibility of a chemical reaction is defined by the free energy of the process, which must have a negative value in order for spontaneous reaction to occur. In practical terms, we can consider free energy as containing two components: enthalpy and entropy. In this section, we will first look at the terminology and types of enthalpy data. Then we will consider entropy measurements, and finally, the calculation of free energy for a reaction.

### Enthalpy of Formation

The enthalpy of a compound is usually listed in data tables as the enthalpy of formation value. The enthalpy of formation is defined as the change in heat content

when 1 mole of a compound is formed from its elements in their standard phases at 298 K and 100 kPa. By definition, the enthalpy of formation of an element is zero. This is an arbitrary standard, just as our geographical measure of altitude is taken as height above mean sea level rather than from the center of the Earth. The symbol for the enthalpy of formation under standard conditions is  $\Delta_f H^\ominus$ . Thus, we find in data tables values such as  $\Delta_f H^\ominus(\text{CO}_2(g)) = -394 \text{ kJ}\cdot\text{mol}^{-1}$ . This information tells us that 394 kJ of energy is released when one mol of carbon (graphite) reacts with one mol of oxygen gas at a temperature of 298 K and a pressure of 100 kPa to give one mol of carbon dioxide:

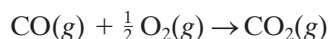


Enthalpies of formation can be combined to calculate the enthalpy change in other chemical reactions.

$$\Delta H^\ominus(\text{reaction}) = \sum \Delta_f H^\ominus(\text{products}) - \sum \Delta_f H^\ominus(\text{reactants})$$

### WORKED EXAMPLE 6.1

Calculate the standard enthalpy change when carbon monoxide burns in air to give carbon dioxide:



#### Answer

First, the necessary data is obtained from tables:

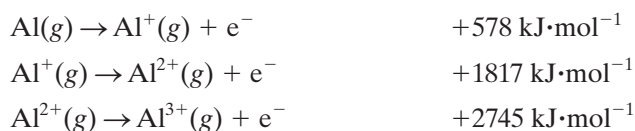
$\Delta_f H^\ominus(\text{CO}_2(g)) = -394 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H^\ominus(\text{CO}(g)) = -111 \text{ kJ}\cdot\text{mol}^{-1}$ ; by definition,  $\Delta_f H^\ominus(\text{O}_2(g))$  is zero.

$$\begin{aligned} \Delta H^\ominus(\text{reaction}) &= [1 \times (-394 \text{ kJ}\cdot\text{mol}^{-1})] - [1 \times (-111 \text{ kJ}\cdot\text{mol}^{-1})] \\ &= -283 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

(Thus, the reaction is exothermic, as are almost all combustion reactions.) ■

## Ionization Energy

As we consider the component thermodynamic factors in the formation of an ionic compound, it is the ionization of the metal atom to form the cation which is a very major component. The concept of ionization energy was introduced as a periodic property in Chapter 2, Section 2.7. In data tables, each ionization step is listed separately. Using the example of aluminum, the formation of a gaseous  $\text{Al}^{3+}$  ion can be represented as:



Thus to ionize all three valence electrons requires over  $5 \text{ MJ}\cdot\text{mol}^{-1}$  of energy input.

### Electron Affinity

Electron affinity, the energy released when an electron is added to an atom, was introduced as a periodic property in Chapter 2, Section 2.6. For many elements, including the alkali metals, formation of an anion is energetically favored. Below we show the energy changes for the formation of the sodide (also called natride) ion and the fluoride ion.



So that we see a contributing reason why the sodide ion is not encountered in “normal” chemistry is that its electron affinity is much lower than that of non-metals such as fluorine.

Just as there are successive ionization energies, there are successive electron affinities. These values, too, have their anomalies. Let us look at the first and second electron affinities for oxygen:



Thus, the addition of a second electron to an oxygen atom is an endothermic process. This energetically unfavorable process is not surprising from the point of view of adding an electron to a species that is already negatively charged, but then one has to explain how the oxide ion exists in chemical compounds. In fact, the oxide ion can only exist where there is some other driving force, such as the formation of a crystal lattice.

### Bond Energies (Enthalpies)

Enthalpies of formation values are very convenient for the calculation of enthalpy changes in reactions. However, inorganic chemists are often interested in the strength of the attraction between atoms in covalent molecules, the bond enthalpy. The term is commonly called *bond energy*, although there are small differences between the two in terms of their definition and numerical values. Bond energy is defined as the energy needed to break 1 mole of the particular covalent bond. Energy is released when bonds are formed, and energy must be supplied when bonds are broken.

We can measure the exact bond energy for a particular pair of atoms joined by a covalent bond. For example, Table 6.1 lists the bond energies in the diatomic molecules of the halogen series. If we look at elements within a group, we see that the bond energies usually decrease as one goes down the group as a result of the increase in atomic size and decrease in orbital overlap of electron density. We will see later in this chapter, and in Chapter 17, that the anomalously low F—F bond energy has a major effect on fluorine chemistry.

The bond energy depends on the other atoms that are present in the molecule. For example, the value of the O—H bond energy is  $492 \text{ kJ}\cdot\text{mol}^{-1}$  in water (HO—H) but  $435 \text{ kJ}\cdot\text{mol}^{-1}$  in methanol,  $\text{CH}_3\text{O—H}$ . Because of this variability, data tables provide average bond energies for a particular covalent bond.



**TABLE 6.1** Bond energies of the diatomic molecules of the halogens

Molecule	Bond energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )
F—F	155
Cl—Cl	242
Br—Br	193
I—I	151

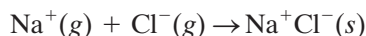
Bond strength depends very strongly on bond order. As the bond order increases, so the energy of a specific bond, and thus the bond strength, increases substantially. Table 6.2 shows this trend for the series of carbon-nitrogen average bond energies.

**TABLE 6.2** Average bond energies for various carbon-nitrogen bonds

Bond	Bond energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )
C—N	305
C=N	615
C≡N	887

### Lattice Energies (Enthalpies)

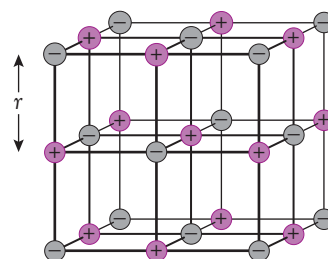
The *lattice energy* is the energy change for the formation of 1 mole of an ionic solid from its constituent gaseous ions (we are really considering lattice enthalpy here, but the difference is negligible). We can illustrate the process with sodium chloride. The lattice energy of sodium chloride corresponds to the energy change for:



The lattice energy is really a measure of the electrostatic attractions and repulsions of the ions in the crystal lattice. This series of interactions can be illustrated by the sodium chloride crystal lattice (Figure 6.1).

Surrounding the central cation are six anions at a distance of  $r$ , where  $r$  is the distance between centers of nearest neighbors. This is the major attractive force holding the lattice together. However, at a distance of  $(2)^{1/2}r$ , there are 12 cations. These will provide a repulsion factor. Adding layers of ions beyond the unit cell, we find that there are eight more anions at a distance of  $(3)^{1/2}r$ , then six more cations at  $2r$ . Hence, the true balance of charge is represented by an infinite series of alternating attraction and repulsion terms, although the size of the contributions drops off rapidly with increasing distance. The summation of all of the attraction and repulsion terms, then, becomes a converging series. Each type of lattice has a different arrangement of cations and anions and hence its own converging series. The numerical values for these series are known as *Madelung constants*,  $A$ . Examples of common lattice types are shown in Table 6.3.

In addition to a dependence on lattice type, lattice energy varies considerably with ion charge. Doubling the charge from  $1+$  to  $2+$  (or  $1-$  to  $2-$ ) approximately triples the lattice energy. For example, the lattice energy of potassium chloride is  $701 \text{ kJ}\cdot\text{mol}^{-1}$ , whereas that of calcium chloride is  $2237 \text{ kJ}\cdot\text{mol}^{-1}$ . In fact, for the series  $\text{MX}$ ,  $\text{MX}_2$ ,  $\text{MX}_3$ ,  $\text{MX}_4$ , the lattice energies are related in the ratios of 1:3:6:10. The lattice energy is also greater if the ions are smaller, a factor that results in closer ion centers.



**FIGURE 6.1** Ionic lattice diagram of the sodium chloride structure, showing the ion charge. [Adapted from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed. (New York: Oxford University Press, 1984), p. 239.]



**TABLE 6.3** The Madelung constants for common lattice types

Type of lattice	Madelung constant, $A$
Sphalerite, ZnS	1.638
Wurtzite, ZnS	1.641
Sodium chloride, NaCl	1.748
Cesium chloride, CsCl	1.763
Rutile, TiO <sub>2</sub>	2.408
Fluorite, CaF <sub>2</sub>	2.519

It is possible to determine the lattice energy of an ionic crystal from experimental measurements, as we will see shortly, but we often need to estimate lattice energy when experimental data are unavailable. To determine a theoretical value, we can use the *Born-Landé equation*. The following equation derives remarkably accurate values of the lattice energy,  $U$ , from combinations of simple functions:

$$U = \frac{NAz^+z^-e^2}{4\pi\epsilon_0r_0} \left(1 - \frac{1}{n}\right)$$

where  $N$  = Avogadro's number ( $6.023 \times 10^{23} \text{ mol}^{-1}$ ),  $A$  = the Madelung constant,  $z^+$  = the relative cation charge,  $z^-$  = the relative anion charge,  $e$  = the actual electron charge ( $1.602 \times 10^{-19} \text{ C}$ ),  $\pi = 3.142$ ,  $\epsilon_0$  = the permittivity of free space ( $8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$ ),  $r_0$  = the sum of the ionic radii, and  $n$  = the average Born exponent (discussed later in the chapter).

The Madelung constant accounts for the attractive forces between ions. But when ions approach each other, their filled electron orbitals begin to add a repulsion factor that increases rapidly when the two nuclei become very close. To account for this repulsive term, the *Born exponent*,  $n$ , is included in the Born-Landé equation. In fact, the sum of the ionic radii represents the equilibrium position between the ion attractions and the interelectron repulsions. Some values of the Born exponent are given in Table 6.4.

**TABLE 6.4** Values for the Born exponent

Electronic configuration of ion	Born exponent, $n$	Examples
He	5	Li <sup>+</sup>
Ne	7	Na <sup>+</sup> , Mg <sup>2+</sup> , O <sup>2-</sup> , F <sup>-</sup>
Ar	9	K <sup>+</sup> , Ca <sup>2+</sup> , S <sup>2-</sup> , Cl <sup>-</sup>
Kr	10	Rb <sup>+</sup> , Br <sup>-</sup>
Xe	12	Cs <sup>+</sup> , I <sup>-</sup>

**WORKED EXAMPLE 6.2**

Calculate the lattice energy of sodium chloride from the Born-Landé equation.

The ionic radii are:  $\text{Na}^+ = 116 \text{ pm}$ ; and  $\text{Cl}^- = 167 \text{ pm}$ .

**Answer**

$$r_0 = (116 \text{ pm} + 167 \text{ pm}) = 283 \text{ pm} = 2.83 \times 10^{-10} \text{ m}.$$

The value for the Born constant will be the average for that of the sodium and chloride ions  $= (7 + 9)/2 = 8$ . Substituting in the equation gives:

$$\begin{aligned} U &= -\frac{(6.02 \times 10^{23} \text{ mol}^{-1}) \times 1.748 \times 1 \times 1 \times (1.602 \times 10^{-19} \text{ C})^2}{4 \times 3.142 \times (8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1})(2.83 \times 10^{-10} \text{ m})} \left(1 - \frac{1}{8}\right) \\ &= -751 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

(This is a value close to the best experimental figure of  $-788 \text{ kJ} \cdot \text{mol}^{-1}$  an error of only 4.7 percent.) ■

The Born-Landé equation can only be used to find the lattice energy if the crystal structure of the compound is known. If it is not, the *Kapustinskii equation* can be used, where  $\nu$  is the number of ions in the empirical formula (for example, for calcium fluoride,  $\nu = 3$ ) and the other symbols have the same meaning and values as the Born-Landé equation except  $r_0$  is in units of picometers (pm):

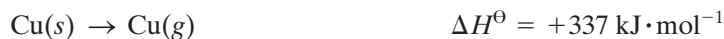
$$U = \frac{1.202 \times 10^5 \nu z^+ z^-}{r_0} \left(1 - \frac{34.5}{r_0}\right) \text{ kJ} \cdot \text{mol}^{-1}$$

When there is a significant difference between the experimental value of lattice energy and that obtained from the Born-Landé or Kapustinskii equation, it is usually an indication that the interaction between the ions is not purely ionic but also contains significant covalent character.

Finally, it should be mentioned that all crystals have a lattice energy. For simple covalent compounds, lattice energy is attributable to intermolecular attractions; for network covalent substances, lattice energy is the energy of the covalent bonds; for metals, it is the attractions that create the metallic bond. However, the energy term for simple covalent molecules is commonly called the enthalpy of sublimation rather than the lattice energy.

**Enthalpies of Atomization**

Another useful measurement is that of *energy of atomization*. This is defined as the energy needed to produce 1 mole of gaseous atoms of that element from the element in its normal phase at room temperature. This energy term can be used to represent the breaking of the metallic bond in metals, such as copper:



or the overcoming of the covalent bonds and intermolecular forces in non-metals, such as diiodine:



In the case of the diiodine atomization, there are two constituent steps to the process: first, overcoming the dispersion forces between the molecules, then second, breaking the covalent bonds within molecules:



### Entropy Changes

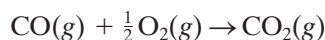
*Entropy* is often related to the degree of disorder of the substance (although the concept of entropy is really more complex). Thus, the solid phase has a lower entropy than the liquid phase, whereas the gas phase, in which there is random motion, has a very high entropy. The entropy change is indicated by the symbol  $\Delta S$ .

Unlike enthalpy, which is usually tabulated as relative values (such as enthalpy of formation), entropy is discussed on an absolute basis. Thus, even elements have a listed value of entropy. The zero point is taken to be that of a perfect crystal of a substance at the absolute zero of temperature. We can calculate the standard entropy change for a reaction in the same way as that of the enthalpy change.

$$\Delta S^\ominus(\text{reaction}) = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$$

#### WORKED EXAMPLE 6.3

Calculate the standard entropy change for the reaction:



#### Answer

First, the necessary data is obtained from tables:

$$S^\ominus(\text{CO}_2(g)) = 214 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}; S^\ominus(\text{CO}(g)) = 198 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1};$$

and  $S^\ominus(\text{O}_2(g)) = 205 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .

Hence,

$$\begin{aligned} \Delta S^\ominus &= [S^\ominus(\text{CO}_2(g))] - [S^\ominus(\text{CO}(g)) + \frac{1}{2} S^\ominus(\text{O}_2(g))] \\ &= [1 \times (+214 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] - [1 \times (+198 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ &\quad + \frac{1}{2} \times (205 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] \\ &= -86 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

(We would expect an entropy decrease for the system in this process because it involves the net loss of  $\frac{1}{2}$  mole of gas. It is usually possible to estimate the sign of the entropy change by counting the moles of gas on each side of the equation since species in the gas phase possess significantly greater entropy than those in liquid, solid, or aqueous phases.) ■

**TABLE 6.5** Factors affecting the spontaneity of a reaction

$\Delta H$	$\Delta S$	$\Delta G$	Result
Negative	Positive	Always negative	Spontaneous
Positive	Negative	Always positive	Nonspontaneous
Positive	Positive	Negative at high $T$	Spontaneous at high $T$
Negative	Negative	Negative at low $T$	Spontaneous at low $T$

### Free Energy: The Driving Force of a Reaction

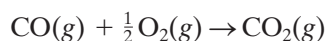
For a spontaneous reaction, there must be an increase in entropy overall (that is, the entropy change of the universe must be positive). The universe, to a physical chemist, consists of the reaction (system) and its surroundings. It is comparatively easy to measure entropy changes of the reaction, but those of the surroundings are more difficult to determine directly. Fortunately, the change in entropy of the surroundings usually results from the heat released to, or absorbed from, the reaction. Heat released to the surroundings (an exothermic reaction) will increase the entropy of the surroundings while absorption of heat (an endothermic reaction) will lead to a decrease in entropy of the surroundings. Thus, we can determine whether a reaction is spontaneous from the entropy and enthalpy changes of the reaction itself. The combination of these two factors gives the free energy change,  $\Delta G^\ominus$ , where:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

The possible sign combinations for the thermodynamic functions are summarized in Table 6.5.

#### WORKED EXAMPLE 6.4

Calculate the free change for the following reaction at 25°C.



given the standard enthalpy change ( $-283 \text{ kJ}\cdot\text{mol}^{-1}$ ) and standard entropy change ( $-86 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) for the reaction.

#### Answer

$$\begin{aligned}\Delta G^\ominus &= (-283 \text{ kJ}\cdot\text{mol}^{-1}) - [(298 \text{ K})(-0.086 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})] \\ &= -257 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

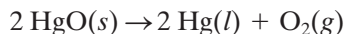
(Since the value of  $\Delta G^\ominus$  is negative, the reaction is thermodynamically spontaneous at this temperature.) ■

As can be seen from Table 6.5, for the combination of  $\Delta H$  and  $\Delta S$  positive and of  $\Delta H$  and  $\Delta S$  negative, the reaction is temperature dependent. This is due to the temperature factor in the free energy equation. In fact, we can

use the free energy equation to obtain a very approximate value of the temperature at which a reaction changes from spontaneous to nonspontaneous or vice versa.

### WORKED EXAMPLE 6.5

Calculate an approximate temperature for the decomposition of mercury(II) oxide to mercury metal and oxygen gas:



Given the standard enthalpy changes ( $+91 \text{ kJ}\cdot\text{mol}^{-1}$ ) and standard entropy change ( $+108 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) for the decomposition.

#### Answer

$$\Delta G^\ominus = (+91 \text{ kJ}\cdot\text{mol}^{-1}) - T(+0.108 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$$

At the point when the direction of reaction changes,  $\Delta G^\ominus = 0$ ,  
 $T = 91/0.108 \text{ K}^{-1} = 843 \text{ K} = 570^\circ\text{C}$

(In fact, mercury(II) oxide decomposes over the range of  $350^\circ\text{C}$  to  $500^\circ\text{C}$ . The difference from our approximate calculation is not surprising. Most of the discrepancy is due to the actual reaction being performed at the atmospheric 20 kPa pressure of oxygen, not the 100 kPa oxygen pressure assumed in the free energy calculation.) ■

The free energy of a reaction at 298 K can also be calculated from the algebraic sum of the free energies of formation in an analogous manner to the calculation for enthalpies:

$$\Delta G^\ominus(\text{reaction}) = \Sigma \Delta_f G^\ominus(\text{products}) - \Sigma \Delta_f G^\ominus(\text{reactants})$$

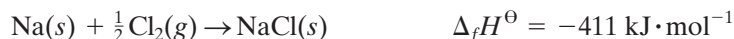
## 6.2 Formation of Ionic Compounds

When an ionic compound is formed from its elements, there is usually a decrease in entropy because the ordered, solid crystalline compound has a very low entropy and often the nonmetal reactant, such as oxygen or chlorine, is a high-entropy gas. For example, in the previous section we determined that the entropy change for the formation of sodium chloride was negative. Thus, for the formation of a thermodynamically stable compound from its constituent elements, a negative enthalpy change of the reaction is usually necessary. It is the exothermicity that becomes the driving force of the reaction.

To attempt to understand why particular compounds form and others do not, we will break the enthalpy of formation process of an ionic compound into a series of theoretical steps: first breaking the reactant bonds, then forming those of the products. In this way, we can identify which enthalpy factors are crucial to the spontaneity of reaction.

### The Enthalpy Changes of the Theoretical Formation of Sodium Chloride

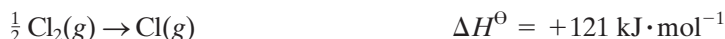
The formation of sodium chloride provides a good example of the theoretical steps involved in the formation of the compound from its constituent elements:



1. The solid sodium is converted to free (gaseous) sodium atoms. This process requires the enthalpy of atomization:



2. The gaseous chlorine molecules must be dissociated into atoms. This transformation requires one-half of the bond energy of chlorine molecules:



3. The sodium atoms must then be ionized. This process requires the first ionization energy. (If we had a metal that formed a divalent cation, such as calcium, then we would have to add both the first and the second ionization energies.)



4. The chlorine atoms must gain electrons. This value is the electron affinity of chlorine atoms.



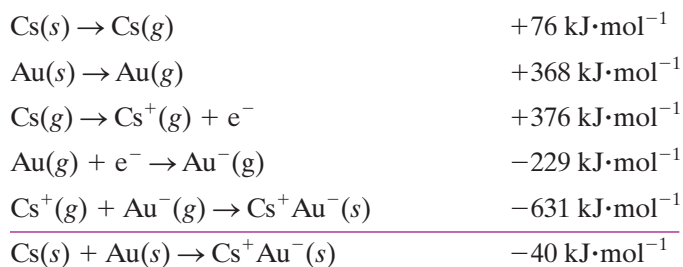
5. The free ions then associate to form a solid ionic compound. This bringing together of ions is a highly exothermic process—the lattice energy. The lattice energy can be looked on as the major driving force for the formation of an ionic compound:



#### WORKED EXAMPLE 6.6

Calculate the standard enthalpy of formation of cesium auride,  $\text{CsAu}(s)$  (see opening Context) given: enthalpy of atomization of cesium =  $76 \text{ kJ} \cdot \text{mol}^{-1}$ ; enthalpy of atomization of gold =  $368 \text{ kJ} \cdot \text{mol}^{-1}$ ; first ionization energy of cesium =  $376 \text{ kJ} \cdot \text{mol}^{-1}$ ; first electron affinity of gold =  $-229 \text{ kJ} \cdot \text{mol}^{-1}$ ; and assume the lattice energy of  $\text{Cs}^+\text{Au}^-$  to be close to that of cesium bromide,  $631 \text{ kJ} \cdot \text{mol}^{-1}$ .

#### Answer



That is,  $\Delta_f H^\ominus(\text{Cs}^+\text{Au}^-(s)) = -40 \text{ kJ} \cdot \text{mol}^{-1}$  ■

### The Born-Haber Cycle for Sodium Chloride

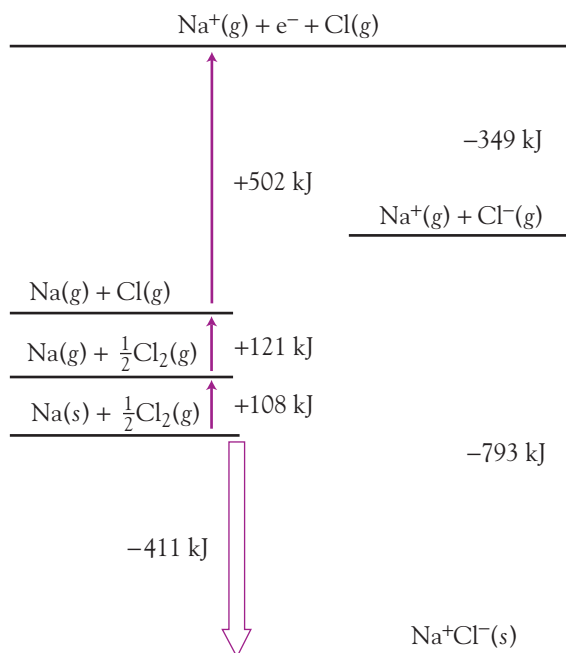
It is usually easier to comprehend information if it is displayed graphically. This representation can be done for the theoretical components of the formation of an ionic compound from its elements. The “up” direction is used to indicate endothermic steps in the process, and the “down” direction corresponds to exothermic steps. The resulting diagram is called a *Born-Haber cycle*. Figure 6.2 shows such a cycle for the formation of sodium chloride. The atomization of the sodium atom, the bond dissociation energy of half a chlorine molecule, and the ionization of the sodium atom are all endothermic processes, while the electron affinity of the chlorine atom and the formation of the crystal lattice are both exothermic processes.

These enthalpy diagrams can be used in two ways: first, to gain a visual image of the key enthalpy terms in the formation of the compound; and second, to determine any one unknown enthalpy value in the thermodynamic cycle since we know that the sum of the component terms should equal the overall enthalpy change for the formation process.

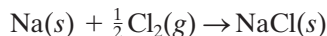
### The Entropy and Free Energy Changes of the Formation of Sodium Chloride

A Born-Haber-type cycle can also be constructed for the entropy changes of each theoretical step. However, as mentioned previously, it is the enthalpy change which is usually the driving force for the formation of a solid ionic compound. We can easily confirm that enthalpy is the predominant factor for the

**FIGURE 6.2** Born-Haber cycle for the formation of sodium chloride.



formation of sodium chloride by calculating the entropy and then free energy for the process under standard conditions:



To find the entropy of formation of sodium chloride, the entropy values of the species can be found from data tables,  $S^\ominus(\text{Na}(s)) = 51 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ;  $S^\ominus(\text{Cl}_2(g)) = 223 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ;  $S^\ominus(\text{NaCl}(s)) = 72 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Thus,

$$\begin{aligned}\Delta_f S^\ominus(\text{NaCl}(s)) &= [1 \times S^\ominus(\text{NaCl}(s))] - [1 \times S^\ominus(\text{Na}(s)) + \frac{1}{2} \times S^\ominus(\text{Cl}_2(g))] \\ &= [1 \times (72 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})] - [1 \times (51 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ &\quad + \frac{1}{2} \times (223 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})] \\ &= -90 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\end{aligned}$$

The free energy of formation of sodium chloride under standard conditions can then be found from:

$$\begin{aligned}\Delta_f G^\ominus(\text{NaCl}(s)) &= \Delta_f H^\ominus(\text{NaCl}(s)) - T\Delta_f S^\ominus(\text{NaCl}(s)) \\ &= [-411 \text{ kJ}\cdot\text{mol}^{-1}] - [(298 \text{ K})(-9.0 \times 10^{-2} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})] \\ &= -384 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The free energy change is negative, and the formation of sodium chloride from its constituent elements is indeed thermodynamically favorable. And, as can be seen, it is the enthalpy factor which is the driving force for the reaction.

## 6.3 Nonexistent Ionic Compounds

The major endothermic step results from the ionization(s) of the metal atom, whereas the most exothermic step derives from the formation of the ionic crystal lattice. From a thermodynamic perspective, it is this balance which determines the ion ratio in the compound which forms. In this section, we will provide two example which show why ionic compounds have the formulas that they do.

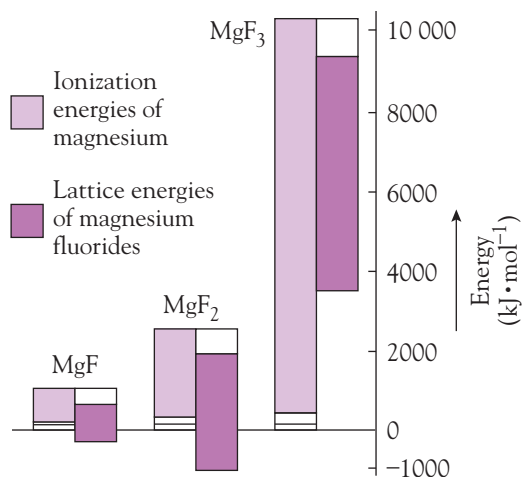
### Why Magnesium Fluoride is $\text{MgF}_2$

Magnesium fluoride,  $\text{MgF}_2$ , can be used to illustrate this point. The sum of the first and second ionization energies of the magnesium ion is  $+2190 \text{ kJ}\cdot\text{mol}^{-1}$ , much higher than the single ionization energy of the monovalent sodium ion. However, with the small, highly charged magnesium ion, the lattice energy is also much higher at  $-2880 \text{ kJ}\cdot\text{mol}^{-1}$ . Incorporating the other terms from the enthalpy cycle results in a relatively large negative enthalpy of formation for magnesium fluoride:  $-1100 \text{ kJ}\cdot\text{mol}^{-1}$ .

If the lattice energy increases so much with greater cation charge, why do magnesium and fluorine form  $\text{MgF}_2$  and not  $\text{MgF}_3$ ? If we estimate the enthalpy of formation of  $\text{MgF}_3$ , the lattice energy will be even greater than that of  $\text{MgF}_2$  because of the greater electrostatic attraction by an  $\text{Mg}^{3+}$  ion. However, for magnesium, the electrons that must be ionized to give the  $3+$  ion are core electrons,



**FIGURE 6.3** Graphical comparison of the Born-Haber cycles for three possible magnesium fluorides.



and the third ionization energy is enormous ( $+7740 \text{ kJ}\cdot\text{mol}^{-1}$ )—far larger than the gain from the lattice energy. Combined with a negative entropy term, there is no possibility that the compound will exist.

Conversely, why does magnesium and fluorine form  $\text{MgF}_2$  and not  $\text{MgF}$ ? As we have seen previously, the two largest energy factors are the ionization energies of magnesium (endothermic) and the lattice energy (exothermic). Far less energy is required to ionize only one electron to form a monpositive magnesium ion than a dipositive ion. However, lattice energy is highly charge dependent; thus, a monpositive cation will result in a much smaller lattice energy. Figure 6.3 compares the values for the thermodynamic components of the Born-Haber cycles for the formation of  $\text{MgF}$ ,  $\text{MgF}_2$ , and  $\text{MgF}_3$ . It can readily be seen that it is the balance of the ionization energies and the lattice energy which dominate the enthalpy terms. In this example, the formation of  $\text{MgF}_2$  is the most favored in terms of enthalpy factors.

### Why Sodium Fluoride is NaF

If  $\text{MgF}_2$  is preferred over  $\text{MgF}$ , then we might expect the compound of sodium and fluorine to be  $\text{NaF}_2$  and not  $\text{NaF}$ . In the case of sodium, however, the second electron to be ionized is a core electron, an extremely endothermic process ( $+4652 \text{ kJ}\cdot\text{mol}^{-1}$ ). The enormous ionization energy would not be balanced by the increased lattice energy. There are also two minor factors that make the enthalpy of formation of  $\text{NaF}$  more negative than what we would expect for  $\text{MgF}$ . With the lower  $Z_{\text{eff}}$ , we find that the first ionization energy of sodium is about  $200 \text{ kJ}\cdot\text{mol}^{-1}$  less than that of magnesium. Furthermore, the  $\text{Mg}^+$  ion, with its one  $3s$  electron remaining, is a larger cation than the  $\text{Na}^+$  ion. Hence, the lattice energy of  $\text{NaF}$  would be higher than that of  $\text{MgF}$ . The combination of lower ionization energy and higher lattice energy results in an enthalpy of formation for sodium fluoride of  $-574 \text{ kJ}\cdot\text{mol}^{-1}$  compared to the estimated value of  $-260 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{MgF}$ .

## 6.4 Thermodynamics of the Solution Process for Ionic Compounds

Just as the formation of a compound from its constituent elements can be considered as a series of theoretical steps, so can the solution process be broken down into several steps. For this analysis, we visualize first that the ions in the crystal lattice are dispersed into the gas phase and then, in a separate step, that water molecules surround the gaseous ions to give the hydrated ions. Thus, ion-ion interactions (ionic bonds) are broken and ion-dipole interactions are formed. The degree of solubility, then, depends on the balance of these two factors, each of which has both enthalpy and entropy components.

There is one key difference between the two analyses. In the formation of a compound, we use the thermodynamic factors simply to determine whether or not a compound will form spontaneously. With the thermodynamics of the solution process, we are concerned with the degree of solubility—that is, where a compound fits on the continuum from very soluble through soluble, slightly soluble, and insoluble to very insoluble. Even for a very insoluble compound, a measurable proportion of aqueous ions will be present in equilibrium with the solid compound.

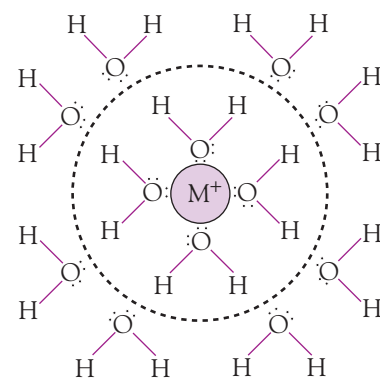
### Lattice Energy

To break the ions free from the lattice—overcoming the ionic bond—requires a large energy input. The value of the lattice energy depends on the strength of the ionic bond, and this, in turn, is related to ion size and charge. That is, magnesium oxide, with dipositive ions, will have a much higher lattice energy than sodium fluoride with its monopositive ions ( $3933 \text{ kJ}\cdot\text{mol}^{-1}$  and  $915 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively). At the same time, the entropy factor will always be highly favorable as the system changes from the highly ordered solid crystal to the disordered gas phase. Consequently, both  $\Delta S$  and  $\Delta H$  for lattice dissociation are always positive.

### Energy of Hydration

In aqueous solution, the ions are surrounded by polar water molecules. A primary hydration sphere of water molecules (usually six) surrounds the cations, with the partially negative oxygen atoms oriented toward the cation. Similarly, the anion is surrounded by water molecules, with the partially positive hydrogen atoms oriented toward the anion. Beyond the first shell of water molecules, we find additional layers of oriented water molecules (Figure 6.4). The total number of water molecules that effectively surround an ion is called the *hydration number*.

The smaller and more highly charged ions will have a larger number of water molecules in hydration spheres than do larger, less highly charged ions. As a result, the effective size of a hydrated ion in solution can be very different from that in the solid phase. This size difference is illustrated in Table 6.6. It is the smaller size of the hydrated potassium ion that enables it to pass through biological membranes more readily than the larger hydrated sodium ions.



**FIGURE 6.4** Primary and secondary hydration spheres of a metal cation. [Adapted from G. Wulfsberg, *Principles of Descriptive Inorganic Chemistry* (New York: University Science Books, 1990), p. 66.]

**TABLE 6.6** Hydration effects on the size of sodium and potassium ions

Ion	Radius (pm)	Hydrated ion	Hydrated radius (pm)
Na <sup>+</sup>	116	Na(OH <sub>2</sub> ) <sub>13</sub> <sup>+</sup>	276
K <sup>+</sup>	152	K(OH <sub>2</sub> ) <sub>7</sub> <sup>+</sup>	232

**TABLE 6.7** Enthalpy of hydration and charge density for three isoelectronic cations

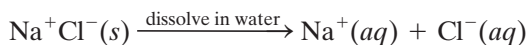
Ion	Hydration enthalpy (kJ·mol <sup>-1</sup> )	Charge density (C·mm <sup>-3</sup> )
Na <sup>+</sup>	-406	24
Mg <sup>2+</sup>	-1920	120
Al <sup>3+</sup>	-4610	364

The formation of the ion-dipole interactions of hydrated ions is highly exothermic. The value of the enthalpy of hydration is also dependent on ion charge and ion size, that is, the charge density. Table 6.7 shows the strong correlation between enthalpy of hydration and charge density for an isoelectronic series of cations.

The entropy of hydration is also negative, mainly because the water molecules surrounding the ions are in a more ordered state than they would be as free water molecules. With the small, more highly charged cations, such as magnesium and aluminum, the hydration spheres are larger than the hydration sphere of sodium; hence, there is a strong ordering of the water molecules around the two higher-charge cations. For these cations, there is a very large decrease in entropy for the hydration process.

### Energy Change of the Solution Process

We can use the solution process for sodium chloride to illustrate an enthalpy of solution cycle. In this cycle, the ionic attraction in the lattice must be overcome by the ion-dipole interactions with the water molecules:



Breaking the process into steps, first, the lattice must be vaporized (dissociate into gaseous ions):



Then the ions are hydrated:

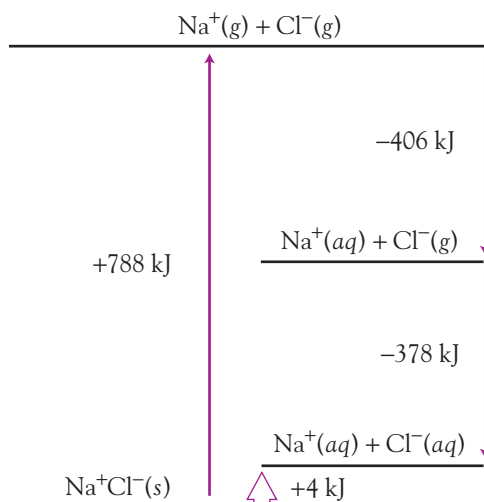


Thus, the enthalpy change  $\Delta H^\ominus$  for the solution process is

$$\begin{aligned} & [(+788 \text{ kJ} \cdot \text{mol}^{-1})] + [(-406 \text{ kJ} \cdot \text{mol}^{-1}) + (-378 \text{ kJ} \cdot \text{mol}^{-1})] \\ & = +4 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

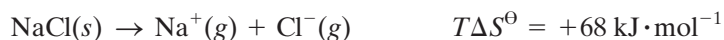
The process can be displayed as a diagram (Figure 6.5).

The enthalpy changes are usually far larger than entropy changes at normal temperatures. However, in this case, the very large enthalpy changes essentially “cancel” each other, making the small entropy change a major factor in

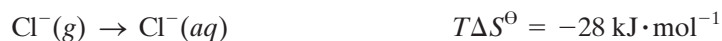


**FIGURE 6.5** Theoretical enthalpy cycle for the solution process for sodium chloride.

determining the solubility of sodium chloride. Thus, we now need to make a similar calculation for the entropy factors. So that we can compare the results with the enthalpy values, we will use  $T\Delta S^\ominus$  data at 298 K. First, the lattice must be vaporized:



Then the ions are hydrated:

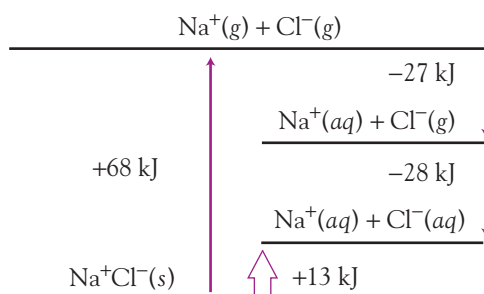


Thus, the entropy change (as  $T\Delta S^\ominus$ ) for the solution process is

$$[(+68 \text{ kJ} \cdot \text{mol}^{-1})] + [(-27 \text{ kJ} \cdot \text{mol}^{-1}) + (-28 \text{ kJ} \cdot \text{mol}^{-1})] \\ = +13 \text{ kJ} \cdot \text{mol}^{-1}$$

The process can be displayed as a diagram (Figure 6.6).

After calculating the free energy change for the solution process, we see that it is the net entropy change that favors solution, whereas the net enthalpy



**FIGURE 6.6** Theoretical entropy (as  $T\Delta S^\ominus$ ) cycle for the solution process for sodium chloride.

change does not; it is the former that is greater than the latter. Hence, as we know from experience, sodium chloride is quite soluble in water at 298 K.

$$\begin{aligned}\Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ &= (+4 \text{ kJ}\cdot\text{mol}^{-1}) - (+13 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= -9 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

## 6.5 Lattice Energies and Comparative Ion Sizes and Charges

In general, there is a dependence of lattice energy upon comparative ion sizes. In some cases, properties of a compound can be explained in terms of a significant mismatch between the anion and cation sizes, usually a large anion with a very small cation. One possible way of coping with this problem is for the compound to absorb moisture and form a hydrate. In the hydration process, the water molecules usually surround the tiny cation. The hydrated cation is then closer in size to the anion. Magnesium perchlorate is a good example of this arrangement. The anhydrous compound absorbs water so readily that it is used as a drying agent. In the crystal of the hydrate, the hexaaquamagnesium ion,  $[\text{Mg}(\text{OH}_2)_6]^{2+}$ , occupies the cation sites and the perchlorate ion occupies the anion sites (see Chapter 5, Section 5.4).

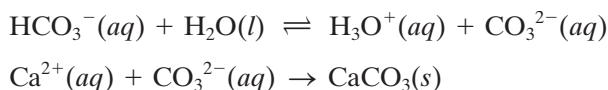
### Existence of Solid Compounds of Large, Low-Charge Anions

The effects of ion mismatch constrain large, low-charge anions to form stable solid compounds with only large, single-charge (low-charge-density) cations. In the opening of this chapter, we mentioned cesium auride,  $\text{Cs}^+\text{Au}^-$ , where it is the large cesium cation (188 pm) which stabilizes the large auride anion (190 pm) in the crystal lattice. The highly-explosive azide ion (181 pm) can similarly be stabilized by a large alkali metal cation (see Chapter 15, Section 15.6).

This concept is particularly important in the context of acid oxoanions, such as hydrogen carbonate. Gently evaporating a solution of sodium hydrogen carbonate ion results, as one might expect, in crystals of the solid compound:



If, however, a solution of calcium ion and a solution of hydrogen carbonate ion are mixed, it is calcium carbonate, not calcium hydrogen carbonate which forms. The hydrogen carbonate ion is in equilibrium with the carbonate ion, so there will always be carbonate ion present in a solution of hydrogen carbonate ion. The calcium ion then forms a precipitate of calcium carbonate:



But how do we explain why the precipitate of the carbonate is formed? The lattice energy of (theoretical) calcium hydrogen carbonate would be the

result of attractions between  $2+$  calcium ions and  $1-$  hydrogen carbonate ions and, because of the charge ratio, any solid compound would have to have alternate cation sites empty. By forming the carbonate instead, there is a much higher lattice energy resulting from the occupancy of all lattice sites by alternating  $2+$  and  $2-$  charge ions. For example, the lattice energy of magnesium fluoride,  $\text{MgF}_2$ , is  $2.9 \text{ MJ}\cdot\text{mol}^{-1}$ , whereas that of magnesium oxide,  $\text{MgO}$ , is  $3.9 \text{ MJ}\cdot\text{mol}^{-1}$ . Thus, the formation of 1 mole of a solid metal carbonate will be approximately  $1 \text{ MJ}\cdot\text{mol}^{-1}$  more exothermic than that of the corresponding solid metal hydrogen carbonate.

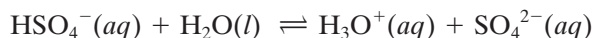
The formation of the oxoanion salt rather than that of the acid-oxoanion holds for dipositive and trippositive cations with all other acid-oxoanions. It is only the large low-charge-density monopositive ions, such as the alkali metal ions (except lithium), which form stable crystalline compounds with the hydrogen sulfate, hydrogen carbonate, hydrogen sulfite, hydrogen phosphate, and dihydrogen phosphate ions.

### WORKED EXAMPLE 6.7

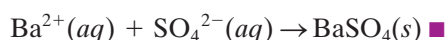
Show by means of net ionic equations why addition of barium ion to hydrogen sulfate ion leads to the formation of barium sulfate.

#### Answer

The hydrogen sulfate ion is in equilibrium with the sulfate ion:

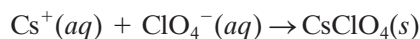


The barium ion then precipitates with the sulfate ion to form a crystal lattice with a high lattice energy. As the sulfate ion is removed from solution, the  $\text{HSO}_4^-/\text{SO}_4^{2-}$  equilibrium produces more sulfate ion, contributing to additional precipitation.



### Formation of Low-Solubility Compounds

It is commonly said that all alkali metal compounds are water soluble. This is not true. The degree of solubility differs widely, depending upon the cation and anion. In particular, insolubility is favored by the combination of large cation with large anion. An explanation is that the large ions will have low hydration enthalpies and, in addition, a moderate lattice enthalpy resulting from the good crystal packing of the ions. The combination of alkali metal ion with the perchlorate ion can be used as an example. Sodium perchlorate has a solubility of over 200 g per 100 mL while cesium perchlorate has a solubility of only 2 g per 100 mL. The perchlorate ion has an approximate ionic radius of 226 pm while those of the sodium ion and the cesium ion are about 116 pm and 181 pm. Thus, using this concept of matching ion sizes would enable us to account for the precipitation of cesium perchlorate when these two ions are mixed:



**TABLE 6.8** Decomposition temperature and cation radius for the Group 2 metal carbonates

Carbonate	Decomposition (°C)	Cation radius (pm)
MgCO <sub>3</sub>	350	86
CaCO <sub>3</sub>	830	114
SrCO <sub>3</sub>	1340	132
BaCO <sub>3</sub>	1450	149

### Thermal Stability of Carbonates

Many metal carbonates undergo thermal decomposition to the metal oxide, for example, magnesium carbonate decomposes to form magnesium oxide and carbon dioxide;



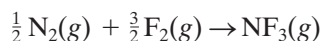
There are trends in the minimum temperature needed for decomposition, such as those for the Group 2 elements and these values correlate with the cation radius (and hence charge density) as shown in Table 6.8.

Comparing the cation radius with that of the carbonate ion (164 pm) and the oxide ion (126 pm) we can see that the best match of ion sizes is that between barium ion and carbonate ion and the earlier Group 2 metal ions with oxide. That is, comparing the carbonate and oxide lattice energies, it will be a less endothermic process for magnesium carbonate decomposing to magnesium oxide than for barium carbonate decomposing to barium oxide.

## 6.6 Formation of Covalent Compounds

To study the thermodynamics of covalent compound formation, it is possible to construct a cycle similar to the Born-Haber cycle that we used for ionic compounds. However, there is a major difference. The cycle does not involve ion formation; instead, we are concerned with covalent bond energies.

The process can be illustrated for the formation of nitrogen trifluoride. Once again, the calculation will focus on the enthalpy terms, and the entropy factor will be considered later.

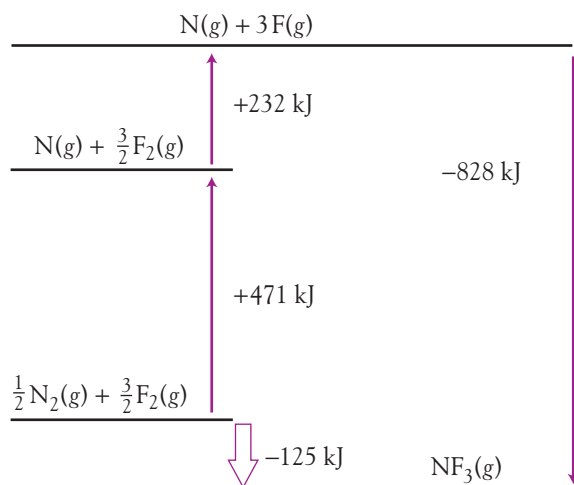


1. The dinitrogen triple bond is broken. This cleavage requires one-half of the N≡N bond energy:



2. The difluorine single bond is broken. For the stoichiometry, three-halves of the F—F bond energy is required:





**FIGURE 6.7** Theoretical enthalpy cycle for the formation of nitrogen trifluoride.

3. The nitrogen-fluorine bonds are formed. This process releases three times the N—F bond energy since three moles of bonds are being formed:



The enthalpy diagram for the formation of nitrogen trifluoride is shown in Figure 6.7. The resulting overall enthalpy change for the reaction will be



Turning to the entropy factor, in the formation of nitrogen trifluoride from its elements, there is a net decrease of 1 mole of gas. Thus, a decrease in entropy would be expected. In fact, this is the case, and the overall entropy change is  $-140 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  (using data from Appendix 1). The resulting free energy change is:

$$\begin{aligned} \Delta_f G^\ominus &= \Delta_f H^\ominus - T \Delta_f H^\ominus \\ &= (-125 \text{ kJ} \cdot \text{mol}^{-1}) - [(298 \text{ K})(-0.140 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] \\ &= -83 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

a value indicating that the compound is quite stable thermodynamically.

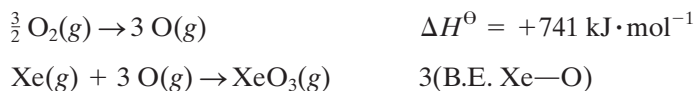
### WORKED EXAMPLE 6.8

Calculate the Xe—O bond energy in xenon trioxide given:

$$\begin{aligned} \Delta_f H^\ominus(\text{XeO}_3\text{(g)}) &= +402 \text{ kJ} \cdot \text{mol}^{-1} \text{ and bond energy}(\text{O}=\text{O}) \\ &= 494 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

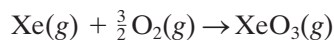
#### Answer

For this enthalpy cycle, we have:





Enthalpy of formation



$$\Delta_f H^\circ(\text{XeO}_3(g)) = +402 \text{ kJ} \cdot \text{mol}^{-1}$$

Thus:

$$(+741 \text{ kJ} \cdot \text{mol}^{-1}) - 3(\text{B.E. Xe—O}) = (+402 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\text{B.E. Xe—O} = 113 \text{ kJ} \cdot \text{mol}^{-1} \blacksquare$$

## 6.7 Thermodynamic versus Kinetic Factors

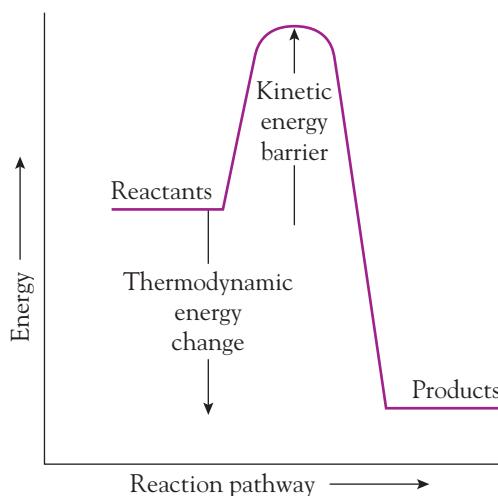
Thermodynamics is concerned with the feasibility of reaction, the position of equilibrium, and the stability of a compound. There is no information about the rate of reaction—the field of kinetics. The rate of a reaction is, to a large extent, determined by the activation energy for the reaction; that is, the energy barrier involved in the pathway for compound formation. This concept is illustrated in Figure 6.8.

A very simple example of the effect of activation energy is provided by the two more common allotropes of carbon, graphite and diamond. Diamond is thermodynamically unstable with respect to graphite:



Yet, of course, diamonds in diamond rings do not crumble into a black powder on a daily basis. They do not because an extremely high activation energy is required to rearrange the covalent bonds from the tetrahedral arrangement in diamond to the planar arrangement in graphite. Furthermore, all forms of carbon are thermodynamically unstable with respect to oxidation to carbon dioxide in the presence of dioxygen. Once again, it is the high activation energy

**FIGURE 6.8** Kinetic and thermodynamic energy factors in a chemical reaction.

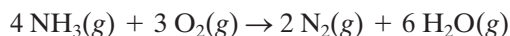


that prevents diamonds in rings and the graphite (“lead”) in pencils from bursting into flame:

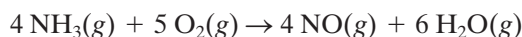


### Pathways for the Oxidation of Ammonia

We can actually make use of kinetics to alter the product of a chemical reaction. A particularly important example is the combustion of ammonia. Ammonia burns in air to form dinitrogen and water vapor:



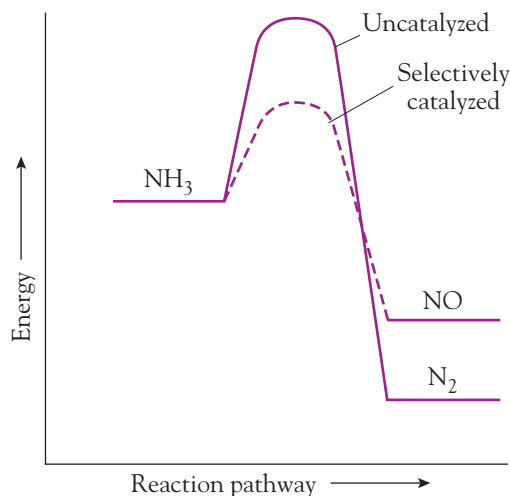
This is the thermodynamically favored path, with a free energy change of  $-1306 \text{ kJ} \cdot \text{mol}^{-1}$ . When the combustion is performed in the presence of a catalyst, the activation energy of a competing reaction, the one to produce nitrogen monoxide, is, in fact, lower than that of the reaction producing dinitrogen gas:



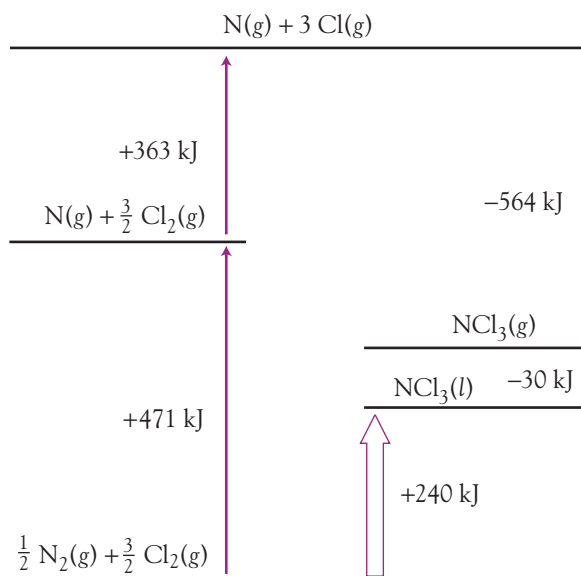
The latter reaction, which is a key step in the industrial preparation of nitric acid, occurs even though the free energy change for the reaction is only  $-958 \text{ kJ} \cdot \text{mol}^{-1}$ . Thus, we are using kinetics to control the products of reaction and overriding the thermodynamically preferred path (Figure 6.9).

### The Existence of Nitrogen Trichloride

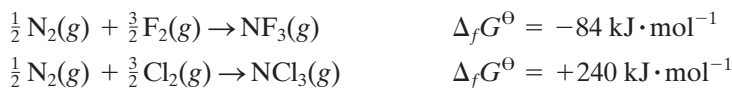
It is also possible to synthesize compounds that have a positive free energy of formation. For example, trioxxygen (ozone) and all the oxides of nitrogen have positive free energies of formation. The synthesis of such substances is feasible if there is a pathway involving a net decrease in free energy and if the decomposition of the compound is kinetically slow. Alternatively, there must be a pathway allowing for the input of energy, such as light in the case of photosynthesis and electrical energy in the case of electrolysis.



**FIGURE 6.9** Diagram (not to scale) of the kinetic and thermodynamic energy factors in the two pathways for the combustion of ammonia.

**FIGURE 6.10** Theoretical enthalpy cycle for the formation of nitrogen trichloride.

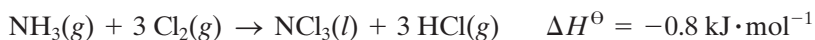
An interesting example is provided by nitrogen trichloride. We saw in the previous section that nitrogen trifluoride is thermodynamically stable. In contrast, nitrogen trichloride is thermodynamically unstable, yet it exists:



To understand this difference, we need to compare the key terms in each energy cycle. First of all, the reduction in the number of moles of gas from reactants to product means that, in both cases, the entropy term will be negative. Hence, for a spontaneous process, the enthalpy change must be negative.

In the synthesis of nitrogen trifluoride, the fluorine-fluorine bond to be broken is very weak ( $158 \text{ kJ} \cdot \text{mol}^{-1}$ ), whereas the nitrogen-fluorine bond to be formed is very strong ( $276 \text{ kJ} \cdot \text{mol}^{-1}$ ). As a result, the enthalpy of formation of nitrogen trifluoride is quite negative. The chlorine-chlorine bond ( $242 \text{ kJ} \cdot \text{mol}^{-1}$ ) is stronger than the fluorine-fluorine bond, and the nitrogen-chlorine bond ( $188 \text{ kJ} \cdot \text{mol}^{-1}$ ) in nitrogen trichloride is weaker than the nitrogen-fluorine bond in nitrogen trifluoride. As a result, the enthalpy change for the formation of nitrogen trichloride is positive (Figure 6.10) and, with a negative entropy change giving a positive  $-T\Delta S$  term, the free energy change will be positive.

How is it possible to prepare such a compound? The reaction between ammonia and dichlorine to give nitrogen trichloride and hydrogen chloride is feasible as a result of the formation of strong hydrogen-chlorine bonds:



The thermodynamically unstable nitrogen trichloride decomposes violently and exothermically when warmed:



Thermodynamics, then, is a useful tool for understanding inorganic chemistry. At the same time, we should always be aware that kinetic factors can cause the product to be other than the most thermodynamically stable one (as in the case of the oxidation of ammonia). In addition, it is sometimes possible to synthesize compounds that have a positive free energy of formation, provided the synthetic route involves a net decrease in free energy and the decomposition of the compound is kinetically slow (as we saw for the existence of nitrogen trichloride).

## KEY IDEAS

- Chemical reactions depend on the balance of enthalpy and entropy changes.
- The formation of an ionic compound can be considered to occur in a series of theoretical steps.
- A diagram can be constructed to display the relative energies of steps in the formation (Born-Haber) cycle.
- The solution process can be considered in terms of an energy cycle.
- The formation of covalent compounds can be displayed graphically.
- Chemical reactions are controlled by kinetic factors in addition to thermodynamic factors.

## EXERCISES

- 6.1** Define the following terms: (a) spontaneous process; (b) entropy; (c) standard enthalpy of formation.
- 6.2** Define the following terms: (a) enthalpy; (b) average bond energy; (c) enthalpy of hydration.
- 6.3** For the formation of solid calcium oxide from solid calcium and gaseous oxygen, what is the probable sign of the entropy change? What, then, must be the sign of the enthalpy change if the formation of the product occurs spontaneously? Do not consult data tables.
- 6.4** At very high temperatures, water will decompose to hydrogen and oxygen gas. Explain why this is to be expected in terms of the formula relating free energy to the other two common thermodynamic functions. Do not consult data tables.
- 6.5** Using enthalpy of formation and absolute entropy values from the data tables in Appendix 1, determine the enthalpy, entropy, and free energy of reaction for the following reaction. Use this information to identify whether the reaction is spontaneous at standard temperature and pressure.
- $$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$$
- 6.6** Using enthalpy of formation and absolute entropy values from the data tables in the appendices, determine the enthalpy, entropy, and free energy of reaction for the following reaction. Use this information to identify whether the reaction is spontaneous at standard temperature and pressure.
- $$\frac{1}{2} \text{N}_2(g) + \text{O}_2(g) \rightarrow \text{NO}_2(g)$$
- 6.7** Deduce whether the synthesis of sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$  ( $\Delta_f G^\circ(\text{SO}_2\text{Cl}_2(g)) = -314 \text{ kJ} \cdot \text{mol}^{-1}$ ), is thermodynamically feasible from phosphorus pentachloride and sulphur trioxide. The other product is phosphoryl chloride,  $\text{POCl}_3$ . Use free energy of formation values from the data tables in Appendix 1.
- 6.8** Use free energy of formation values from Appendix 1 to determine whether the following reaction is thermodynamically feasible:
- $$\text{PCl}_5(g) + 4 \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{PO}_4(s) + 4 \text{HCl}(g)$$
- 6.9** Which one of the N—N or N=N bonds will be stronger? Do not look at data tables. Explain your reasoning.
- 6.10** The molecules of dinitrogen and carbon monoxide are isoelectronic. Yet the C≡O bond energy ( $1072 \text{ kJ} \cdot \text{mol}^{-1}$ )

is stronger than that of the  $\text{N}\equiv\text{N}$  bond ( $942\text{ kJ}\cdot\text{mol}^{-1}$ ). Suggest an explanation.

**6.11** Use bond energy data from Appendix 3 to calculate an approximate value for the enthalpy of reaction for:



**6.12** Use bond energy data from Appendix 3 to decide whether the following reaction is thermodynamically possible:



**6.13** Place the following compounds in order of increasing lattice energy: magnesium oxide, lithium fluoride, and sodium chloride. Give the reasoning for this order.

**6.14** Calculate the first three terms of the series for the Madelung constant for the sodium chloride lattice. How does this compare with the limiting value?

**6.15** Calculate the first two terms of the series for the Madelung constant for the cesium chloride lattice. How does this compare with the limiting value?

**6.16** Using the Born-Landé equation, calculate the lattice energy of cesium chloride.

**6.17** Using the Born-Landé equation, calculate the lattice energy of calcium fluoride.

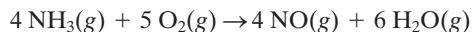
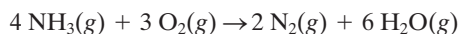
**6.18** Construct a Born-Haber cycle for the formation of aluminum fluoride. Do not perform any calculation.

**6.19** Construct a Born-Haber cycle for the formation of magnesium sulfide. Do not perform any calculation.

**6.20** Calculate the enthalpy of formation of copper(I) fluoride. This compound adopts a sphalerite structure.

**6.21** The lattice energy of sodium hydride is  $2782\text{ kJ}\cdot\text{mol}^{-1}$ . Using additional data from the appendices, calculate a value for the electron affinity of atomic hydrogen.

**6.22** In the discussion of thermodynamic and kinetic factors, we compared the two reactions

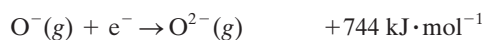


Without consulting data tables:

(a) Is there any major difference in entropy factors between the two reactions? Explain.

(b) Considering your answer to (a) and the fact that the free energy for the second reaction is less negative than for the first, deduce the sign of the enthalpy of formation of nitrogen monoxide, NO.

**6.23** The electron affinities of the oxygen atom are



If the second electron affinity is so endothermic, why are ionic oxides so prevalent?

**6.24** For an ionic compound, MX, the lattice energy is  $1205\text{ kJ}\cdot\text{mol}^{-1}$  and the enthalpy of solution is  $-90\text{ kJ}\cdot\text{mol}^{-1}$ . If the enthalpy of hydration of the cation is 1.5 times that of the anion, what are the enthalpies of hydration of the ions?

## BEYOND THE BASICS

**6.25** The Born-Landé equation utilizes a term called “the permittivity of free space.” Use a physics text to explain the significance of this term in physical science.

**6.26** Calculate the enthalpy of formation of calcium oxide using a Born-Haber cycle. Obtain all necessary information from the data tables in the appendices. Compare the value that you obtain with the actual measured value of  $\Delta_f H^\circ(\text{CaO}(\text{s}))$ . Then calculate a similar cycle assuming that calcium oxide is  $\text{Ca}^+\text{O}^-$  rather than  $\text{Ca}^{2+}\text{O}^{2-}$ . Take the lattice energy of  $\text{Ca}^+\text{O}^-$  to be  $-800\text{ kJ}\cdot\text{mol}^{-1}$ . Discuss why the second scenario is less favored in enthalpy terms.

**6.27** Construct Born-Haber cycles for the theoretical compounds  $\text{NaCl}_2$  and  $\text{NaCl}_3$ . Calculate the enthalpy of formation for both of these two compounds using information

from the data tables in the appendices plus the following values: theoretical lattice energy,  $\text{NaCl}_2 = -2500\text{ kJ}\cdot\text{mol}^{-1}$ ; theoretical lattice energy,  $\text{NaCl}_3 = -5400\text{ kJ}\cdot\text{mol}^{-1}$ ; second ionization energy (IE),  $\text{Na} = 4569\text{ kJ}\cdot\text{mol}^{-1}$ ; third IE,  $\text{Na} = 6919\text{ kJ}\cdot\text{mol}^{-1}$ . Compare the cycles and suggest why  $\text{NaCl}_2$  and  $\text{NaCl}_3$  are not the preferred products.

**6.28** The lattice energy of sodium tetrahydridoborate(III),  $\text{NaBH}_4$ , is  $2703\text{ kJ}\cdot\text{mol}^{-1}$ . Using additional data from the appendices, calculate the enthalpy of formation of the tetrahydridoborate ion.

**6.29** Magnesium chloride is very soluble in water, whereas magnesium oxide is very insoluble in water. Offer an explanation for this difference in terms of the theoretical steps of the solution process. Do not use data tables.

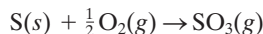
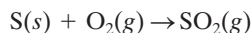
**6.30** Using lattice energy and enthalpy of hydration values from data tables, determine the enthalpy of solution of (a) lithium chloride; (b) magnesium chloride. Explain the major difference in the two values in terms of the theoretical steps.

**6.31** Construct an energy diagram, similar to a Born-Haber cycle, for the formation of carbon tetrafluoride. Then calculate the enthalpy of formation from the steps, using numerical values from the data tables in the appendices. Finally, compare your value with the tabulated value of  $\Delta_f H^\circ(\text{CF}_4(g))$ .

**6.32** Construct an energy diagram, similar to a Born-Haber cycle, for the formation of sulfur hexafluoride. Then calculate the enthalpy of formation from the steps, using numerical values from data tables. Finally, compare your value with the tabulated value of  $\Delta_f H^\circ(\text{SF}_6(g))$ .

**6.33** Calculate the chlorine-fluorine bond energy in chlorine monofluoride, ClF, using an energy diagram.

**6.34** Using enthalpy of formation and absolute entropy values from data tables, determine the free energy of formation for the following reactions:



(a) Account for the sign of the entropy change in the formation of sulfur trioxide.

(b) Which combustion leads to the greatest decrease in free energy (that is, which reaction is thermodynamically preferred)?

(c) Which of the oxides of sulfur is most commonly discussed?

(d) Suggest an explanation to account for the conflict between your answers to parts (b) and (c).

**6.35** Although the hydration energy of the calcium ion,  $\text{Ca}^{2+}$ , is much greater than that of the potassium ion,  $\text{K}^+$ , the molar solubility of calcium chloride is much less than that of potassium chloride. Suggest an explanation.

**6.36** The enthalpy of solution for sodium chloride is +4  $\text{kJ}\cdot\text{mol}^{-1}$  while that of silver chloride is +65  $\text{kJ}\cdot\text{mol}^{-1}$ .

(a) What would you suspect about the comparative solubilities of the two compounds? In drawing this conclusion, what assumption do you have to make?

(b) Using enthalpy of hydration data, calculate values for the two lattice energies. (Both adopt the sodium chloride structure.)

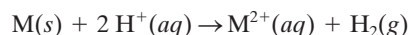
(c) Calculate values for the lattice energies using the Born-Landé equation and compare to the values calculated in part (b). Suggest a reason for the significant discrepancy in the case of one of the compounds.

**6.37** Using the following data, plus any other necessary data from the appendices, calculate three values for the hydration enthalpy of the sulfate ion. Are the values consistent?

Compound	$\Delta_f H^\circ$ solution ( $\text{kJ}\cdot\text{mol}^{-1}$ )	Lattice energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\text{CaSO}_4$	-17.8	-2653
$\text{SrSO}_4$	-8.7	-2603
$\text{BaSO}_4$	-19.4	-2423

**6.38** It is possible to calculate standard enthalpy/entropy of solution values from the difference between the standard enthalpy/entropy of formation of the solid compound and the standard enthalpy/entropy of formation of the constituent aqueous ions. Thus, determine the free energy of solution of calcium phosphate at 20°C. Suggest what your value means in terms of the solubility of calcium phosphate.

**6.39** Magnesium and lead have similar first and second ionization energies, yet their reactivity with acid:



(where M = Mg, Pb)

is very different. Construct a suitable cycle and obtain the appropriate data from the appendices (*hint*: since the reduction of hydrogen ion is common to both cycles, you need only consider the formation of the aqueous metal cations), and then deduce the factor that causes the reactivity difference. Suggest a fundamental reason for this difference.

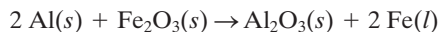
**6.40** For the main group elements, the most thermodynamically stable compound is the one when all of the valence electrons have been lost. Yet for all of the lanthanoids, it is the 3+ state that provides the most stable state. Explain in terms of ionization energies and their role in Born-Haber cycles.

**6.41** Use the Kapustinskii equation to calculate a lattice energy for cesium chloride and compare it to the experimental value and to that obtained from the Born-Landé equation (Exercise 6.16).

**6.42** Thallium has the two oxidation numbers of +1 and +3. Use the Kapustinskii equation to calculate values for the lattice energies of TlF and  $\text{TlF}_3$ . The radii of  $\text{Tl}^+$  and  $\text{Tl}^{3+}$  are 164 pm and 102 pm, respectively.

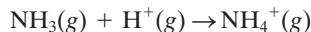
**6.43** Under very high pressure, rubidium chloride will adopt a cesium chloride structure. Calculate the enthalpy change for the transition from its sodium chloride lattice structure to that of the cesium chloride lattice structure.

**6.44** One of the most spectacular chemical demonstrations is the thermite reaction:



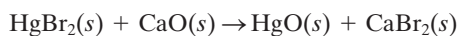
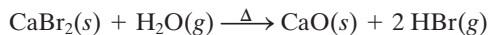
This reaction is so exothermic that molten iron is produced, and the reaction was formerly used as a means of welding railroad track. Using the data tables in the appendices, account for the enormous exothermicity of this reaction.

**6.45** Calculate the proton affinity of ammonia:



given that ammonium fluoride,  $\text{NH}_4\text{F}$ , crystallizes in a wurtzite structure, with a distance of 256 pm between ammonium ion and fluoride ion centers, and that the Born exponent for the crystal lattice is 8. The ionization energy for the hydrogen atom is  $+1537 \text{ kJ}\cdot\text{mol}^{-1}$ . *Hint:* Among the additional data that you will need from the appendices are the enthalpy of formation of ammonia, hydrogen fluoride, and ammonium fluoride.

**6.46** The following reaction sequence has been proposed as a thermochemical method for the production of dihydrogen and dioxygen from water. Calculate the free energy changes for each step at 298 K and those for the overall process.



Suggest reasons why the process has little possibility of commercial adoption.

**6.47** The ionic bond is often described as being formed as a result of metals “wanting to lose electrons” and nonmetals “wanting to gain electrons.” Critique this statement using appropriate thermodynamic values.

## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



# SOLVENT SYSTEMS AND ACID-BASE BEHAVIOR

## CHAPTER 7

Many chemical reactions are performed in solution. What determines our choice of solvent? How do solvents function? The most commonly used solvent is water, where acid-base chemistry becomes important. For most purposes, the Brønsted-Lowry interpretation of acid-base properties is quite adequate, although Lewis concepts are also discussed. The latter part of the chapter focuses on the hard-soft acid-base concept, a particularly useful way of explaining some of the properties of inorganic compounds.

### Context: Green Solvents for the Future

The solution chemistry of our planet is dominated by water. Thus, our view of what is soluble and why things dissolve is based on the properties of this very polar covalent molecule. For many inorganic chemistry reactions, water cannot be used because a large range of reactants and/or products react with water as we discuss in Section 7.4. When we do use other solvents, they are often low-polarity, toxic, flammable, volatile organic compounds (see Section 7.1). Yet solvent systems without these disadvantages exist and play crucial roles in laboratory and industrial chemical synthesis. We are now aware, too, that common solvents, including water, can behave very differently under conditions of high temperature and pressure (see Chapter 10, Section 10.6).

One of the major developments in recent years is the discovery of ionic liquids and their use as solvents. Ionic liquids (ILs) are composed of a very large mono-positive organic cation with a large mono-negative anion. As a result, in ILs, the cation-anion attraction is very weak and the lattice energies of such compounds is so low that thermal energy at room temperature is sufficient to collapse the crystal structure to a liquid. At the same time, the ionic nature of the bonding makes the energy of vaporization very high; thus ILs have very low vapor pressures at room temperature. It is the combination of properties which make ILs potentially recyclable and give them their “green” credentials.

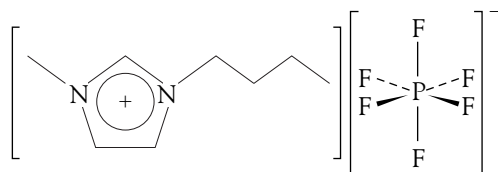
The most widely studied ionic liquid, and the first to be produced commercially, is 1-butyl-3-methylimidazolium hexafluorophosphate, known as BMIMPF<sub>6</sub> (see figure below). Ionic liquids of this type are

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 7.1 Solvents
- 7.2 Brønsted-Lowry Acids and Bases
- 7.3 Trends in Acid-Base Behavior
- 7.4 Acid-Base Reactions of Oxides
- 7.5 The Lewis Theory
- 7.6 Pearson Hard-Soft Acid-Base Concepts
- 7.7 Applications of the HSAB Concept
- 7.8 Biological Aspects



expensive so they find most use in applications where reuse is possible. With their unique ionic solvent properties, ILs dissolve a wide range of both inorganic and organic compounds; thus new high-yield “green” pathways are being devised for many organic syntheses. In particular, ILs can be used as solvents for many traditional organic chemistry syntheses, such as Diels-Alder reactions and Friedel-Crafts reactions.



The structure of the ionic liquid  $[\text{BMIM}]^+(\text{PF}_6)^-$

## 7.1 Solvents

Solvents function by interacting with solid solutes so that the reactant molecules and/or ions are free to collide and react. In order for a solvent to dissolve a solute, the solvent-solute bonding interaction must be strong enough to overcome the lattice energy, the attraction between the particles in the solid crystal.

Highly polar solvents are necessary to dissolve ionic compounds, whereas most covalent compounds are soluble in low-polarity solvents. The best measure of the molecular polarity of the solvent is the dielectric constant for the compound. The term *dielectric constant* refers to the ability of the compound to distort an electrostatic field. Table 7.1 provides a list of some solvents and their corresponding dielectric constants. We can categorize common solvents as *polar protic*

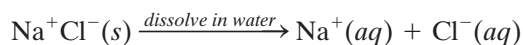
**TABLE 7.1** Some solvents and their dielectric constants

Common name	Formula	Dielectric constant
Hydrofluoric acid	HF	84
Water	H <sub>2</sub> O	78
Dimethylsulfoxide (DMSO)	(CH <sub>3</sub> ) <sub>2</sub> SO	47
<i>N,N</i> -dimethylformamide (DMF)	(CH <sub>3</sub> ) <sub>2</sub> NCHO	38
Acetonitrile	CH <sub>3</sub> CN	37
Methanol	CH <sub>3</sub> OH	32
Ammonia	NH <sub>3</sub>	27
Acetone	(CH <sub>3</sub> ) <sub>2</sub> CO	21
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	9
Tetrahydrofuran (THF)	C <sub>4</sub> H <sub>8</sub> O	8
Diethylether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	4
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	2
Hexane	C <sub>6</sub> H <sub>14</sub>	2

(dielectric constant usually between 50 and 100), *dipolar aprotic* (dielectric constant usually between 20 and 50), or *nonpolar* (dielectric constant close to zero).

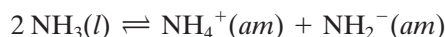
### Polar Protic Solvents

Polar protic solvents contain one of the three very polar bonds H—F, O—H, or N—H. Solvation occurs by the strong ion-dipole forces between the anion and the hydrogen of the solvent and between the cation and the fluorine/oxygen/nitrogen of the solvent. Solubility depends on the ion-dipole attractions being stronger than the lattice energy (see Chapter 6, Section 6.1), the electrostatic cation-anion attractions in the crystal lattice. For the solution of sodium chloride in water:



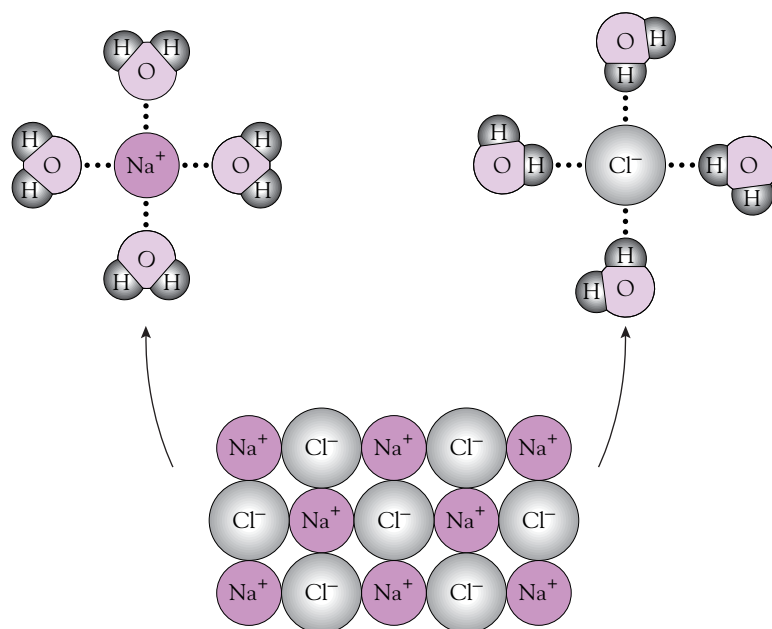
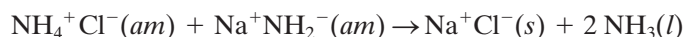
We can picture the solvation process as in Figure 7.1.

Most protic solvents undergo *autoionization*; that is, a small proportion of the solvent molecules undergo hydrogen ion exchange reactions to give their conjugate acid and conjugate base simultaneously. For water and ammonia, these equilibria are



where *am* represents liquid ammonia, parallel to the use of *aq* for water.

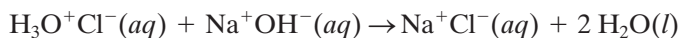
Although ammonia boils at  $-33^\circ\text{C}$ , it has a high enthalpy of vaporization. As a result, it is quite practicable to work with liquid ammonia provided this is done within a fume hood (ammonia is a toxic, noxious gas). Acid-base reactions can be performed in ammonia. For example, ammonium chloride and sodium amide,  $\text{NaNH}_2$ , react to give sodium chloride and ammonia:



**FIGURE 7.1** Representation of the dissolving process for sodium chloride in water. [From G. Rayner-Canham et al., *Chemistry: A Second Course* (Don Mills, ON, Canada: Addison-Wesley, 1989), p. 350.]

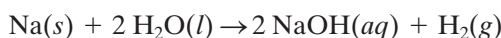
It is possible to define acids and bases in terms of the solvent employed. Thus, an acid is a solute that, either by direct dissociation or by reaction with the solvent, gives the cation characteristic of the solvent. In this case, the ammonium ion is the cation characteristic of ammonia and so the ammonium ion is classified as an acid in ammonia solution. Similarly, a base is a solute that, either by direct dissociation or by reaction with the solvent, gives the anion characteristic of the solvent. Here it is the amide ion that is the anion characteristic of ammonia. The amide ion is therefore categorized as a base in ammonia solution.

The reaction above parallels the acid-base reaction in water between hydrochloric acid and sodium hydroxide. The similarity can be seen more clearly if we write hydrochloric acid as hydronium chloride,  $\text{H}_3\text{O}^+\text{Cl}^-$ :

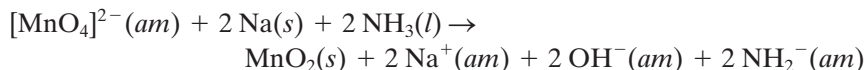


Sodium chloride is soluble in water but insoluble in ammonia. Ammonia is less polar than water; thus, the formation of weaker ion-dipole interactions makes ammonia unable to compensate for the sodium chloride lattice energy.

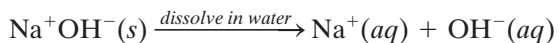
Water is such a convenient, inexpensive solvent, but it constrains the chemistry that we perform. For example, we cannot use sodium as a reducing agent in aqueous solution because sodium reacts with water:



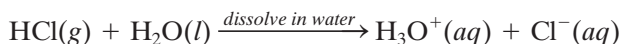
However, in liquid ammonia, it is possible to use sodium metal to reduce the permanganate ion to the manganate ion,  $[\text{MnO}_4]^{2-}$  (see Chapter 20, Section 20.6), and then to manganese(IV) oxide:



When we say an ionic compound “dissolves” in water, the process is actually one of dissociation. The term *dissociation* means “separation” and is used when a solvent such as water separates the ions that are present in ionic compounds. As an example, we can use sodium hydroxide. The crystal lattice of this white solid contains alternating sodium ions and hydroxide ions. The solution process can be represented as

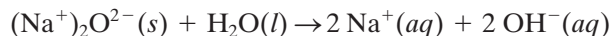


The dissolving of an inorganic acid in water occurs by a different process. Inorganic acids contain covalent bonds. Solution in water results in *ionization*, the breaking of the covalent bonds resulting in ion formation. That is, for ionization to occur, the ion-dipole attractions formed must be stronger than the covalent bonds broken in the molecular acids. We can illustrate this process with hydrochloric acid:



In defining the term *solvent*, we have also to differentiate between “dissolves in” and “reacts with.” For example, when we add water to solid white

sodium oxide, the solid “disappears” just as the sodium hydroxide “disappeared,” but in this case, a chemical reaction has occurred:

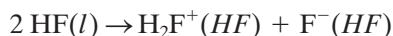


### WORKED EXAMPLE 7.1

Give an equation for the autoionization reaction of  $\text{HF}(l)$  and identify the conjugate acid and conjugate base.

#### Answer

Some of the  $\text{HF}$  molecule will autoionize to give  $\text{H}_2\text{F}^+$  and  $\text{F}^-$ .

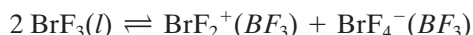


$\text{H}_2\text{F}^+$  is the conjugate acid and  $\text{F}^-$  is the conjugate base. ■

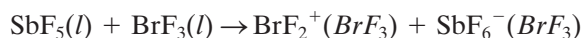
### Dipolar Aprotic Solvents

As we mentioned earlier, to dissolve an ionic compound, the solvent must have a stronger interaction with the ions than the lattice energy. Aprotic solvents function by being strong Lewis acids or bases. They are most often Lewis bases with lone pairs that can be attracted toward the cation, since the small cation usually contributes the greater share to the lattice energy. For example, lithium chloride is soluble in acetone,  $(\text{CH}_3)_2\text{CO}$ . In this solvent, the lithium ion in solution is actually present as the  $[\text{Li}[\text{OC}(\text{CH}_3)_2]_4]^+$  ion with a lone pair on each oxygen bonded to the lithium ion.

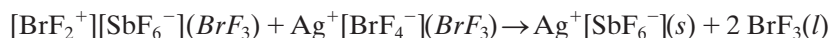
A very few aprotic solvents autoionize in the same manner as a protic solvent. A good example is bromine trifluoride:



Bromine trifluoride can act as a Lewis acid (with silver fluoride as a base) or as a Lewis base (with antimony pentafluoride as an acid):



It is even possible to have a Lewis neutralization reaction of the acid  $[\text{BrF}_2]$   $[\text{SbF}_6]$  with the base  $\text{Ag}[\text{BrF}_4]$ :



### Nonpolar Solvents

This class of solvents will not dissolve ionic compounds but will dissolve a wide range of covalently bonded uncharged species. For example, octasulfur,  $\text{S}_8$ , and tetraphosphorus,  $\text{P}_4$ , are both insoluble in water but dissolve readily in nonpolar carbon disulfide,  $\text{CS}_2$ . In each of these cases, the dispersion-force interaction between solute and solvent is greater than that between molecules of the

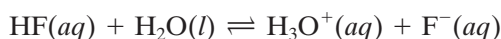
elements themselves. The enthalpy of solution tends to be small for low-polar and nonpolar solutes. This can be explained in terms of the only attraction within the solute or between solute and solvent being that of dispersion and, in some cases, weak dipole-dipole interactions. With such a small enthalpy change, the (usually positive) entropy of mixing becomes a significant factor in the solution process.

Many metals form covalent compounds. For example, the bonding in solid mercury(II) nitrate is best considered as ionic, but that in liquid dimethylmercury,  $\text{Hg}(\text{CH}_3)_2$ , is covalent. Thus, mercury(II) nitrate is soluble in water, whereas dimethylmercury is miscible with almost all of the nonpolar, low-dielectric constant solvents. It is the preference for nonpolar solvents, such as in the fatty tissues of fish and of our brain, that causes toxic dimethylmercury to bioaccumulate (see the opening context in Chapter 23).

## 7.2 Brønsted-Lowry Acids and Bases

Although nonpolar solvents are important for compounds of nonmetals and for organometallic compounds (see Chapter 23), water is still the most common solvent for simple compounds of metal salts. Thus, for our discussions of aqueous acids and bases, we will still use Brønsted-Lowry theory; that is, an acid is a hydrogen ion donor and a base is a hydrogen ion acceptor.

Acid behavior usually depends on a chemical reaction with the solvent—in most cases, water. This behavior can be illustrated for hydrofluoric acid:



In this reaction, water functions as a base. The hydronium ion is the conjugate acid of water and the fluoride ion is the conjugate base of hydrofluoric acid. Although chemists often say that the acid has donated its hydrogen ion to the base, the language is somewhat misleading, for it is more accurately a competition for the hydrogen ion between two chemical substances (with the base winning). The acid does not “donate” the hydrogen ion any more willingly than you would “donate” your wallet or purse to a mugger.

Because the values of acid ionization constants,  $K_a$ , can involve very large or very small exponents, the most useful quantitative measure of acid strength is the  $\text{p}K_a$ , where  $\text{p}K_a = -\log_{10}K_a$ . The stronger the acid, the more negative the  $\text{p}K_a$ . Typical values are shown in Table 7.2.

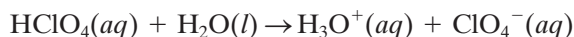
**TABLE 7.2** Acid ionization constants of various inorganic acids

Acid	HA	$\text{A}^-$	$K_a$ (at 25°C)	$\text{p}K_a$
Perchloric acid	$\text{HClO}_4$	$\text{ClO}_4^-$	$10^{10}$	−10
Hydrochloric acid	$\text{HCl}$	$\text{Cl}^-$	$10^2$	−2
Hydrofluoric acid	$\text{HF}$	$\text{F}^-$	$3.5 \times 10^{-4}$	3.45
Ammonium ion	$\text{NH}_4^+$	$\text{NH}_3$	$5.5 \times 10^{-10}$	9.26

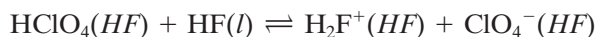
## Strengths of Acids

For an inorganic chemist, it is trends in the strengths of acids that are interesting. The common acids with  $K_a > 1$  (negative  $\text{p}K_a$  values), such as hydrochloric acid, nitric acid, sulfuric acid, and perchloric acid, are all regarded as strong acids. Those with  $K_a < 1$  (positive  $\text{p}K_a$  values), such as nitrous acid, hydrofluoric acid, and most of the other inorganic acids, are weak acids; that is, there are appreciable proportions of the molecular acid present in solution.

In water, all the strong acids seem equally strong, undergoing close to 100 percent ionization; that is, water acts as a *leveling solvent*. A stronger acid, such as perchloric acid,  $\text{HClO}_4$ , will ionize to give hydronium ion, the strongest possible acid in aqueous solution:



To qualitatively identify the stronger acid, we dissolve the acids in a base weaker than water. A weaker base—often a pure weak acid—will function as a *differentiating solvent* for acids. This test can be illustrated by the equilibrium for perchloric acid in hydrofluoric acid:



where  $HF$  represents the pure solvent, hydrogen fluoride. The weaker acid, hydrofluoric acid, functions in this case as a hydrogen ion acceptor (base) for the stronger perchloric acid. A substance that can act either as an acid or as a base is said to be *amphiprotic*. Since hydrofluoric acid is a weaker base than water, the equilibrium does not lie completely to the right, as does that for the reaction of perchloric acid with water. The experiment can be repeated with the other strong acids, and the strongest acid is the acid that causes the equilibrium to lie farthest to the right. Of the common acids, this is perchloric acid.

## Binary Acids

The most common binary acids are the hydrohalic acids, whose  $\text{p}K_a$  values are shown in Table 7.3. With a positive  $\text{p}K_a$ , hydrofluoric acid is clearly a much weaker acid than the other three. The others are all strong acids, and they

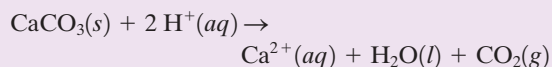
**TABLE 7.3** Correlation between the acid strengths of the hydrohalic acids and the energies of the hydrogen-halogen bonds

Acid	$\text{p}K_a$	H—X bond energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\text{HF}(aq)$	+3	565
$\text{HCl}(aq)$	−7	428
$\text{HBr}(aq)$	−9	362
$\text{HI}(aq)$	−10	295

## Antacids

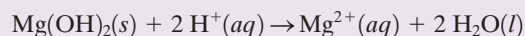
One of the major categories of over-the-counter medications is antacids. In fact, the treatment of upset stomachs is a billion-dollar business. Antacids are the most common of the types of inorganic pharmaceuticals. The stomach contains acid—hydrochloric acid—since the hydronium ion is an excellent catalyst for the breakdown of complex proteins (hydrolysis) into the simpler peptide units that can be absorbed through the stomach wall. Unfortunately, some people's stomachs overproduce acid. To ameliorate the unpleasant effects of excess acid, a base is required. But the choice of bases is not as simple as in a chemistry lab. For example, ingestion of sodium hydroxide would cause severe and possibly life-threatening throat damage.

Some proprietary antacids contain calcium carbonate. An obvious disadvantage is that the neutralization reaction produces carbon dioxide:



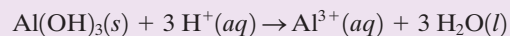
Although the beneficial aspects of increasing one's calcium intake are mentioned by companies selling such antacid compositions, they rarely mention that calcium ion acts as a constipative.

Another popular antacid compound is magnesium hydroxide. This is available in tablet formulations, but it is also marketed as a finely ground solid mixed with colored water to form a slurry called “milk of magnesia.” The low solubility of the magnesium hydroxide means that there is a negligible concentration of free hydroxide ion in the suspension. In the stomach, the insoluble base reacts with acid to give a solution of magnesium ion.



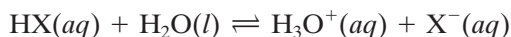
Whereas calcium ion is a constipative, magnesium ion is a laxative. For this reason, some formulations contain a mixture of calcium carbonate and magnesium hydroxide, balancing the effects of the two ions.

Aluminum hydroxide is the active ingredient in a few antacid formulations. This base is also water insoluble; thus, the hydroxide ions are not released until the tablet reaches the stomach.



As we will discuss in Chapter 13, Section 13.11, the aluminum ion is toxic. There is no evidence that the occasional intake of an aluminum-containing antacid tablet will cause long-term health effects, but regular users of antacids might consider using calcium and/or magnesium formulations.

ionize almost completely, hydroiodic being the strongest. When HX is used to generically represent each hydrohalic acid, the ionization equilibrium is:



We find the predominant thermodynamic factors to be the enthalpy of the H—X bond breaking and the enthalpy of formation of an additional O—H bond as the water molecule becomes the hydronium ion. The values of the various H—X bond energies are also given in Table 7.3, while for comparison, the O—H bond energy is  $459 \text{ kJ}\cdot\text{mol}^{-1}$ . Because the tendency of any reaction is toward the formation of the stronger bond, it is apparent that ionization is not energetically favored for hydrofluoric acid but is favored for the other hydrohalic acids. In fact, the bond energy differences correlate remarkably well with the trends in acid strength.

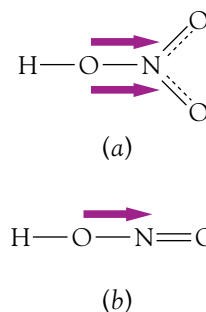
## Oxoacids

Oxoacids are ternary acids containing oxygen. For all the common inorganic acids, the ionizable hydrogen atoms are covalently bonded to oxygen

atoms. For example, nitric acid,  $\text{HNO}_3$ , is more appropriately written as  $\text{HONO}_2$ .

In a series of oxoacids of one element, there is a correlation between acid strength and the number of oxygen atoms. Thus, nitric acid is a strong acid ( $\text{p}K_{\text{a}} = -1.4$ ), whereas nitrous acid,  $\text{HONO}$ , is a weak acid ( $\text{p}K_{\text{a}} = +3.3$ ). Electronegativity arguments can be used to provide an explanation. Oxoacids are like the hydrohalic acids in that their acid strength depends on the weakness of the covalent bond between the ionizable hydrogen atom and its neighbor. For the oxoacids, the greater the number of highly electronegative oxygen atoms in the molecule, the more the electron density is pulled away from the hydrogen atom and the weaker the hydrogen-oxygen bond. As a result, an acid with numerous oxygen atoms is more easily ionized and hence stronger. This tendency is illustrated in Figure 7.2.

The considerable dependence of acid strength on the number of oxygen atoms can actually be used in a semiquantitative fashion. If the formula of an oxoacid is written as  $(\text{HO})_n\text{XO}_m$ , then when  $m = 0$ , the value of  $\text{p}K_{\text{a}}$  for the first ionization is about 8; for  $m = 1$ , it is about 2; for  $m = 2$ , it is about  $-1$ ; and for  $m = 3$ , it is about  $-8$ .



**FIGURE 7.2** Nitric acid (a) is a stronger acid than nitrous acid (b) because the electron flow away from the H—O bond is greater in nitric acid.

### WORKED EXAMPLE 7.2

Place the following oxoacids of chlorine in order of increasing acid strength;  $\text{HClO}_4$ ,  $\text{HClO}$ ,  $\text{HClO}_3$ ,  $\text{HClO}_2$ .

#### Answer

The greater the number of electronegative oxygen atoms, the greater the acidity.

So the order of acidity will be  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ . ■

### WORKED EXAMPLE 7.3

Estimate approximately the  $\text{p}K_{\text{a}}$  of (a) chlorous acid,  $\text{HClO}_2$  and (b) boric acid,  $\text{H}_3\text{BO}_3$ .

#### Answer

a) Chlorous acid has the structure  $(\text{HO})\text{ClO}$ , so  $m = 1$  and the  $\text{p}K_{\text{a}}$  is likely to be about 2.

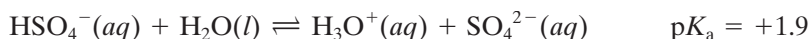
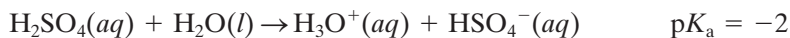
b) Boric acid has the structure  $(\text{HO})_3\text{B}$ , so  $m = 0$  and the  $\text{p}K_{\text{a}}$  is likely to be about 8. ■

## Polyprotic Acids

There are several acids, including sulfuric acid and phosphoric acid, that have more than one ionizable hydrogen atom. The successive ionizations always



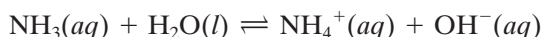
proceed to a lesser and lesser extent. This trend can be illustrated by the two ionization steps for sulfuric acid:



The first step proceeds essentially to completion; hence, sulfuric acid is identified as a strong acid. The equilibrium for the second step lies slightly to the left at common acid concentrations. Thus, in an aqueous solution of sulfuric acid, the hydrogen sulfate ion,  $\text{HSO}_4^-$ , is one of the major species. We can explain the decreasing values of successive ionizations in terms of the increasing negative charge of the resulting anion, making the loss of an additional hydronium ion more difficult.

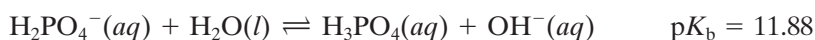
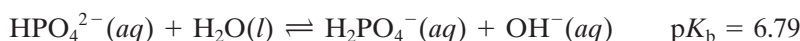
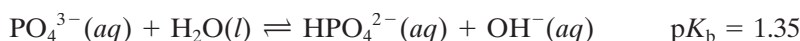
### Brønsted-Lowry Bases

A Brønsted-Lowry base is a hydrogen ion acceptor. After the hydroxide ion itself, ammonia is the next most important Brønsted-Lowry base. This compound reacts with water to produce the hydroxide ion. Here water is acting as an acid with hydroxide ion its conjugate base, and the ammonium ion is the conjugate acid of ammonia. It is the production of the hydroxide ion that makes ammonia solutions a useful glass cleaner (the hydroxide ion reacts with fat molecules to form water-soluble salts):



There are many other common bases, including the conjugate bases of weak acids (Table 7.4). It is these anions that are present in many metal salts and yield basic solutions when the salts are dissolved in water, as we explore more in the next section.

An anion with a multiple negative charge has a  $\text{p}K_b$  value corresponding to each of the hydrolysis steps. For example, there are three equilibria for the phosphate ion:



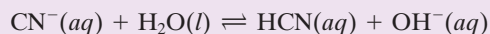
Because the second  $\text{p}K_b$  is less than 7.00, the hydrogen phosphate ion acts as a base, not an acid.

**TABLE 7.4** Base ionization constants of various inorganic bases

Base	$\text{A}^-$	HA	$K_b$ (at 25°C)	$\text{p}K_b$
Phosphate ion	$\text{PO}_4^{3-}$	$\text{HPO}_4^{2-}$	$4.7 \times 10^{-2}$	1.33
Cyanide ion	$\text{CN}^-$	HCN	$1.6 \times 10^{-5}$	4.79
Ammonia	$\text{NH}_3$	$\text{NH}_4^+$	$1.8 \times 10^{-5}$	4.74
Hydrazine	$\text{N}_2\text{H}_4$	$\text{N}_2\text{H}_5^+$	$8.5 \times 10^{-7}$	6.07

## Cyanide and Tropical Fish

Cyanide ion is the conjugate base of the weak acid hydrocyanic acid. Thus, a solution of sodium cyanide is not only toxic from the presence of the base and its conjugate acid but is also very basic:



Cyanide is used as a complexing agent in the extraction of precious metals (see Chapter 21, Section 20.11). The accidental release of cyanide-containing solutions from mining operations can cause major localized damage to aquatic organisms. However, the greatest environmental catastrophe involving cyanide has resulted from the tropical fish trade.

Saltwater tropical fish are prized for their brilliant colors. Since they are almost impossible to breed in captivity, collectors rely on the harvesting of fish from tropical coral reefs. It is estimated that about 35 million tropical fish are collected each year for the aquarium trade. In the United States alone, about 700,000 households and businesses keep marine aquariums.

The trade started in 1957 in the Philippines. Cyanide poisoning was the simplest method of collecting the fish, and it is estimated that over the past 40 years, in Philippine waters alone, over 1 million kg of sodium cyanide has been squirted onto tropical reefs. Divers crush one or two tablets of sodium cyanide and mix the powder with water, then squirt the solution over part of the reef. The hydrogen cyanide is absorbed through the mouth or gills, immediately disabling enzymes such as cytochrome oxidase, resulting in diminished oxygen uptake. The agile

fish become asphyxiated, making it easy to capture them before they can flee into crevices in the coral. It is estimated that about half of the fish are killed immediately. Of the remainder, the long-term effects of liver-absorbed cyanide will kill about 40 percent, leaving only about 10 percent to make it to the collector's tank.

In addition to the fish kill, cyanide has a major effect on the reef organisms themselves. Concentrations of cyanide as low as  $50 \text{ mg} \cdot \text{L}^{-1}$  are enough to cause the death of corals. About 30 percent of coral reefs are in Southeast Asian waters, and they have the greatest diversity of marine life anywhere on the planet. It is believed that the effects of cyanide on the reefs in the Philippines and Indonesia, the sources of 85 percent of tropical fish, have contributed to the destruction of vast areas of reef. In fact, only 4 percent of Philippine reefs and 7 percent of Indonesian reefs are in excellent condition. There are suspicions of cyanide use in Vietnam and Kiribati.

Cyanide is still the easiest way to collect the fish. Fishing practices are difficult to change when livelihoods are at stake. To discourage the trade, it is the fish purchaser who must be targeted. The Marine Aquarium Council (MAC) has been founded to develop methods of cyanide-free collection of marine fish. MAC officials are hoping that collectors of marine fish will insist on purchasing from their pet stores only fish that have been MAC-certified. It is hoped that insistence on certified fish will effectively destroy the market for cyanide-caught fish and require the harvesters to adopt less ecologically damaging methods.

## 7.3 Trends in Acid-Base Behavior

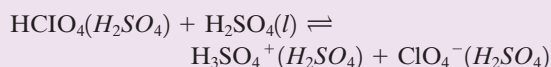
### The Acidity of Metal Ions

Dissolving sodium chloride in water provides an essentially neutral solution, while dissolving aluminum chloride in water gives a strongly acidic solution. As we have discussed in Chapter 5, Section 5.2, and Chapter 6, Section 6.4, ions are hydrated in solution. Most commonly, the first solvation sphere around a metal ion consists of six water molecules. We account for the ions forming a neutral solution by considering those water molecules to be comparatively weakly held, such as in the case of the sodium ion.

As the charge density increases, that is, with smaller ions and more highly charged ions, the lone pairs on the oxygen become strongly attracted to the

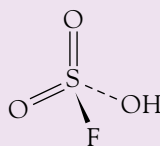
## Superacids

A superacid can be defined as an acid that is stronger than 100 percent sulfuric acid. In fact, chemists have synthesized superacids that are from  $10^7$  to  $10^{19}$  times stronger than sulfuric acid. There are four categories of superacids: Brønsted, Lewis, conjugate Brønsted-Lewis, and solid superacids. A common Brønsted superacid is perchloric acid. When perchloric acid is mixed with pure sulfuric acid, the sulfuric acid actually acts like a base:



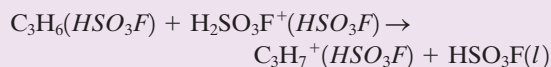
Fluorosulfuric acid,  $\text{HSO}_3\text{F}$ , is the strongest Brønsted superacid; it is more than 1000 times more acidic than sulfuric acid. This superacid, which is an ideal solvent because it is liquid from  $-89^\circ\text{C}$  to  $+164^\circ\text{C}$ , has the structure shown in Figure 7.3.

A Brønsted-Lewis superacid is a mixture of a powerful Lewis acid and a strong Brønsted-Lowry acid. The most potent combination is a 10 percent solution of antimony pentafluoride,  $\text{SbF}_5$ , in fluorosulfuric acid. The addition of antimony pentafluoride increases the acidity



**FIGURE 7.3** The structure of fluorosulfuric acid.

of the fluorosulfuric acid several thousand times. The reaction between the two acids is very complex, but the super-hydrogen ion donor present in the mixture is the  $\text{H}_2\text{SO}_3\text{F}^+$  ion. This acid mixture will react with many substances, such as hydrocarbons, that do not react with normal acids. For example, propene,  $\text{C}_3\text{H}_6$ , reacts with this ion to give the propyl cation:



The solution of antimony pentafluoride in fluorosulfuric acid is commonly called “Magic Acid.” The name originated in the Case Western Reserve University laboratory of George Olah, a pioneer in the field of superacids (and recipient of the Nobel Prize in Chemistry in 1994). A researcher working with Olah put a small piece of Christmas candle left over from a lab party into the acid and found that it dissolved rapidly. He studied the resulting solution and found that the long-chain hydrocarbon molecules of the paraffin wax had added hydrogen ions and the resulting cations had rearranged themselves to form branched-chain molecules. This unexpected finding suggested the name “Magic Acid,” and it is now a registered trade name for the compound. This family of superacids is used in the petroleum industry for the conversion of the less important straight-chain hydrocarbons to the more valuable branched-chain molecules, which are needed to produce high-octane gasoline.

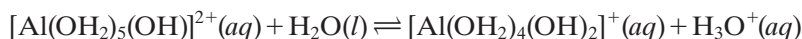
metal ion, essentially forming a covalent bond. As a result the hydrogen atoms become increasingly positively charged to the point where they act as hydrogen ion donors to a neighboring water molecule (previously mentioned in Chapter 5, Section 5.3). The process can be illustrated using the aluminum ion:



VIDEO CLIP

Thus, the higher the charge density of the metal ion, the more the equilibrium shifts toward the production of hydronium ion, leaving the metal ion as a hydroxy species. As a result of this equilibrium, metal ions with a  $3+$  or higher positive charge will only exist as the true hydrated ion at very low pH. This process of reaction with water is sometimes called *hydrolysis*.

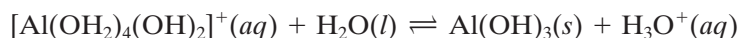
There will be as many  $\text{p}K_a$  values as the ion has charge. Thus, for the aluminum ion, the next equilibrium is:



**TABLE 7.5** A comparison of sodium, magnesium, and aluminum species

	Very acidic	Acidic	Basic	Very basic
Sodium	$\text{Na}^+(aq)$			
Magnesium	$\text{Mg}^{2+}(aq)$			$\text{Mg}(\text{OH})_2(s)$
Aluminum	$\text{Al}^{3+}(aq)$	$\text{Al}(\text{OH})_3(s)$		$\text{Al}(\text{OH})_4^-(aq)$

Then, as the pH increases, the series of equilibria shift to the right, ultimately resulting in precipitation of the metal hydroxide.



Unlike many of the other metal hydroxides, for the aluminum ion, at even higher pH values, exhibits amphoteric behavior with the metal hydroxide redissolving to form an oxoanion (see Chapter 13, Section 13.6):

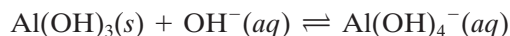
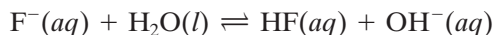


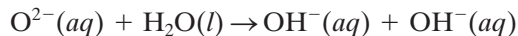
Table 7.5 compares the acid-base properties of the aqueous sodium, magnesium, and aluminum cations. For simplicity, all aluminum cation species are shown as the generic “ $\text{Al}^{3+}$ ”.

### The Basicity of Nonmetal Anions

Just as there are patterns in the acidity of cations, so are there patterns in the basicity of simple anions. In fact, the pattern is almost the mirror image of that of the cations. Thus, just as the alkali metals are neutral, the halide ions (with the exception of fluoride) are neutral. For the fluoride ion, partial hydrolysis to hydrofluoric acid occurs. The predominant species for fluoride ion and chloride ion by pH are shown in Table 7.6:



For Group 16, the oxide ion,  $\text{O}^{2-}$ , is so basic that in contact with water, the hydroxide ion is immediately formed:



The sulfide ion is the corresponding base to the very weak hydrosulfuric acid,  $\text{H}_2\text{S}(aq)$ —better known as aqueous hydrogen sulfide. As a result, hydrolysis to

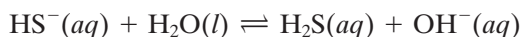
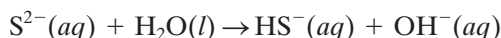
**TABLE 7.6** A comparison of fluoride and chloride aqueous species

	Very Acidic	Acidic	Basic	Very Basic
Fluoride	HF(aq)	F <sup>-</sup> (aq)		
Chloride	Cl <sup>-</sup> (aq)			

**TABLE 7.7** A comparison of oxide and sulfide aqueous species

	Very acidic	Acidic	Basic	Very basic
Oxide	$\text{H}_3\text{O}^+(aq)$	$\text{H}_2\text{O}(aq)$		$\text{OH}^-(aq)$
Sulfide	$\text{H}_2\text{S}(aq)$		$\text{HS}^-(aq)$	$\text{S}^{2-}(aq)$

the hydrogen sulfide ion is almost totally complete, with some of the hydrogen sulfide ion, in turn, hydrolyzing to (di)hydrogen sulfide:



It is these hydrolysis reactions which result in the characteristic “rotten-egg” hydrogen sulfide odor above sulfide ion solutions. The predominant species for oxide ion and sulfide ion by pH are shown in Table 7.7.

### The Basicity of Oxoanions

Just as the acidity of oxoacids depends on the number of oxygen atoms and on the number of hydrogen atoms, so the basicity of the corresponding anion depends on the number of oxygen atoms and on the ion charge. Again, the ions can be categorized according to neutral, slightly basic, moderately basic, and strongly basic.

First, looking at the series  $\text{XO}_n^-$ , we see that the basicity increases as  $n$  decreases. This is the converse of the series for oxoacids, where the acidity decreases for  $\text{HXO}_n$   $n$  decreases. The cause of these two trends has the same origin. That is, the greater the number of oxygen atoms around the element X, the weaker any O—H bond and the less prone the anion will be toward hydrolysis (Table 7.8).

For the series of oxoacids having the common formula  $\text{XO}_4^{n-}$ , as the charge increases, so the basicity increases (Table 7.9). This pattern resembles that of the monatomic anions, where the higher the charge, the more basic the ion.

This trend is illustrated in Table 7.10 by the pH dependence of the predominant species of the Period 3 isoelectronic oxoanions,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{ClO}_4^-$ . The silicate ion has been excluded from the series since its chemistry is very complex. At very high pH values, the orthosilicate ion,  $\text{SiO}_4^{4-}$ , predominates; at

**TABLE 7.8** Basicity of some common  $\text{XO}_n^-$  oxoanions

Classification	Type	Examples
Neutral	$\text{XO}_4^-$	$\text{ClO}_4^-$ , $\text{MnO}_4^-$
	$\text{XO}_3^-$	$\text{NO}_3^-$ , $\text{ClO}_3^-$
Weakly basic	$\text{XO}_2^-$	$\text{NO}_2^-$ , $\text{ClO}_2^-$
Moderately basic	$\text{XO}^-$	$\text{ClO}^-$

**TABLE 7.9** Basicity of some common  $\text{XO}_4^{n-}$  oxoanions

Classification	Type	Examples
Neutral	$\text{XO}_4^-$	$\text{ClO}_4^-$ , $\text{MnO}_4^-$
Weakly basic	$\text{XO}_4^{2-}$	$\text{SO}_4^{2-}$ , $\text{CrO}_4^{2-}$ , $\text{MoO}_4^{2-}$
Moderately basic	$\text{XO}_4^{3-}$	$\text{PO}_4^{3-}$ , $\text{VO}_4^{3-}$
Strongly basic	$\text{XO}_4^{4-}$	$\text{SiO}_4^{4-}$

**TABLE 7.10** A comparison of phosphate, sulfate, and perchlorate aqueous species

	Very acidic	Acidic	Basic	Very basic
Phosphate	$\text{H}_3\text{PO}_4(aq)$	$\text{H}_2\text{PO}_4^-(aq)$	$\text{HPO}_4^{2-}(aq)$	$\text{PO}_4^{3-}(aq)$
Sulfate	$\text{HSO}_4^-(aq)$	$\text{SO}_4^{2-}(aq)$		
Perchlorate	$\text{ClO}_4^-(aq)$			

**TABLE 7.11** A comparison of carbonate and nitrate aqueous species

	Very acidic	Acidic	Basic	Very basic
Carbonate	CO <sub>2</sub> (aq)	HCO <sub>3</sub> <sup>-</sup> (aq)		CO <sub>3</sub> <sup>2-</sup> (aq)
Nitrate	NO <sub>3</sub> <sup>-</sup> (aq)			

a very low pH, hydrated silicon dioxide; however, over the middle of the pH range there are numerous polymeric ions whose proportions depend on the solution concentration as well as the pH.

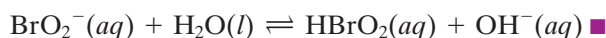
The pattern among  $\text{XO}_4^{n-}$  ions can also be seen in the  $\text{XO}_3^{n-}$  ions, with the basicity increasing as the oxoanion charge increases as is shown in Table 7.11 for carbonate and nitrate species.

**WORKED EXAMPLE 7.4**

Suggest which of one of bromate and bromite ions would hydrolyze in aqueous solution and write a hydrolysis equation for that ion.

**Answer**

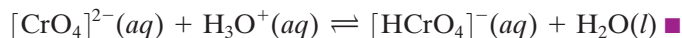
The ions are  $\text{BrO}_3^-$  and  $\text{BrO}_2^-$ . According to Table 7.8, an  $\text{XO}_3^-$  oxoanion will be neutral, while an  $\text{XO}_2^-$  oxoanion will be weakly basic. The bromate ion will be neutral, while the bromite ion will undergo hydrolysis:

**WORKED EXAMPLE 7.5**

What would you expect as the predominant species in neutral solution and in acid solution for the chromate ion?

**Answer**

According to Table 7.9, an anion of the type  $\text{XO}_4^{2-}$  is weakly basic. Thus, in neutral solution, the chromate ion should be predominantly present as  $[\text{CrO}_4]^{2-}$ , while in acid solution, the acid anion should be expected:

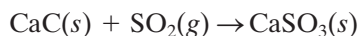


## 7.4 Acid-Base Reactions of Oxides

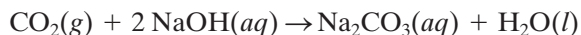
In this section, we will focus specifically on the acid-base reactions involving oxides. Oxides can be classified as basic (most metal oxides), acidic (generally nonmetal oxides), amphoteric (the “weak” metal oxides with both acidic and basic properties), and neutral (a few nonmetal and metal oxides). In Chapter 16, Section 16.5, we will see how the acid-base behavior relates to the oxidation state of the non-oxygen atom.



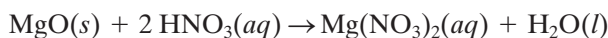
The most typical of the oxide reactions is the reaction of an acidic oxide with a basic oxide to form a salt. For example, sulfur dioxide (an acidic oxide) is a major waste product from metal smelters and other industrial processes. Traditionally, it was released into the atmosphere, but now a number of acid-base reactions have been devised to remove the acidic gas from the waste emissions. The simplest of these reacts with basic calcium oxide to give solid calcium sulfite:



Acidic oxides often react with bases. For example, carbon dioxide reacts with sodium hydroxide solution to produce sodium carbonate:

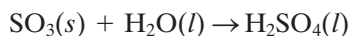
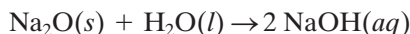


Conversely, many basic oxides react with acids. For example, magnesium oxide reacts with nitric acid to form magnesium nitrate:

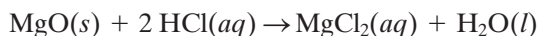


### Highest Oxides of the Second and Third Periods

Progressing across a period, there is a transition from basic oxide for the metals to acidic oxide for the nonmetals (Table 7.12). For example, sodium oxide reacts with water to give sodium hydroxide, while sulfur trioxide reacts with water to give sulfuric acid:



Not all oxides react with water; some are insoluble. For example, magnesium oxide is water insoluble but will react with acids:



**TABLE 7.12** Acid-base properties of the highest oxides of the Period 3 elements

Compound	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>10</sub>	(SO <sub>3</sub> ) <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>
Acid-base behavior	Basic	Basic	Amphoteric	Acidic	Acidic	Acidic	Acidic

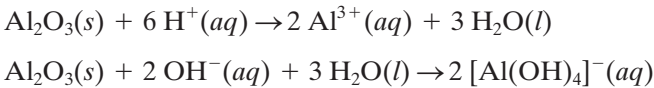
TABLE 7.13 Acid-base properties of the highest oxides of the Group 15 elements

Compound	N <sub>2</sub> O <sub>5</sub>	P <sub>4</sub> O <sub>10</sub>	As <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>
Acid-base behavior	Acidic	Acidic	Acidic	Amphoteric	Basic

while acidic oxides, such as silicon dioxide, will react with bases:



Aluminum is one of the borderline, or weak, metals. These metals (other examples are zinc and tin) have chemical properties of both metals and nonmetals. Thus, their oxides react with acids (like metals) and bases (like nonmetals). For example, aluminum oxide reacts with acids to give the hexaaquaaluminum cation,  $[\text{Al}(\text{OH}_2)_6]^{3+}$ , which we can simply represent as  $\text{Al}^{3+}(aq)$ , and it reacts with bases to give the tetrahydroxoaluminate,  $[\text{Al}(\text{OH})_4]^-$ , anion:



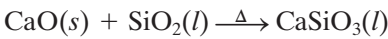
Highest Oxides of the Group 15 Elements

Just as there is a transition from basic oxide to acidic oxide across a period, so there is a similar pattern down a group in the middle of the periodic table. Here we have chosen the Group 15 elements to illustrate the pattern showing that as the elements change from nonmetal through metalloid to nonmetal, the oxides change from acidic to amphoteric to basic (Table 7.13).

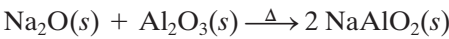
The Lux-Flood Theory

The *Lux-Flood theory* is a special theory that is devoted to solventless acid-base reactions, such as those of oxides. Oxides are classified as acids or bases according to their location in the periodic table (Table 7.14).

For example, in Chapter 20, Section 20.6, we show that a crucial reaction in the synthesis of iron is the high-temperature removal of sand with calcium oxide. According to the Lux-Flood theory, this is the reaction of a base, calcium oxide, with an acid, silicon dioxide:



Note that it is the non-oxygen element in the acid oxide that becomes part of the oxoanion; in this case, silicate. Thus, the reaction of sodium oxide (base) with aluminum oxide (acid) would produce sodium aluminate:



Acid-Base Concepts in Geochemistry

Traditionally, geochemists classified silicate rocks on an acid-base scale. Such rocks contain metal ions, silicon, and oxygen, and we can think of them according

TABLE 7.14 Lux-Flood assignment of acidity and basicity of oxides

Acids	p-block oxides Early transition metal oxides
Bases	s-block oxides Later transition metal oxides



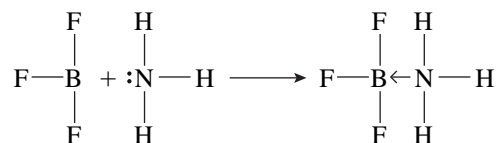
to the Lux-Flood theory as a combination of basic metal oxides and acidic silicon dioxide. We consider a rock such as granite, with more than 66 percent silicon dioxide, to be acidic; those with 52 to 66 percent  $\text{SiO}_2$ , intermediate; those with 45 to 52 percent  $\text{SiO}_2$ , such as basalt, basic; and those with less than 45 percent, ultrabasic. For example, the mineral olivine, a common component of ultrabasic rocks, has the chemical composition  $\text{Mg}_x\text{Fe}_{(2-x)}\text{SiO}_4$ , which can be thought of as a combination of oxides,  $(\text{MgO})_x(\text{FeO})_{(2-x)}(\text{SiO}_2)$ . Silicon dioxide constitutes approximately 35 percent of the mass (depending on the Mg-to-Fe ratio); therefore, this mineral is classified as ultrabasic. In general, the acidic silicate rocks tend to be light in color (granite is pale gray), whereas the basic rocks are dark (basalt is black).

## 7.5 The Lewis Theory

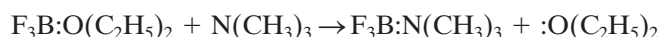
As we mentioned at the beginning of the chapter, the Lewis theory is much broader than the Brønsted-Lowry theory. A Lewis acid is an electron-pair acceptor, while a Lewis base is an electron-pair donor. Here, we will mention two particular contexts in which the Lewis theory is particularly useful: main group reactions and transition metal ion reactions.

### Main Group Reactions

The classic example of a Lewis acid-base reaction is that between boron trifluoride and ammonia. Using electron-dot diagrams, we can see that boron trifluoride, with its empty p orbital, is the Lewis acid; ammonia, with its available lone pair, is the Lewis base. In organic chemistry, the Lewis acid would be referred to as an *electrophile* and the Lewis base as a *nucleophile*. The combination reaction results in a coordinate covalent bond between the two component species:



A stronger Lewis base will replace a weaker one. For example, ethoxyethane (diethyl ether),  $(\text{C}_2\text{H}_5)_2\text{O}$ , can be displaced by trimethylamine,  $(\text{CH}_3)_3\text{N}$ :



### Metal Ion Complex Formation

In Chapter 3, Section 3.14, we demonstrated that bonding falls on a continuum. This is also true of the solvation phenomenon. For example, when cesium chloride dissolves in water, we assume that the water molecules around the cesium ion are essentially electrostatically attracted. However, the interaction seems to become less electrostatic and more covalent as the charge density increases

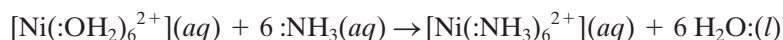
or when the cation does not have a noble gas electron configuration (as per Fajans' rules; see Chapter 5, Section 5.2).

As an example, liquid ammonia dissolves silver chloride (which is insoluble in water), but on evaporation, the compound obtained is diamminesilver(I) chloride,  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ . Thus, the solvation process is best pictured as the ammonia acting not electrostatically but as a Lewis base (lone-pair donor) toward the silver ion:



Water, too, can solvate cations by means of its lone pair, although it is a weaker Lewis base than ammonia.

As we mentioned in Chapter 5, Section 5.4, solid-state hydrates are common among higher-charge density cations and those of transition metal ions. For example, the green color of the nickel(II) ion in solution is actually the color of the hexaaquanickel(II) ion,  $[\text{Ni}(\text{OH}_2)_6]^{2+}(aq)$ . The bonding in these hydrated cations appears to have significant covalent character. As would be expected from the principles of Lewis acid-base theory, the water molecules can be displaced. For example, addition of the stronger base, ammonia, to the hexaaquanickel(II) ion gives the blue color of the hexamminenickel(II) ion:



The bonding in transition metal complexes is covered in more detail in Chapter 19.

## 7.6 Pearson Hard-Soft Acid-Base Concepts

In Chapter 6, we saw that thermodynamics can be used to predict the feasibility of chemical reactions. However, we need complete thermodynamic data with which to perform the calculations, and these are not always available. Chemists have therefore tried to find a more qualitative empirical approach to reaction prediction. For example, will sodium iodide react with silver nitrate to give silver iodide and sodium nitrate, or will silver iodide react with sodium nitrate to give sodium iodide and silver nitrate? To make such predictions of reaction, a very effective method was devised by R. G. Pearson, known as the *hard-soft acid-base (HSAB) concept*.

Pearson proposed that Lewis acids and bases could be categorized as either “hard” or “soft.” Using these categories, he showed that a reaction generally proceeded in the direction that would pair the softer acid with the softer base and the harder acid with the harder base. The elements were divided as follows:

1. The *hard acids*, also known as *class a metal ions*, consist of most of the metal ions in the periodic table. They are characterized by low electronegativities and often high charge densities. The charge density is sometimes the better guide to hardness, since we categorize the theoretical  $\text{H}^+$ ,  $\text{B}^{3+}$ , and  $\text{C}^{4+}$  ions as hard acids, and these have extremely high charge densities.



**TABLE 7.15** Common hard, borderline, and soft bases

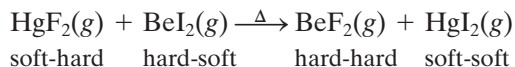
Hard	Borderline	Soft
$F^-$ , $O^{2-}$ , $OH^-$ , $H_2O$ , $CO_3^{2-}$ , $NH_3$ , $NO_3^-$ , $SO_4^{2-}$ , $ClO_4^-$ , $PO_4^{3-}$ , $(Cl^-)$	$Br^-$ , $N_3^-$ , $NCS^-$	$I^-$ , $S^{2-}$ , $P^{3-}$ , $H^-$ , $CN^-$ , $CO$ , $SCN^-$ , $S_2O_3^{2-}$

when bonding through the sulfur atom ( $-SCN$ ) (Table 7.15). Ions that can bond through different elements are called *ambidentate ligands*. The topic of ambidentate ligands is discussed more fully in Chapter 19.

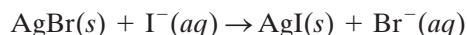
## 7.7 Applications of the HSAB Concept

In this section, we will review some of the applications of the HSAB concept to simple inorganic chemistry. In Chapter 19, Section 19.14, we return to the concept in the context of transition metal complexes.

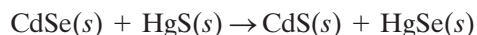
The most important application of the HSAB concept is in the prediction of chemical reactions. For example, we can predict the gas-phase reaction of mercury(II) fluoride with beryllium iodide because the soft-acid mercury(II) ion is paired with the hard-base fluoride ion, while the hard-acid beryllium ion is paired with the soft-base iodide ion. According to the HSAB concept, the ions would prefer to be partnered with their own type. Hence, the following reaction would be expected, and it does, in fact, occur:



The HSAB concept can be used even when less than half of the species are hard. That is, one can say that softer acids prefer softer bases. Among the nonmetallic elements, softness increases from the upper right in the periodic table to the lower left. For example, iodine is the softest of the halogens. Thus, we expect iodide ion to react with silver bromide since the soft-acid silver ion will prefer the soft-base iodide ion over the borderline-base bromide ion.



Another example is the reaction of cadmium selenide with mercury(II) sulfide, where the soft-acid mercury(II) ion prefers the softer-base selenide ion, while the borderline-acid cadmium ion prefers the less-soft sulfide ion:



We can also use the HSAB concept in the interpretation of solubility patterns. Table 7.16 shows that the solubility trend for sodium halides is the complete reverse of that for silver halides. The difference can be explained as the hard-acid sodium preferring the harder bases, while the soft-acid silver prefers

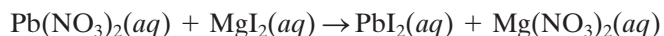
**TABLE 7.16** Solubilities of sodium and silver halides ( $\text{mol}\cdot\text{L}^{-1}$ )

	Fluoride	Chloride	Bromide	Iodide
<b>Sodium</b>	1.0	6.1	11.3	12.3
<b>Silver</b>	14.3	$1.3 \times 10^{-5}$	$72 \times 10^{-7}$	$9.1 \times 10^{-9}$

softer bases. This is one approach to the discussion of solubility patterns. In Chapter 11, Section 11.3, we examine the trend in solubilities of the sodium halides in terms of thermodynamic contributions.

**WORKED EXAMPLE 7.6**

Predict whether the following reaction will occur:

**Answer**

The  $\text{Pb}^{2+}$  and  $\text{I}^-$  ions are soft and the  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$  ions are hard. The favored species are hard-hard and soft-soft pairs. Therefore, the reaction will occur. ■

**The HSAB Concept in Geochemistry**

In 1923, the geochemist V. M. Goldschmidt devised a classification of the chemical elements that were a part of the geological history of the Earth. As the Earth cooled, some elements separated into the metallic phase of the Earth's core (the *siderophiles*), some formed sulfides (the *chalcophiles*), some formed silicates (the *lithophiles*), while others escaped to provide the atmosphere (the *atmosphiles*). The classification is still used today in various modified forms.

Here we will consider the categories in terms of the element forms on the surface of the Earth. Using this modification of Goldschmidt's classification, we consider atmosphiles as the unreactive nonmetals found solely in the atmosphere in their elemental forms (the noble gases and dinitrogen); lithophiles as the metals and nonmetals that occur mainly as oxides, silicates, sulfates, or carbonates; chalcophiles as the elements that are usually found as sulfides; and siderophiles as the metals that, on the surface of the Earth, are usually found in elemental form. The distributions of the lithophiles, chalcophiles, and siderophiles in the periodic table according to this assignment are shown in Figure 7.5.

If we compare the geochemical classification with the HSAB classification, we see that the metallic lithophiles are hard acids. They would therefore be expected to prefer the hard-base oxygen, either as the oxide ion or as an oxygen-bonded oxoanion, such as silicate. For example, the common



## 7.8 Biological Aspects

The thiol group ( $-\text{SH}$ ) part of the amino acid cysteine is a common component of enzymes. Normally, zinc would bind to many of the thiol sites, but the toxic metals (except for beryllium) are softer than zinc and will bind preferentially. Beryllium, on the other hand, is a hard acid, and as such, it preferentially binds to sites occupied by another Group 2 element, hard-acid magnesium. The environmentally toxic nonmetals and semimetals arsenic, selenium, and tellurium are very soft bases. The biochemical form of their toxicity is not well understood, but it may arise from preferential binding to borderline acids such as iron(II) and zinc, preventing the metals from performing their essential roles in enzymes. Selenium is a particularly interesting case for, as mentioned in Chapter 2, very small concentrations of selenium-containing enzymes are essential for our health. Many diseases are linked with low selenium levels in diets. Higher levels cause the disease selenosis, the symptoms of which include garlic-smelling breath, upset stomach, tiredness, and hair loss.

																		H																			He
Li		Be															B		C	N	O	F	Ne														
Na		Mg															Al	Si	P	S	Cl	Ar															
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																				
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																				
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub																										

## KEY IDEAS

- Aqueous acid-base behavior can be interpreted in terms of the Brønsted-Lowry theory.
- Patterns exist in strengths of acids and bases.
- Oxides can be classified according to their acid-base behavior.
- In nonaqueous solvents, the Lewis theory is applicable.
- Pearson hard-soft acid-base concepts can often be used to predict a reaction.
- The toxicity of elements can be linked to their HSAB properties.

## EXERCISES

- 7.1** Explain briefly the differences among the three different solvent types: polar protic, dipolar aprotic, and nonpolar.
- 7.2** Which type of solvent would you use to dissolve (a) phosphorus pentachloride; (b) cesium chloride; (c) tin(IV) chloride? Give your reasoning in each case.
- 7.3** Write net ionic equations to correspond with each of the following molecular equations:
- (a)  $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$
- (b)  $\text{Na}_2\text{CO}_3(aq) + \text{CoCl}_2(aq) \rightarrow 2 \text{NaCl}(aq) + \text{CoCO}_3(s)$
- (c)  $\text{NH}_4\text{OH}(aq) + \text{CH}_3\text{COOH}(aq) \rightarrow \text{CH}_3\text{COONH}_4(aq) + \text{H}_2\text{O}(l)$
- 7.4** Write net ionic equations to correspond with each of the following molecular equations:
- (a)  $\text{Na}_2\text{S}(aq) + 2 \text{HCl}(aq) \rightarrow 2 \text{NaCl}(aq) + \text{H}_2\text{S}(g)$
- (b)  $\text{HF}(aq) + \text{NaOH}(aq) \rightarrow \text{NaF}(aq) + \text{H}_2\text{O}(l)$
- (c)  $\text{Na}_4\text{HPO}_4(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{NaH}_2\text{PO}_4(aq) + \text{NaHSO}_4(aq)$
- 7.5** Define the following terms: (a) conjugate acid-base pairs; (b) self-ionization; (c) amphiprotic.
- 7.6** Define the following terms: (a) acid ionization constant; (b) leveling solvent; (c) polyprotic.
- 7.7** Write a balanced net ionic equation for the reaction of each of the following compounds with water: (a)  $\text{NH}_4\text{NO}_3$ ; (b)  $\text{KCN}$ ; (c)  $\text{NaHSO}_4$ .
- 7.8** Write a balanced net ionic equation for the reaction of each of the following compounds with water: (a)  $\text{Na}_3\text{PO}_4$ ; (b)  $\text{NaHSO}_4$ ; (c)  $[(\text{CH}_3)_3\text{NH}]\text{Cl}$ .
- 7.9** Write an equilibrium equation to represent the reaction of chloramine,  $\text{ClNH}_2$ , a base, with water.
- 7.10** Write an equilibrium equation to represent the reaction of fluorosulfonic acid,  $\text{HSO}_3\text{F}$ , with water.
- 7.11** Pure sulfuric acid can be used as a solvent. Write an equilibrium equation to represent the self-ionization reaction.
- 7.12** The following species are amphiprotic. Write the formulas of the corresponding conjugate acids and bases: (a)  $\text{HSe}^-$ ; (b)  $\text{PH}_3$ ; (c)  $\text{HPO}_4^{2-}$ .
- 7.13** Using liquid ammonia as a solvent, what is (a) the strongest acid? (b) the strongest base?
- 7.14** Hydrogen fluoride is a strong acid when dissolved in liquid ammonia. Write a chemical equation to represent the acid-base equilibrium.
- 7.15** Hydrogen fluoride behaves as a base when dissolved in pure sulfuric acid. Write a chemical equation to represent the acid-base equilibrium and identify the conjugate acid-base pairs.
- 7.16** Identify the conjugate acid-base pairs in the following equilibrium:
- $$\text{HSeO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SeO}_4^{2-}(aq)$$
- 7.17** Identify the conjugate acid-base pairs in the following equilibrium:
- $$\text{HSeO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{SeO}_4(aq)$$
- 7.18** Which will be the stronger acid, sulfurous acid,  $\text{H}_2\text{SO}_3(aq)$  or sulfuric acid,  $\text{H}_2\text{SO}_4(aq)$ ? Use electronegativity arguments to explain your reasoning.
- 7.19** Hydrogen selenide,  $\text{H}_2\text{Se}$ , is a stronger acid than hydrogen sulfide. Use bond strength arguments to explain your reasoning.
- 7.20** Addition of copper(II) ion to a hydrogen phosphate,  $\text{HPO}_4^{2-}$ , solution results in precipitation of copper(II) phosphate. Use two chemical equations to suggest an explanation.
- 7.21** The hydrated zinc ion,  $[\text{Zn}(\text{OH}_2)_6]^{2+}$ , forms an acidic solution. Use a chemical equation to suggest an explanation.
- 7.22** A solution of the cyanide ion,  $\text{CN}^-$ , is a strong base. Write a chemical equation to illustrate this. What can you deduce about the properties of hydrocyanic acid,  $\text{HCN}$ ?



**7.23** The weak base hydrazine,  $\text{H}_2\text{NNH}_2$ , can react with water to form a diprotic acid,  $^+\text{[H}_3\text{NNH}_3]^+$ . Write chemical equations to depict the two equilibrium steps. When hydrazine is dissolved in water, which of the three hydrazine species will be present in the lowest concentration?

**7.24** When dissolved in water, which of the following salts will give neutral, acidic, or basic solutions: (a) potassium fluoride; (b) ammonium chloride? Explain your reasoning.

**7.25** When dissolved in water, which of the following salts will give neutral, acidic, or basic solutions: (a) aluminum nitrate; (b) sodium iodide? Explain your reasoning.

**7.26** When two sodium salts,  $\text{NaX}$  and  $\text{NaY}$ , are dissolved in water to give solutions of equal concentration, the pH values obtained are 7.3 and 10.9, respectively. Which is the stronger acid,  $\text{HX}$  or  $\text{HY}$ ? Explain your reasoning.

**7.27** The  $\text{p}K_b$  values of the bases  $\text{A}^-$  and  $\text{B}^-$  are 3.5 and 6.2, respectively. Which is the stronger acid,  $\text{HA}$  or  $\text{HB}$ ? Explain your reasoning.

**7.28** Pure liquid sulfuric acid can be dissolved in liquid acetic (ethanoic) acid,  $\text{CH}_3\text{COOH}$ . Write a balanced chemical equation for the equilibrium. Will the acetic acid act as a differentiating or leveling solvent? Explain your reasoning.

**7.29** Write a net ionic equation for the equilibrium reaction between aqueous phosphoric acid and aqueous disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ .

**7.30** In a damp climate, sodium sulfide has a strong “rotten egg” smell characteristic of hydrogen sulfide. Write two net ionic equilibria to indicate how the gas is produced.

**7.31** Identify the oxides corresponding to the following acids: (a) nitric acid; (b) chromic acid,  $\text{H}_2\text{CrO}_4$ ; (c) periodic acid,  $\text{H}_5\text{IO}_6$ .

**7.32** Identify the oxides corresponding to the following bases: (a) potassium hydroxide; (b) chromium(III) hydroxide,  $\text{Cr}(\text{OH})_3$ .

**7.33** For each of the following nonaqueous reactions, identify the acid and the base.

- (a)  $\text{SiO}_2 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3$
- (b)  $\text{NOF} + \text{ClF}_3 \rightarrow \text{NO}^+ + \text{ClF}_4^-$
- (c)  $\text{Al}_2\text{Cl}_6 + 2 \text{PF}_3 \rightarrow 2 \text{AlCl}_3\text{:PF}_3$

**7.34** For each of the following nonaqueous reactions, identify the acid and the base.

- (a)  $\text{PCl}_5 + \text{ICl} \rightarrow \text{PCl}_4^+ + \text{ICl}_2^-$
- (b)  $\text{POCl}_3 + \text{Cl}^- \rightarrow \text{POCl}_4^-$
- (c)  $\text{Li}_3\text{N} + 2 \text{NH}_3 \rightarrow 3 \text{Li}^+ + 3 \text{NH}_2^-$

**7.35** What will be the effect on the pH of the water (if anything) when you add the following salt? Write a chemical equation where appropriate: (a)  $\text{CsCl}$ ; (b)  $\text{K}_2\text{Se}$ ; (c)  $\text{ScBr}_3$ ; (d)  $\text{KF}$ . In the cases where the pH does change, would you expect a large or small change?

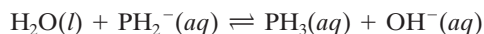
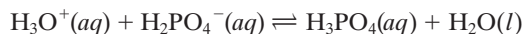
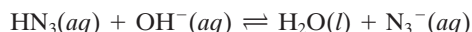
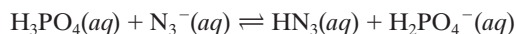
**7.36** What will be the effect on the pH of the water (if anything) when you add the following salt? Write a chemical equation where appropriate: (a)  $\text{Na}_2\text{O}$ ; (b)  $\text{Mg}(\text{NO}_3)_2$ ; (c)  $\text{K}_2\text{CO}_3$ .

**7.37** Identify the following oxoanions as neutral, weakly basic, moderately basic, or strongly basic: (a)  $\text{WO}_4^{2-}$ ; (b)  $\text{TcO}_4^-$ ; (c)  $\text{AsO}_4^{3-}$ ; (d)  $\text{GeO}_4^{4-}$ .

**7.38** Identify the following oxoanions as neutral, weakly basic, or moderately basic: (a)  $\text{BrO}_3^-$ ; (b)  $\text{BrO}^-$ ; (c)  $\text{BrO}_2^-$ .

**7.39** The ion  $\text{XeO}_6^{4-}$  is moderately basic. What degree of basicity would you expect for the isoelectronic ions (a)  $\text{IO}_6^{5-}$ ? (b)  $\text{TeO}_6^{6-}$ ?

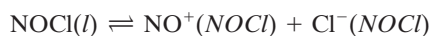
**7.40** Each of the following reactions lies toward the product side. On this basis, arrange all of the Brønsted acids in order of decreasing strength.



**7.41** From free energy of formation values, determine the free energy of reaction of magnesium oxide with water to give magnesium hydroxide and then deduce whether magnesium oxide is more or less basic than calcium oxide.

**7.42** From free energy of formation values, determine the free energy of reaction of silicon dioxide with calcium oxide to give calcium silicate,  $\text{CaSiO}_3$ , and then deduce whether silicon dioxide is more or less acidic than carbon dioxide.

**7.43** Nitrosyl chloride,  $\text{NOCl}$ , can be used as a nonaqueous solvent. It undergoes the following self-ionization:



Identify which of the ions is a Lewis acid and which is a Lewis base. Also, write a balanced equation for the reaction between  $(\text{NO})^+(\text{AlCl}_4)^-$  and  $[(\text{CH}_3)_4\text{N}]^+\text{Cl}^-$ .

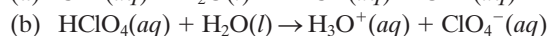
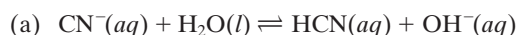
**7.44** Liquid bromine trifluoride,  $\text{BrF}_3$ , undergoes self-ionization. Write a balanced equilibrium equation to represent this process.

**7.45** In pure liquid ammonia, the self-ionization constant is  $1 \times 10^{-33}$ .

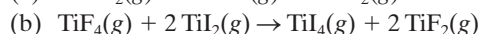
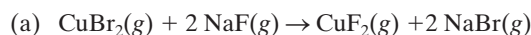
(a) Calculate the concentration of ammonium ion in liquid ammonia.

(b) Calculate the concentration of ammonium ion in a  $1.0 \text{ mol}\cdot\text{L}^{-1}$  solution of sodium amide,  $\text{NaNH}_2$ .

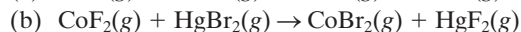
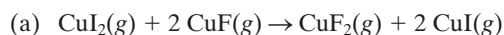
**7.46** Each of the following reactions in aqueous solution can also be performed using liquid hydrogen fluoride as a solvent and reactant in place of the water. Write the corresponding equations for reactions in hydrogen fluoride. Will the position of equilibrium be the same, farther to the right, or farther to the left than those for the aqueous reactions?



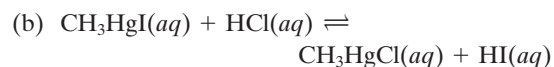
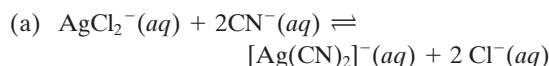
**7.47** Will either of the following high-temperature gas-phase reactions be feasible? Give your reasoning in each case.



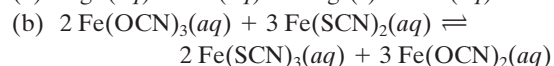
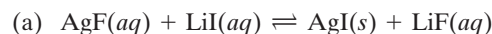
**7.48** Will either of the following high-temperature gas-phase reactions be feasible? Give your reasoning in each case.



**7.49** In the following solution equilibria, suggest whether the equilibrium constant is likely to be greater or less than 1.



**7.50** In the following solution equilibria, will the products or reactants be favored? Give your reasoning in each case.



**7.51** Predict to which group in the common cation analysis each of the following ions will belong and write a formula for the probable precipitate (if any): (a) thallium(I),  $\text{Tl}^+$ ; (b) rubidium,  $\text{Rb}^+$ ; (c) radium,  $\text{Ra}^{2+}$ ; (d) iron(III),  $\text{Fe}^{3+}$ .

**7.52** Deduce which compound is a common ore of the element listed:

(a) thorium:  $\text{ThS}_2$  or  $\text{ThO}_2$

(b) platinum:  $\text{PtAs}_2$  or  $\text{PtSiO}_4$

(c) fluorine:  $\text{CaF}_2$  or  $\text{PbF}_2$

**7.53** Deduce which compound is a common ore of the element listed and give your reasoning:

(a) magnesium:  $\text{MgS}$  or  $\text{MgSO}_4$

(b) cobalt:  $\text{CoS}$  or  $\text{CoSO}_4$

**7.54** For the three most common antacids, magnesium hydroxide, calcium carbonate, and aluminum hydroxide, calculate which provides the greatest neutralization per gram of antacid. Would you use this factor as the sole reason for choosing an antacid?

## BEYOND THE BASICS

**7.55** Calculate the concentration of sulfide ion in a  $0.010 \text{ mol}\cdot\text{L}^{-1}$  solution of hydrogen sulfide in  $1.0 \text{ mol}\cdot\text{L}^{-1}$  strong acid. The values of the acid ionization constants,  $K_{a1}$  and  $K_{a2}$ , are  $8.9 \times 10^{-8}$  and  $1.2 \times 10^{-13}$ , respectively. If the solution contained cadmium and iron(II) ions at concentrations of  $0.010 \text{ mol}\cdot\text{L}^{-1}$ , would either of their sulfides precipitate? The solubility products of cadmium and iron(II) sulfides are  $1.6 \times 10^{-28}$  and  $6.3 \times 10^{-18}$ , respectively.

**7.56** What pH would be required in a  $0.010 \text{ mol}\cdot\text{L}^{-1}$  solution of hydrogen sulfide to just start to precipitate tin(II) sulfide from a  $0.010 \text{ mol}\cdot\text{L}^{-1}$  tin(II) ion solution? The values of the acid ionization constants,  $K_{a1}$  and  $K_{a2}$ , are  $8.9 \times 10^{-8}$  and  $1.2 \times 10^{-13}$ , respectively. The solubility of tin(II) sulfide is  $1.0 \times 10^{-25}$ .

**7.57** The only common ore of mercury is mercury(II) sulfide. Zinc, however, is found as the sulfide, carbonate, silicate, and oxide. Comment on this.

**7.58** In Figure 7.5, we saw how acid-base properties change across a period. Research the change in acid-base behavior of the highest oxidation states of the Group 15 elements as the group is descended.

**7.59** Silicic acid, often written as  $\text{SiO}_2 \cdot x\text{H}_2\text{O}(s)$ , is a weaker acid than carbonic acid,  $\text{H}_2\text{CO}_3(aq)$ . Write a balanced equation for the reaction of carbonic acid with a simple silicate, such as  $\text{Mg}_2\text{SiO}_4(s)$ . Explain how this reaction is relevant to the reduction of atmospheric carbon dioxide levels over geologic time.

**7.60** Boric acid,  $\text{B}(\text{OH})_3(\text{aq})$ , acts as an acid in water. However, it does not do so as a hydrogen ion donor; instead, it acts as a Lewis acid toward the hydroxide ion. Depict this process in an equation for the reaction of boric acid with sodium hydroxide solution.

**7.61** Copper(I) ion undergoes the following disproportionation reaction for which the equilibrium constant is about  $10^6$ :



If the copper(I) ion is dissolved in dimethylsulfoxide,  $(\text{CH}_3)_2\text{SO}$ , as a solvent, the equilibrium constant is only about 2. Suggest an explanation.

**7.62** The molecule  $(\text{CH}_3)_2\text{N}-\text{PF}_2$  has two atoms that can act as Lewis bases. With boron compounds,  $\text{BH}_3$  attaches to phosphorus, while  $\text{BF}_3$  attaches to nitrogen. Give your reasoning.

**7.63** The molar solubility of calcium chloride is about four times greater than that of barium chloride. Suggest an explanation in terms of the HSAB concept and an explanation in terms of thermodynamic factors.

**7.64** The reaction between calcium oxide and silicon dioxide to give calcium silicate,  $\text{CaSiO}_3$ , is an important reaction in a blast furnace for the production of iron in that it removes silicate impurities as low-density slag that can be poured off. What would be the theoretical oxidation number of the silicon? Then explain the transfer of the oxide ion to the silicon dioxide in terms of HSAB theory.

**7.65** Using the Lux-Flood theory, what would you expect the formula of the product to be in the reaction of iron(III) oxide with aluminum oxide?

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# OXIDATION AND REDUCTION

## CHAPTER 8

A large proportion of chemical reactions involves changes in the oxidation state. In this chapter, we show how oxidation states can be determined. We then examine redox reactions. The redox properties of a particular oxidation state of an element can be displayed graphically, giving us information about the thermodynamic stability of that compound or ion.

### Context: Unraveling Nature's Secrets

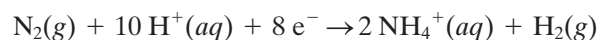
Two of the major challenges of the twenty-first century are food supplies and energy. These two problems come together in the context of fertilizer production. To produce ever-greater yield of crops, we rely more and more on synthetic fertilizers to provide the nutrients for fast-growing high-yield foodstuffs. Yet the method of synthesis of ammonia-based fertilizers (see Chapter 15, Section 15.5) has not essentially changed in the last 100 years.

Most of the atmosphere is dinitrogen,  $N_2$ . Hydrogen can be obtained relatively easily, although in reactions also producing carbon dioxide. The problem is that what seems to be a simple redox reaction:



is kinetically controlled (see Chapter 6, Section 6.7) as it has a very high activation energy,  $E_a$ , of  $420 \text{ kJ} \cdot \text{mol}^{-1}$ . Catalysts and high pressures and temperatures are needed in the industrial fertilizer production facilities.

In nature, on land and in the seas, a group of organisms called the *diazomorphs* reduce atmospheric nitrogen to the ammonium ion in the natural environment with ease. All the enzymes need is mildly reducing, slightly acid conditions (see Section 8.11). Overall, we know the biological reduction process is:

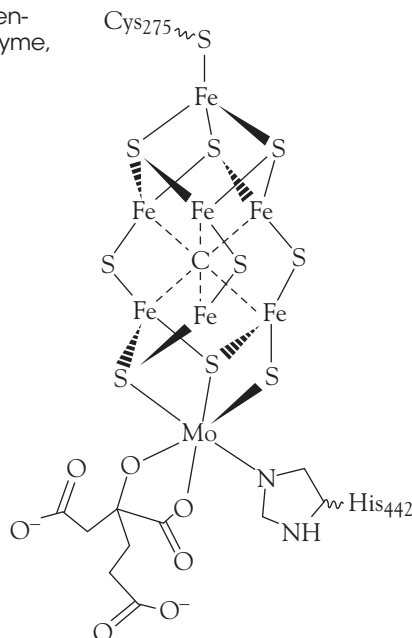


And we know that 16 moles of adenosine triphosphate, ATP, are oxidized to adenosine diphosphate, ADP, in the multistep pathway. To bypass the high energy of activation of breaking the  $N \equiv N$  bond, the organisms use enzymes (biological catalyst) named the *nitrogenases*. The enzymes contain molybdenum and iron at the core reaction site(s)

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 8.1** Redox Terminology
- 8.2** Oxidation Number Rules
- 8.3** Determination of Oxidation States from Electronegativities
- 8.4** The Difference between Oxidation State and Formal Charge
- 8.5** Periodic Variations of Oxidation States
- 8.6** Redox Equations
- 8.7** Quantitative Aspects of Half-Reactions
- 8.8** Electrode Potentials as Thermodynamic Functions
- 8.9** Latimer (Reduction Potential) Diagrams
- 8.10** Frost (Oxidation State) Diagrams
- 8.11** Pourbaix ( $E^\circ$ –pH) Diagrams
- 8.12** Redox Synthesis
- 8.13** Biological Aspects

The core of the nitrogen-fixing factor in the enzyme, nitrogenase.



(see figure above), but how the reaction proceeds is still to be unraveled. If chemists could synthesize a simple molecule—perhaps of similar structure to the nitrogenase core—we could produce fertilizer more inexpensively and without significant environmental impact.

## 8.1 Redox Terminology

Many inorganic reactions are redox reactions, and, like so many fields of chemistry, the study of oxidation and reduction has its own vocabulary and definitions. Traditionally, oxidation and reduction were each defined in three different ways, as shown in Table 8.1.

In modern chemistry, we use more general definitions of oxidation and reduction:

Oxidation: Increase in oxidation number

Reduction: Decrease in oxidation number

**TABLE 8.1** Traditional definitions of oxidation and reduction

Oxidation	Reduction
Gain of oxygen atoms	Loss of oxygen atoms
Loss of hydrogen atoms	Gain of hydrogen atoms
Loss of electrons	Gain of electrons

## 8.2 Oxidation Number Rules

Of course, now we have to define an oxidation number. Oxidation numbers are simply theoretical values used to simplify electron bookkeeping. We assign these values to the common elements on the basis of a simple set of rules:

1. The oxidation state,  $N_{\text{ox}}$ , of an atom as an element is zero.
2. The oxidation state of a monatomic ion is the same as its ion charge.
3. The algebraic sum of the oxidation states in a neutral polyatomic compound is zero; in a polyatomic ion, it is equal to the ion charge.
4. In combinations of elements, the more electronegative element has its characteristic negative oxidation state (for example,  $-3$  for nitrogen,  $-2$  for oxygen,  $-1$  for chlorine), and the more electropositive element has a positive oxidation state.
5. Hydrogen usually has an oxidation state of  $+1$  (except with more electropositive elements, when it is  $-1$ ).

Once we consider atoms in molecules we refer to them as having an *oxidation state*. The oxidation state is the physical state of the element corresponding to its oxidation number. So we can calculate the theoretical oxidation number of an atom in a molecule but say that it is in that oxidation state. Be aware that these two terms are sometimes used interchangeably but are subtly different. For example, to find the oxidation state of sulfur in sulfuric acid,  $\text{H}_2\text{SO}_4$ , we can use rule 3 to write:

$$2[N_{\text{ox}}(\text{H})] + [N_{\text{ox}}(\text{S})] + 4[N_{\text{ox}}(\text{O})] = 0$$

Because oxygen usually has an oxidation state of  $-2$  (rule 4) and hydrogen,  $+1$  (rule 5), we write:

$$2(+1) + [N_{\text{ox}}(\text{S})] + 4(-2) = 0$$

Hence,  $[N_{\text{ox}}(\text{S})] = +8 - 2 = +6$ .

### WORKED EXAMPLE 8.1

Determine the oxidation state of manganese in  $\text{KMnO}_4$ .

#### Answer

Using rule 3, we can write  $[N_{\text{ox}}(\text{K})] + [N_{\text{ox}}(\text{Mn})] + 4[N_{\text{ox}}(\text{O})] = 0$ .

Oxygen usually has an oxidation state of  $-2$  (rule 4) and potassium,  $+1$  (rule 2).

Substituting:  $(+1) + [N_{\text{ox}}(\text{Mn})] + 4(-2) = 0$ .

Thus,  $[N_{\text{ox}}(\text{Mn})] = +8 - 1 = +7$ . ■

**WORKED EXAMPLE 8.2**

Determine the oxidation state of iodine in the ion  $\text{ICl}_4^-$ .

**Answer**

For this polyatomic ion, we can use rule 3 to write:

$$[N_{\text{ox}}(\text{I})] + 4[N_{\text{ox}}(\text{Cl})] = -1$$

Chlorine is more electronegative than iodine, so chlorine will have the conventional negative oxidation state of  $-1$  (rule 4).

$$\text{So, } [N_{\text{ox}}(\text{I})] + 4(-1) = -1$$

$$\text{Rearranging: } [N_{\text{ox}}(\text{I})] = -1 + 4 = +3. \blacksquare$$

### 8.3 Determination of Oxidation Numbers from Electronegativities

Memorizing rules does not necessarily enable us to understand the concept of oxidation number. Furthermore, there are numerous polyatomic ions and molecules for which there is no obvious way of applying the “rules.” Rather than mechanically apply simplistic algebraic rules, we can always deduce an oxidation number from relative electronegativities. This method is particularly useful for cases in which there are two atoms of the same element in a molecule or ion that have different chemical environments. Using the electronegativity approach, we can identify the oxidation number of each atom in its own unique environment, whereas the algebraic method simply gives an average number.

To assign oxidation numbers to covalently bonded atoms, we draw the electron-dot formula of the molecule and refer, for simplicity, to the Pauling electronegativity values of the elements involved (Figure 8.1). Although the electrons in a polar covalent bond are unequally shared, for the purpose of assigning oxidation numbers, we assume that they are completely “owned” by

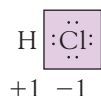
**FIGURE 8.1** Pauling electronegativity values of various nonmetals and semimetals.

<div>H 2.2</div>					<div>He —</div>
B 2.0	C 2.5	N 3.0	O 3.4	F 4.0	Ne —
	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar —
	Ge 2.0	As 2.2	Se 2.6	Br 3.0	Kr 3.0
			Te 2.1	I 2.7	Xe 2.6
				At 2.2	Rn —

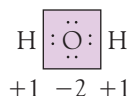
the more electronegative atom. Then we compare how many outer (valence) electrons an atom “possesses” in its molecule or ion with the number it has as a free monatomic element. The difference—the number of valence electrons “possessed” by the free atom minus the number of valence electrons “possessed” by molecular or ionic atom—is the oxidation number.

### Deducing an Oxidation Number in a Covalently Bonded Molecule

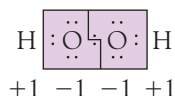
The hydrogen chloride molecule will serve as an example. Figure 8.1 shows that chlorine has a higher electronegativity than hydrogen, so we assign the bonding electrons to chlorine. A chlorine atom in hydrogen chloride will “have” one more electron in its outer set of electrons than a neutral chlorine atom has. Hence, we assign it an oxidation number of  $[7 - 8] = -1$ . The hydrogen atom has “lost” its one electron; thus, it has an oxidation number of  $[1 - 0] = +1$ . This assignment is illustrated as:



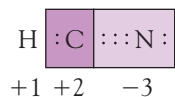
When we construct a similar electron-dot diagram for water, we see that each hydrogen atom has an oxidation number of  $[1 - 0] = +1$ , and the oxygen atom,  $[6 - 8] = -2$ , as in rules 4 and 5.



In hydrogen peroxide, oxygen has an “abnormal” oxidation number. This is easy to comprehend if we realize that when pairs of atoms of the same electronegativity are bonded together, we must assume that the bonding electron pair is split between them. In this case, each oxygen atom has an oxidation number of  $[6 - 7] = -1$ . The hydrogen atoms are  $+1$  as in the water molecule.



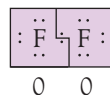
This method can be applied to molecules containing three (or more) different elements. Hydrogen cyanide, HCN, illustrates the process. Nitrogen is more electronegative than carbon, so it “possesses” the electrons participating in the C—N bond  $[5 - 8] = -3$ . And carbon is more electronegative than hydrogen, so it “possesses” the electrons of the H—C bond  $[4 - 2] = +2$ .



Rule 1 states that the oxidation number of any element is 0. How do we arrive at this value? In a molecule consisting of two identical atoms, such as difluorine, the electrons in the covalent bond will always be shared equally. Thus, we divide the shared electrons between the fluorine atoms. Each fluorine

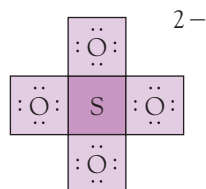


atom had seven valence electrons as a free atom and now it still has seven; hence  $[7 - 7] = 0$ .

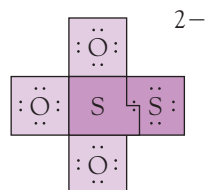


### Deducing an Oxidation Number in a Polyatomic Ion

Polyatomic ions can be treated in the same way as neutral molecules. We can use the simple electron-dot structure of the sulfate ion to illustrate this. (However, in Chapter 16, Section 16.18, we will see that bonding in the sulfate ion is actually more complex.) Following the same rules of assigning bonding electrons to the more electronegative atom, we assign an oxidation number of  $-2$  to each oxygen atom. But sulfur has six outer electrons in the neutral atom and none in this structure. Hence, according to the rules, the sulfur atom is assigned an oxidation number of  $[6 - 0] = +6$ . Note that this same oxidation number was assigned earlier to the sulfur atom in sulfuric acid.



As already mentioned, two atoms of the same element can actually have different oxidation states within the same molecule. The classic example of this situation is the thiosulfate ion,  $\text{S}_2\text{O}_3^{2-}$ , which has sulfur atoms that are in different environments. Each oxygen atom has an oxidation number of  $-2$ . But according to rule 4 stated earlier, the two equally electronegative sulfur atoms divide the two electrons participating in the  $\text{S}-\text{S}$  bond. Hence, the central sulfur atom has an oxidation state of  $[6 - 1] = 5$ , and the other sulfur atom has an oxidation state of  $[6 - 7] = -1$ . These assignments correlate with this ion's chemical reactions, in which the two sulfur atoms behave differently.



## 8.4 The Difference between Oxidation Number and Formal Charge

In Chapter 3, Section 3.8, we mentioned the concept of formal charge as a means of identifying feasible electron-dot structures for covalent molecules. To calculate formal charge, we divided the bonding electrons equally between the constituent atoms. The favored structures were generally those with the lowest formal charges.



**TABLE 8.2** Oxidation number of chlorine in common oxyanions

<b>Ion</b>	<b>Oxidation number</b>
$\text{ClO}^-$	+1
$\text{ClO}_2^-$	+3
$\text{ClO}_3^-$	+5
$\text{ClO}_4^-$	+7

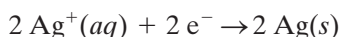
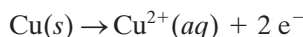
Many of the nonmetals and metalloids exhibit more than one oxidation number. For example, in its different compounds, nitrogen assumes every oxidation state between  $-3$  and  $+5$ . The common oxidation numbers of nonmetals, however, tend to decrease in units of two. This pattern can be seen in the oxidation numbers assigned to chlorine in the various oxyanions it forms (Table 8.2).

## 8.6 Redox Equations

In a redox reaction, one substance is oxidized and another is reduced. This process is sometimes easy to see; for example, when a rod of copper metal is placed in a silver nitrate solution, shiny crystals of silver metal are formed on the copper surface and the solution turns blue. In this case, the oxidation state of copper has increased from 0 to  $+2$ , and that of silver has decreased from  $+1$  to 0:

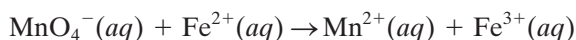


We can think of the process as two separate half-reactions, the loss of electrons by the copper metal and the gain of electrons by the silver ions:

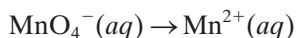
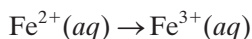


### Balancing Redox Equations in Acidic Solution

We have just seen that a redox equation can be divided into oxidation and reduction half-reactions. The half-reaction concept is particularly useful as a means of balancing complex redox reactions. For example, a solution of purple permanganate ion oxidizes an iron(II) ion solution to iron(III) ion in acid solution, itself being reduced to the very pale pink (almost colorless) manganese(II) ion. We can write the following skeletal (unbalanced) equation:



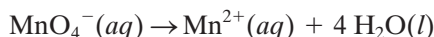
The first step is to identify the two half-reactions:



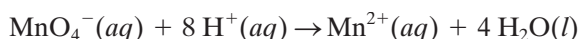
We can balance the iron half-reaction first because it is very simple, requiring just one electron:



But in the reduction equation, we have oxygen atoms on the left, but none on the right. We can remedy this by adding the appropriate number of water molecules to the side lacking oxygen atoms:

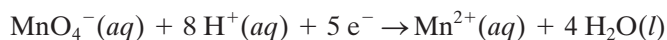


This addition has balanced the oxygen atoms, but it has introduced hydrogen atoms in the process. To balance these, we add hydrogen ions to the left-hand side:



VIDEO CLIP

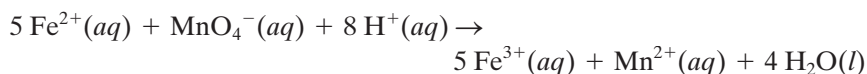
Finally, we balance the charges by adding electrons as needed:



Before adding the two half-reactions, the number of electrons required for the reduction must match the number of electrons produced during the oxidation. In this case, we achieve this balance by multiplying the iron oxidation half-reaction by 5:

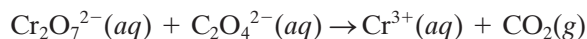


The final balanced reaction will be:



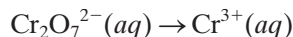
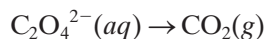
### WORKED EXAMPLE 8.3

Balance the following reaction in acidic solution:

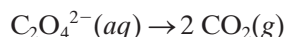


#### Answer

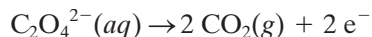
We can identify the two half-reactions:



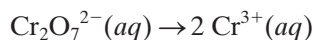
The first reaction, the oxidation reaction, requires the carbon atoms to be balanced:



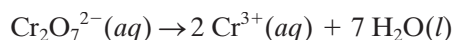
Then the charge:



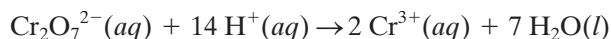
In the reduction equation, the chromium needs to be balanced first:



Then to balance the oxygen atoms, the appropriate number of water molecules must be added to the product side:

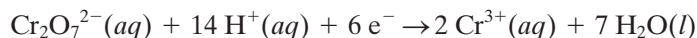


This addition has balanced the oxygen atoms, but it has introduced hydrogen atoms in the process. To balance these, hydrogen ions are added to the reactant side:

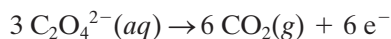


(Continued)

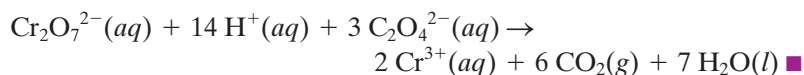
Finally, the charges are balanced by adding electrons:



Before adding the two half-reactions, the number of electrons required for the reduction must match the number of electrons produced during the oxidation. In this case, the balance is achieved by multiplying the oxalate oxidation half-reaction by 3:

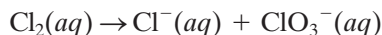


The final balanced reaction will be:

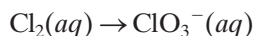
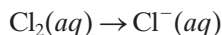


### Balancing Redox Equations in Basic Solution

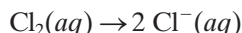
To balance a redox equation in basic solution, the procedure above is followed, then an additional step is added at the end. To illustrate, we will use the disproportionation reaction of dichlorine to chloride ion and chlorate ion in basic solution:



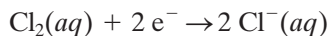
A *disproportionation reaction* occurs when some ions (or molecules) are oxidized, while others of the same species are reduced. In the case of dichlorine, some of the chlorine atoms are oxidized, changing their oxidation state from 0 to +5; the remainder are reduced, changing from 0 to -1. As before, we can construct the two half-reactions:



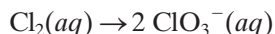
Choosing the reduction half-reaction first, we balance the number of atoms of chlorine:



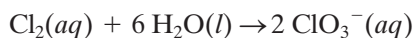
Then we can balance for charge:



For the oxidation half-reaction, the number of chlorine atoms also has to be balanced:



As we did in the previous example, we balance the oxygen atoms with water molecules:



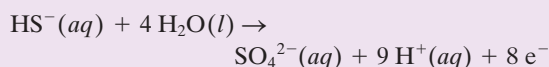
And then the water molecules with hydrogen ions:



## Chemosynthesis: Redox Chemistry on the Seafloor

The bottom of the oceans is a cold and black place. Long thought to be lifeless, apart from scavenger species living off dead organisms falling from the upper water layers, these depths are now known to support novel life-forms relying on exotic biochemical processes. On the surface of the Earth, life relies on photosynthesis to drive redox cycles. What, then, drives the biological cycles at the ocean floor? Life there is actually concentrated around vents in the seafloor, which issue plumes of superheated water saturated with toxic hydrogen sulfide and heavy metal sulfides. On the edge of this environment, a tremendous range of organisms flourishes.

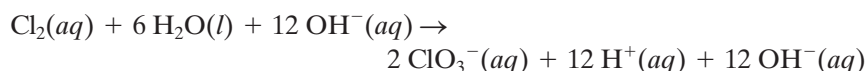
The most interesting life-form is the mouthless, gutless tube worms. These enormous creatures rely on bacteria living inside them to obtain energy by the oxidation of the hydrogen sulfide ion to sulfate ion, the process of *chemosynthesis*:



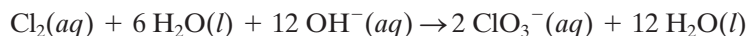
The energy from this reaction is then used by the worms for the conversion of seawater-dissolved carbon dioxide to the complex carbon-based molecules in their structures. As can be seen from the half-reaction, for every mole of hydrogen sulfide ion consumed, 9 moles of hydrogen (hydronium) ion are produced. Hence, the worms must possess an efficient biochemical mechanism to pump out the excess acid, or they would die from low pH.

Scientists at the University of California at Santa Barbara have managed to build an aquarium that duplicates the extreme pressure, low temperature, and high-hydrogen sulfide concentration at the seafloor vents so that these tube worms can be studied in the laboratory. Learning the secrets of these organisms at deep-sea vents may reveal more about the origins of life on Earth, since some scientists believe that the first organisms on this planet originated at such vents.

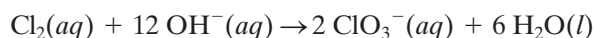
However, because the reaction takes place in basic solution, we add the same number of moles of hydroxide ion to each side as there are hydrogen ions on the right:



Since  $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ , we can write



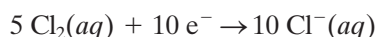
which simplifies to



Next, we balance the equation with respect to charge by adding electrons:



The reduction half-reaction must be multiplied by 5 to balance the moles of electrons:



The sum of the two half-reactions will be



Finally, the coefficients of the equation can be divided by 2:



## 8.7 Quantitative Aspects of Half-Reactions

The relative oxidizing or reducing power of a half-reaction can be determined from the half-cell potential, which is the potential of the half-reaction relative to the potential of a half-reaction in which hydrogen ion ( $1 \text{ mol} \cdot \text{L}^{-1}$ ) is reduced to hydrogen gas (100 kPa pressure on a finely divided black platinum surface). This reference half-reaction is assigned a standard potential,  $E^\ominus$ , of zero:



The more positive the half-cell reduction potential, the stronger the oxidizing power of the species. For example, difluorine is an extremely strong oxidizing agent (or electron acceptor):



Conversely, the lithium ion has a very negative reduction potential:



For lithium, the reverse half-reaction has a positive potential; hence lithium metal is a very strong reducing agent (or electron provider):



The strongest oxidizing agent is oxygen difluoride,  $\text{OF}_2$  ( $E^\ominus = +3.29 \text{ V}$  in acid solution). The strongest reducing agent is the azide ion,  $\text{N}_3^-$  ( $E^\ominus = -3.33 \text{ V}$  in acid solution).

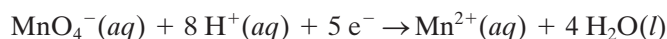
### Dependence of Half-Cell Potential upon Concentration

Half-cell potentials are concentration dependent. Thus, it is possible for a reaction to be spontaneous under certain conditions but not under others. The variation of potential with concentration is given by the Nernst equation:

$$E = E^\ominus - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]}$$

where  $R$  is the ideal gas constant ( $8.31 \text{ V} \cdot \text{C} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ),  $T$  is the temperature in kelvins,  $n$  is the moles of transferred electrons according to the redox equation,  $F$  is the Faraday constant ( $9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}$ ), and  $E^\ominus$  is the potential under standard conditions of  $1 \text{ mol} \cdot \text{L}^{-1}$  for species in solution and 100 kPa pressure for gases.

To see the effects of nonstandard conditions, consider the permanganate ion to manganese(II) ion half-cell. This half-cell is represented by the half-reaction we balanced earlier:



The corresponding Nernst equation will be:

$$E = +1.51 \text{ V} - \frac{RT}{5F} \ln \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8}$$

Suppose the pH is increased to 4.00 (that is,  $[\text{H}^+]$  is reduced to  $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ), but the concentrations of permanganate ion and manganese(II) ion are kept at  $1.0 \text{ mol}\cdot\text{L}^{-1}$ . Under the new conditions (first, solving for  $RT/5F$ ), the half-cell potential becomes:

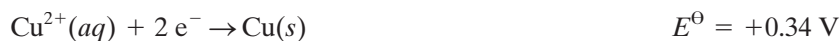
$$E = +1.51 \text{ V} - (5.13 \times 10^{-3} \text{ V}) \ln \frac{(1.00)}{(1.00)(1.0 \times 10^{-4})^8}$$

$$= +1.13 \text{ V}$$

Thus, permanganate ion is a significantly weaker oxidizing agent in less acid solutions. The concentration effect is exceptionally large in this particular half-reaction because the stoichiometry requires 8 moles of hydrogen ion. Hence, in the Nernst equation, the hydrogen ion concentration is raised to the eighth power; as a result, the potential is exceptionally sensitive to pH.

### Thermodynamic Spontaneity of a Redox Reaction

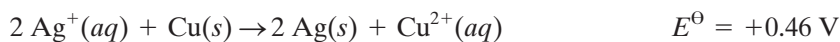
For a redox reaction to be spontaneous, the sum of its half-cell reduction potentials must be positive. For example, consider the reaction of copper metal with silver ion, which we discussed earlier. The values of the half-cell reduction potentials are



Adding the silver ion reduction potential to the copper metal oxidation potential,



gives a positive cell potential:



Thus, when a strip of copper metal is placed in silver nitrate solution, reaction will occur to give silver metal and a solution of copper(II) nitrate (the nitrate ion being a spectator ion).

## 8.8 Electrode Potentials as Thermodynamic Functions

As we have just seen in the equation for the silver ion–copper metal reaction, electrode potentials are not altered when coefficients of equations are changed. The potential is the force driving the reaction, and it is localized either at the surface of an electrode or at a point where two chemical species come in contact. Hence, the potential does not depend on stoichiometry. Potentials are simply a measure of the free energy of the process. The relationship between free energy and potential is:

$$\Delta G^\ominus = -nFE^\ominus$$



where  $\Delta G^\ominus$  is the standard free energy change,  $n$  is the moles of electrons,  $F$  is the Faraday constant, and  $E^\ominus$  is the standard electrode potential. The Faraday constant is usually expressed as  $9.65 \times 10^4 \text{ C}\cdot\text{mol}^{-1}$ , but for use in this particular formula, it is best written in units of joules:  $9.65 \times 10^4 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$ . For the calculations in this section, however, it is even more convenient to express the free energy change as the product of moles of electrons and half-cell potentials. In this way, we do not need to evaluate the Faraday constant.

To illustrate this point, let us repeat the previous calculation of the copper-silver reaction, using free energies instead of just standard potentials:

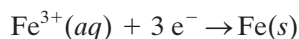


The free energy change for the process, then, is  $(-1.60F + 0.68F) \text{ V}$ , or  $-0.92F \text{ V}$ . Converting this value back to a standard potential gives:

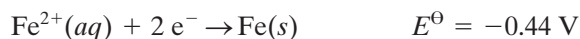
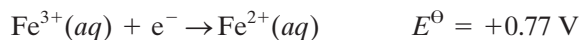
$$E^\ominus = -\frac{\Delta G^\ominus}{nF} = -\frac{-0.92F \text{ V}}{2F} = +0.46 \text{ V}$$

or the same value obtained by simply adding the standard potentials.

But suppose we want to combine two half-cell potentials to derive the value for an unlisted half-cell potential; then the shortcut of using standard electrode potentials does not work. Note that we are adding half-reactions to get another half-reaction, not a balanced redox reaction. The number of electrons in the two reduction half-reactions will not balance. Consequently, we must work with free energies. As an example, we can determine the half-cell potential for the reduction of iron(III) ion to iron metal,



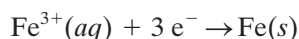
given the values for the reduction of iron(III) ion to iron(II) ion and from iron(II) ion to iron metal:



First, we calculate the free energy change for each half-reaction:



Adding the two equations results in the “cancellation” of the  $\text{Fe}^{2+}$  species. Hence, the free energy change for



will be  $(-0.77F + 0.88F) \text{ V}$ , or  $+0.11F \text{ V}$ . Converting this  $\Delta G^\ominus$  value back to potential for the reduction of iron(III) to iron metal gives

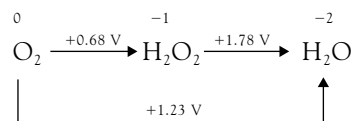
$$E^\ominus = -\frac{\Delta G^\ominus}{nF} = -\frac{+0.11F \text{ V}}{3F} = -0.04 \text{ V}$$

## 8.9 Latimer (Reduction Potential) Diagrams

It is easier to interpret data when they are displayed in the form of a diagram. The standard reduction potentials for a related set of species can be displayed in a reduction potential diagram, or what is sometimes called a *Latimer diagram*. Latimer diagrams display the redox information about a series of oxidation states in a very compact form. More than that, they enable us to predict the redox behavior of the species.

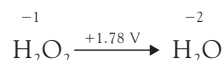
### Latimer Diagram for Oxygen in Acidic Solution

A simple example of a Latimer diagram is that for oxygen in acid solution:

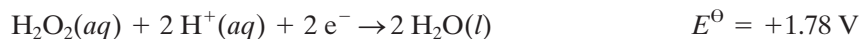


The diagram includes the two common oxidation states of oxygen (0 and  $-2$ ) and the uncommon oxidation state of  $-1$ . The number between each pair of species is the standard reduction potential for the reduction half-reaction involving those species.

Notice that although the species are indicated, to use the information, we have to write the corresponding complete half-reaction. For the simple ions, writing the half-reaction is very easy. For example, we can consider the right part of the Latimer diagram for oxygen:



The diagram shows that, with a reduction potential of  $+1.78 \text{ V}$ , hydrogen peroxide is a strong oxidizing agent with respect to water. The corresponding full half-reaction can be written as:

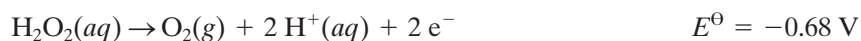
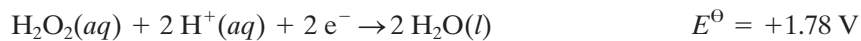


From reduction potential tables, we can see that many species have reduction potentials less than this value, including that for the iron(II)/(III) pair:



So we can confidently predict, from a thermodynamic perspective, hydrogen peroxide solution will oxidize a solution of iron(II) ion to iron(III) ion.

The diagram tells us something else about hydrogen peroxide. The sum of the potentials for the reduction and oxidation of hydrogen peroxide is positive ( $+1.78 \text{ V} - 0.68 \text{ V}$ ). This value indicates that hydrogen peroxide will disproportionate:

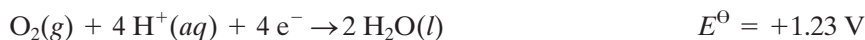


Summing the two half-equations gives the overall equation



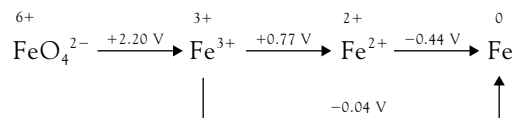
Even though the disproportionation is thermodynamically spontaneous, it is kinetically very slow. The decomposition happens rapidly, however, in the presence of a catalyst such as iodide ion or many transition metal ions. Our bodies contain the enzyme *catalase* to catalyze this reaction and destroy harmful hydrogen peroxide in our cells.

Finally, we see that oxygen gas is, itself, a strong oxidizing agent, as we see in Chapter 20, Section 20.9.



### Latimer Diagram for Iron in Acidic Solution

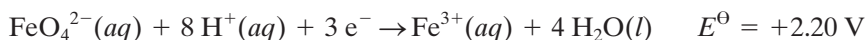
Similarly, a Latimer diagram can be constructed for the various iron oxidation states in acid solution. The diagram includes the three common oxidation states of iron (+3, +2, 0) and the uncommon oxidation state of +6. The high positive value between the ferrate ion and the iron(III) ion indicates that the ferrate ion is a strong oxidizing agent (that is, it is very easily reduced). A negative number indicates that the species to the right is a reducing agent. In fact, iron metal can be used as a reducing agent, itself being oxidized to the iron(II) ion.



We can write the half-reactions corresponding to each of the arrows on the iron Latimer diagram. For example, for the reduction of iron(III) ion to iron(II) ion, we simply write:

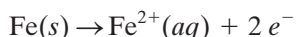


However, for the reduction of ferrate ion,  $\text{FeO}_4^{2-}$ , we have to balance the oxygen with water, then the hydrogen in the added water with hydrogen ion, and finally the charge with electrons:

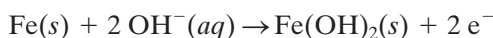


### Latimer Diagram for Iron in Basic Solution

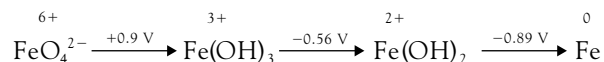
In all the examples used so far in this section, the reactions occur in acid solution. The values are sometimes quite different in basic solution, because of the presence of different chemical species at high pH. For example, as the diagram above shows, iron metal is oxidized in acid solution to the soluble iron(II) cation:



However, in basic solution, the iron(II) ion immediately reacts with the hydroxide ion present in high concentration to give insoluble iron(II) hydroxide:



Thus, the Latimer diagram for iron in basic solution (shown in the following figure) contains several different species from the diagram under acid conditions, and, as a result, the potentials are different:



We see that, in basic solution, iron(II) hydroxide is easily oxidized to iron(III) hydroxide (+0.56 V), and the ferrate ion is now a very weak oxidizing agent (+0.9 V in basic solution compared with +2.20 V in acid solution).

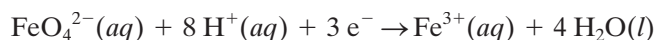
Although Latimer diagrams are useful for identifying reduction potentials for specific redox steps, they can become very complex. For example, a diagram for the five species of manganese has 10 potentials relating the various pairs of the five species. It is tedious to sort out the information that is stored in such a complex diagram. For this reason, it is more useful to display the oxidation states and their comparative energies as a two-dimensional graph. This is the topic of the next section.

### WORKED EXAMPLE 8.4

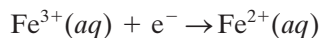
Calculate the value of  $E^\ominus$  for the reduction of  $\text{FeO}_4^{2-}$  to  $\text{Fe}^{2+}$  in acid solution.

#### Answer

We can see from the Latimer diagram that we can find this value by adding the free energy changes for:



and:



For the first equation  $E^\ominus = +2.20 \text{ V}$ ,  
so  $\Delta G^\ominus = -3(F)(+2.20 \text{ V}) = -6.60F \text{ V}$ .

For the second equation  $E^\ominus = +0.77 \text{ V}$ ,  
so  $\Delta G^\ominus = -1(F)(+0.77 \text{ V}) = -0.77F \text{ V}$

Hence, the free energy for  $\text{FeO}_4^{2-}$  to  $\text{Fe}^{2+}$  will be  $(-6.60) + (-0.77) = -7.37 \text{ V}$ .

Converting this back to an electrode potential gives:

$$E^\ominus = -\frac{\Delta G^\ominus}{nF} = -\frac{-7.37F \text{ V}}{3F} = 2.46 \text{ V.} \blacksquare$$

## 8.10 Frost (Oxidation State) Diagrams

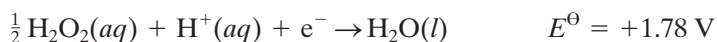
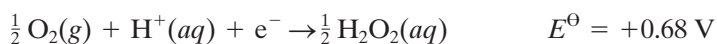
It is preferable to display the information about the numerous oxidation states of an element as an oxidation state diagram, or a *Frost diagram*, as it is sometimes called, the diagrams having been devised by Arthur Frost of Northwestern University. Such a diagram enables us to extract information

about the properties of different oxidation states visually, without the need for calculations.

A Frost diagram shows the relative free energy (rather than potential) on the vertical axis and the oxidation state on the horizontal axis. Energy is expressed as  $-nE^\ominus$ ; sometimes called the *volt equivalent*. Thus, energy values are usually plotted in units of volts times moles of electrons for that redox step ( $\text{V} \cdot \text{mol e}^-$ ). We obtain the same value by dividing the free energy by the Faraday constant,  $\Delta G^\ominus/F$ . For consistency, the element in oxidation state 0 is considered to have zero free energy. Lines connect species of adjacent oxidation states. We have adopted the convention that the positive oxidation states are to the right and the negative to the left, but the reader should be aware that some figures are reversed, with positive oxidation states to the left.

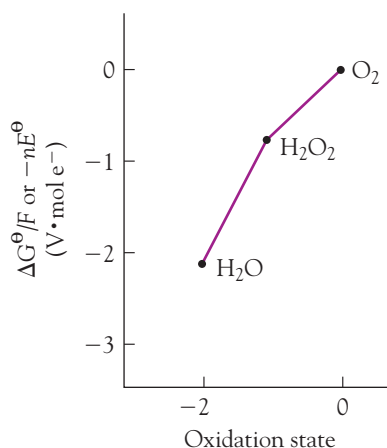
### Frost Diagram for Oxygen in Acidic Solution

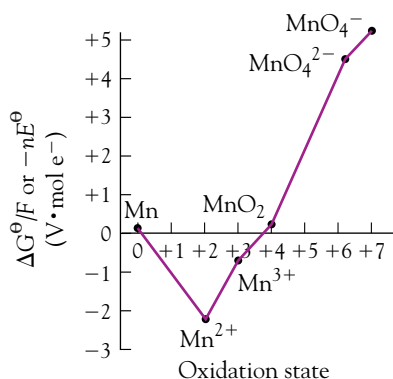
From the Latimer diagram for oxygen shown in the previous section, we can construct a Frost diagram for oxygen species in acid solution (Figure 8.3). The first point will simply be 0, 0 for dioxygen because its free energy is taken to be 0 when its oxidation state is 0. We consider the changes per mole of oxygen *atoms*:



Thus, the point for hydrogen peroxide will then be  $-1$ ,  $-0.68$  because the oxidation state for oxygen in hydrogen peroxide is  $-1$  and its free energy is  $-1$  times the product of the moles of electrons (1) and the half-cell reduction potential ( $+0.68 \text{ V}$ ). The point for water will be at  $-2$ ,  $-2.46$  because the oxygen has an oxidation state of  $-2$  and the free energy of the oxygen in water will be  $-(1 \times 1.78)$  units below the hydrogen peroxide point. This diagram enables us to obtain a visual image of the redox chemistry of oxygen in acid solution. Water, at the lowest point on the plot, must be the most thermodynamically stable. Hydrogen peroxide, on a convex curve, will disproportionate.

**FIGURE 8.3** Frost diagram for oxygen in acid solution.





**FIGURE 8.4** Frost diagram for manganese in acid solution.

### Frost Diagram for Manganese in Acidic Solution

All the features of a Frost diagram can be appreciated by studying the redox chemistry of manganese in acid conditions (Figure 8.4).

From this diagram, we can identify the following features:

1. More thermodynamically stable states will be found lower in the diagram. Thus, manganese(II) is the most stable (from a redox perspective) of all the manganese species.
2. A species that is high and on the right of the plot (such as the permanganate ion,  $\text{MnO}_4^-$ ) will be strongly oxidizing.
3. A species that is high and on the left of the plot will be strongly reducing. Thus, manganese metal is moderately reducing.
4. A species on a convex curve (such as the manganate ion,  $\text{MnO}_4^{2-}$ , and the manganese(III) ion) will tend to disproportionate.
5. A species on a concave curve (such as manganese(IV) oxide,  $\text{MnO}_2$ ) will not disproportionate. The species on either side of a species on a concave curve will comproportionate (such as mixing solutions of manganese(III) ion and manganate ion will form a precipitate of manganese(IV) oxide).
6. An oxoanion remaining as the anionic species in acid conditions indicates that the anion is a conjugate base of a strong acid. Thus, permanganic acid,  $\text{HMnO}_4$ , and manganic acid,  $\text{HMnO}_3$ , must be strong acids.

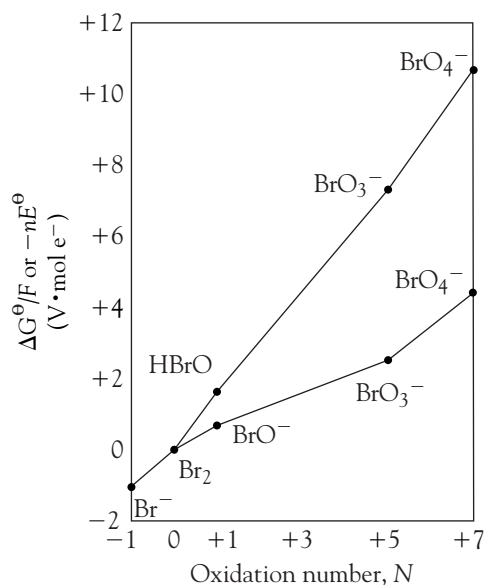
However, interpretation of Frost diagrams has caveats. First, the diagram represents the comparative free energy for standard conditions; that is, a solution of concentration  $1 \text{ mol}\cdot\text{L}^{-1}$  at pH 0 (a hydrogen ion concentration of  $1 \text{ mol}\cdot\text{L}^{-1}$ ). If the conditions are changed, then the energy will be different, and the relative stabilities might be different.

As pH changes, the potential of any half-reaction that includes the hydrogen ion also changes. But even more important, often the actual species involved will change. For example, the aqueous manganese(II) ion does not exist at high pH values. Under these conditions, insoluble manganese(II) hydroxide,  $\text{Mn}(\text{OH})_2$ , is formed. It is this compound, not  $\text{Mn}^{2+}$ , that appears on the Frost diagram for manganese(II) in basic solution (see Chapter 20, Section 20.6).

Finally, we must emphasize that the Frost diagrams are thermodynamic functions and do not contain information about the rate of decomposition of a thermodynamically unstable species. Potassium permanganate,  $\text{KMnO}_4$ , is a good example. Even though the reduction of permanganate ion to a more stable lower oxidation state of manganese(II) ion is favored, the reaction is kinetically slow (except in the presence of a catalyst). Thus, we can still work with permanganate ion solutions (though it is wise to freshly prepare them as needed).

### WORKED EXAMPLE 8.5

Using the following Frost diagram, discuss the redox chemistry of bromine in acidic solution (upper line) and basic solution (lower line).



### Answer

In both acid and base, the bromide ion is the most thermodynamically stable. In basic solution, the hypobromite ion will disproportionate. In acid solution, both bromate and perbromate are strongly oxidizing, but less so in basic solution. Both perbromic acid and bromic acid are strong acids, but hypobromous acid is a weak acid. ■

## 8.11 Pourbaix ( $E^\circ$ -pH) Diagrams

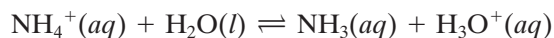
In the last section, we saw how a Frost diagram could be used to compare the thermodynamic stabilities of different oxidation states of an element. Frost diagrams can be constructed for both acid ( $\text{pH} = 0$ ) and basic ( $\text{pH} = 14$ ) conditions.

It would be useful to be able to identify the thermodynamically stable species at any particular permutation of half-cell potential,  $E$ , and pH. The French chemist Marcel Pourbaix devised such a plot; hence, such plots are usually called Pourbaix diagrams after him, although they are also called  $E^\ominus$ -pH diagrams and *predominance-area diagrams*.

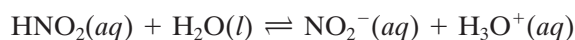
### Pourbaix Diagram for Nitrogen

The Pourbaix diagram for nitrogen (mentioned in the Context for this chapter) is shown in Figure 8.5. Oxidizing conditions are shown toward the top; reducing conditions toward the bottom. Acidic conditions are shown toward the left; basic conditions are shown toward the right.

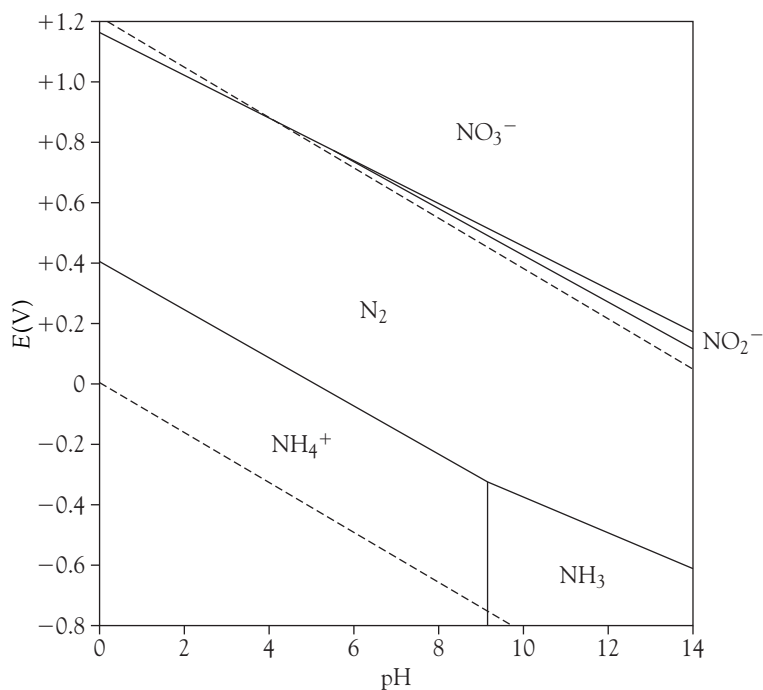
The Pourbaix diagram shows that, under reducing conditions, the thermodynamically preferred species are the ammonium ion (at lower pH values) and the ammonia molecule (at higher pH values). The vertical line between the two indicates that the equilibrium of weak base/weak acid is solely dependent upon pH:



There is a narrow range over which the +3 oxidation state of nitrogen is viable, and this too, is an acid base equilibrium:



Then, in stronger oxidizing conditions, the nitrate ion, the conjugate base of a very strong acid, predominates. If the boundary were horizontal, then the transition would be solely on the basis of an electron transfer only. A sloping



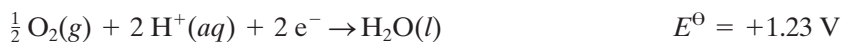
**FIGURE 8.5** Pourbaix diagram showing the thermodynamically stable nitrogen species as a function of standard potential,  $E^\ominus$ , and pH.



boundary indicates that the two species differ in a half-reaction which is also pH dependent. For example, from nitrite ion to nitrate ion, this would be:



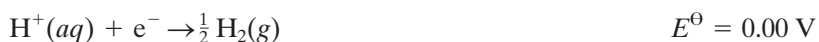
The diagram also shows two shaded lines. The upper shaded line represents the oxidation of water:



while the lower shaded line represents the reduction of water to hydrogen gas:



which under conditions of  $1 \text{ mol} \cdot \text{L}^{-1} \text{H}^+$  is represented as:

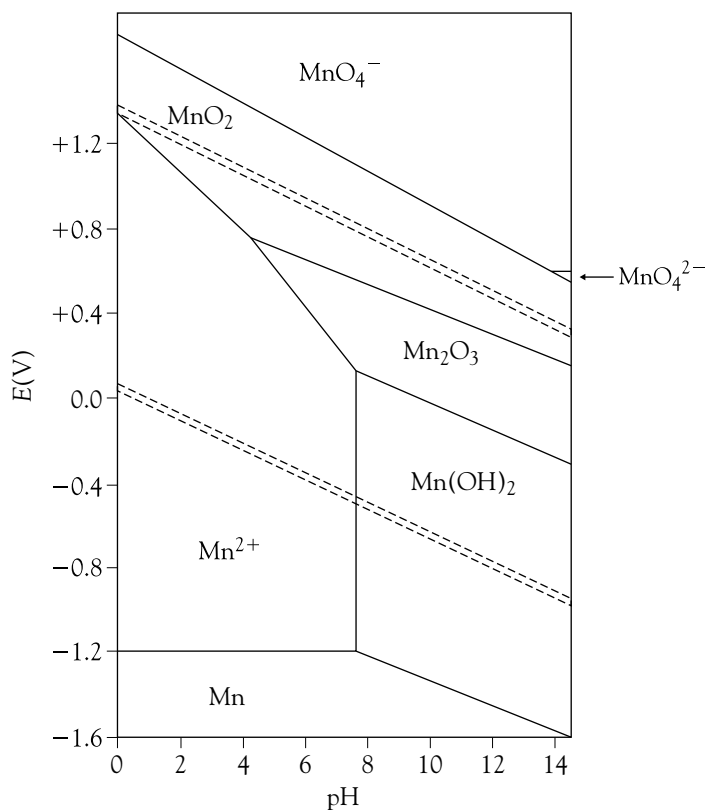


These two shaded lines represent the boundaries within which reactions in aqueous solution are possible. A higher potential and the water will start oxidizing; a lower potential and the water will start reducing.

### Pourbaix Diagram for Manganese

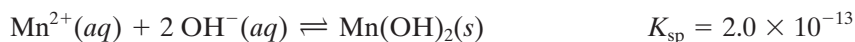
Figure 8.6 shows a Pourbaix diagram for the manganese system. Having discussed the Pourbaix diagram for nitrogen qualitatively, for manganese, we

**FIGURE 8.6** Pourbaix diagram showing the thermodynamically stable manganese species as a function of standard potential,  $E^\ominus$ , and pH.



will see how a Pourbaix diagram is constructed from tabulated data, such as standard oxidation potentials, solubility products, acid-base equilibrium constants, and so on.

We will start by deriving the boundary between the manganese(II) ion and manganese(II) hydroxide, the vertical divide indicating an equilibrium that is dependent solely on pH and not on a redox process:

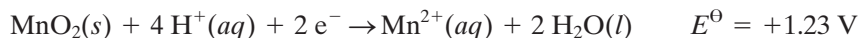


Hence, when manganese(II) is in its standard concentration of  $1 \text{ mol}\cdot\text{L}^{-1}$ , as  $K_{\text{sp}} = [\text{Mn}^{2+}][\text{OH}^{-}]^2$ , then  $[\text{OH}] = \sqrt{(2.0 \times 10^{-13})}$  and  $\text{pH} = 7.65$ . Thus, at a pH greater than this, the hydroxide is the preferred form of manganese(II).

Conversely, as was described for the nitrogen Pourbaix diagram, a horizontal line will represent a pure redox transformation. An example of a horizontal line is found in the manganese Pourbaix diagram between manganese metal and the manganese(II) ion:



Most boundaries lie between these extremes since they are both pH and potential dependent. For example, the reduction of manganese(IV) oxide to manganese(II) ion is represented as:



The Nernst expression can then be used to plot the boundary between the two states:

$$E = E^\ominus - \frac{RT}{2F} \ln \frac{[\text{Mn}^{2+}]}{[\text{H}^{+}]^4}$$

Inserting the values of  $R$ ,  $T$ , and  $F$ , setting  $[\text{Mn}^{2+}]$  as  $1 \text{ mol}\cdot\text{L}^{-1}$ , and converting  $\ln$  to  $\log_{10}$  (by multiplying by 2.303) gives

$$E = 1.23 \text{ V} - (0.118)\text{pH}$$

Substituting different values of pH, we can calculate the corresponding value of  $E$  and construct the boundary line on the Pourbaix diagram.

So we can see that the permanganate ion lies outside the limit of aqueous solutions. However, as we mentioned in the previous section, permanganate ion can exist in aqueous solution because the decomposition of permanganate ion has a high activation energy barrier, providing kinetic stability and slowing the rate of decomposition. The manganate ion,  $\text{MnO}_4^{2-}$ , occupies a tiny niche at very high pH and also outside the water limits. Thus, to synthesize this ion, we resort to the oxidation of manganese(IV) oxide in molten potassium hydroxide:

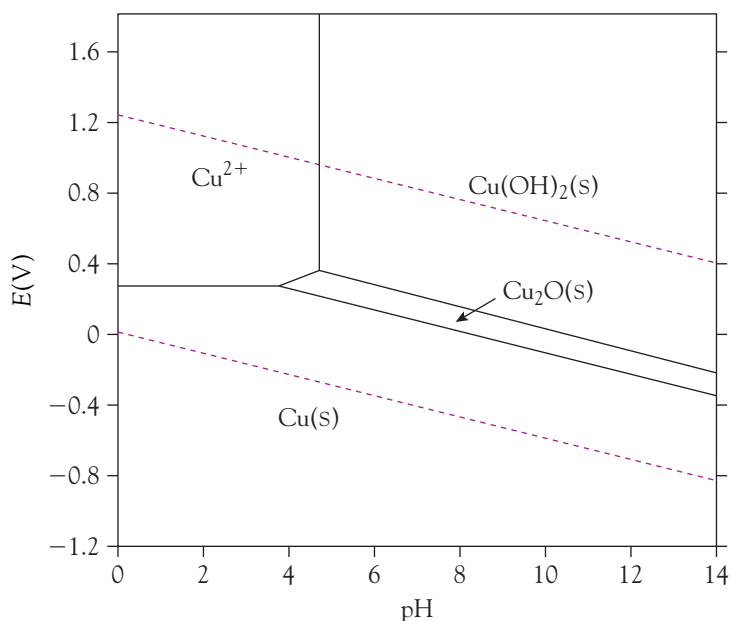


We chose to discuss manganese so that the information in the Pourbaix diagram (Figure 8.6) can be contrasted with that which can be obtained from the Frost diagram (Figure 8.4). It is easier to identify the major aqueous species under different pH and  $E$  conditions from a Pourbaix diagram, but the study of

the relative stabilities of different oxidation states is best accomplished from a Frost diagram. It is important to realize that Pourbaix diagrams display only the common thermodynamically preferred species. Sometimes species are left off the diagram for simplicity. For example, Figure 8.6 does not include the mixed manganese(II) manganese(III) oxide,  $\text{Mn}_3\text{O}_4$ . Other species do not come in the range of the Pourbaix diagram. For example, the aqueous manganese(III) ion only becomes the thermodynamically stable species when  $[\text{H}^+]$  is about  $10 \text{ mol}\cdot\text{L}^{-1}$  and the potential is about  $+1.5 \text{ V}$ .

### WORKED EXAMPLE 8.5

Use the Pourbaix diagram below to summarize the chemistry of copper.



### Answer

In aqueous solution, copper mostly exhibits a 2+ oxidation state, usually as the  $\text{Cu}^{2+}$  ion. In basic solution, copper(II) hydroxide is formed. The copper(II) ion is readily reduced to copper metal, but in basic conditions, copper(I) oxide is formed when copper(II) hydroxide is reduced. ■

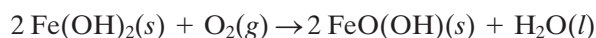
## 8.12 Redox Synthesis

Redox reactions are an important means of chemical synthesis. These reactions can be accomplished by chemical or electrochemical means. In the case of oxidation reactions, we have many useful chemical reagents, including ozone, hydrogen peroxide, and dioxygen (Table 8.3). Thus, we can choose the oxidizing agent appropriate to our needs and according to the pH requirements of the reaction.

**TABLE 8.3** Some common oxidizing agents with their corresponding half-reactions and potentials in acidic and basic solution

<b>Ozone</b>		
Acid	$\text{O}_3(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	$E^\ominus = +2.08 \text{ V}$
Base	$\text{O}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{O}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	$E^\ominus = +1.24 \text{ V}$
<b>Hydrogen peroxide</b>		
Acid	$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	$E^\ominus = +1.78 \text{ V}$
Base	$\text{HO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow 3 \text{OH}^-(\text{aq})$	$E^\ominus = +0.88 \text{ V}$
<b>Dioxygen</b>		
Acid	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	$E^\ominus = +1.23 \text{ V}$
Base	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	$E^\ominus = +0.40 \text{ V}$

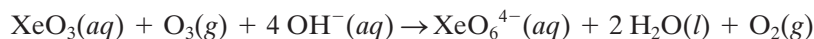
To illustrate, iron(II) hydroxide is oxidized to iron(III) oxide hydroxide in the presence of atmospheric oxygen:



But a stronger oxidizing agent such as hydrogen peroxide is needed to oxidize chromium(III) hydroxide to chromate ion:



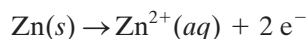
and an extremely strong oxidizing agent to convert xenon trioxide to the perxenate ion:



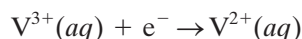
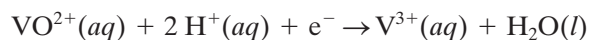
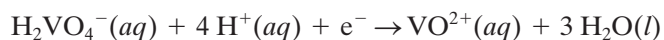
Electrolytic methods allow the potential to be adjusted to favor the production of the required ion. For example, sulfate can be electrolytically oxidized to the peroxodisulfate ion:



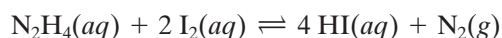
There is a similarly wide repertoire of reducing agents. Metals, such as zinc, are commonly used for the reduction of transition metals in higher oxidation states to lower states:



For example, we can reduce vanadium stepwise from its +5 state in the dihydrogen vanadate ion,  $\text{H}_2\text{VO}_4^-$ , to the vanadium(II) ion:



Hydrazine,  $\text{N}_2\text{H}_4$ , is a very convenient strong reducing agent since it is oxidized to dinitrogen gas, leaving the other product in the reaction vessel. An example is the reduction of iodine to hydrogen iodide:

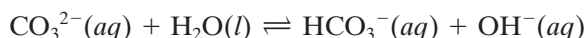


### 8.13 Biological Aspects

In all biological systems, we have to consider both the potential,  $E$ , and the acidity, pH, simultaneously when trying to decide what species of an element might be present (and we have to consider kinetic factors as well). Thus, Pourbaix diagrams have a particular importance for bioinorganic chemistry and inorganic geochemistry. Figure 8.7 shows the limits of pH and  $E$  that we find in natural waters. The upper dashed line, representing water in contact with the atmosphere, corresponds to a partial pressure of dioxygen of 20 kPa, the oxygen gas pressure at sea level. Rain tends to be slightly acidic as a result of the absorption of carbon dioxide from the atmosphere:



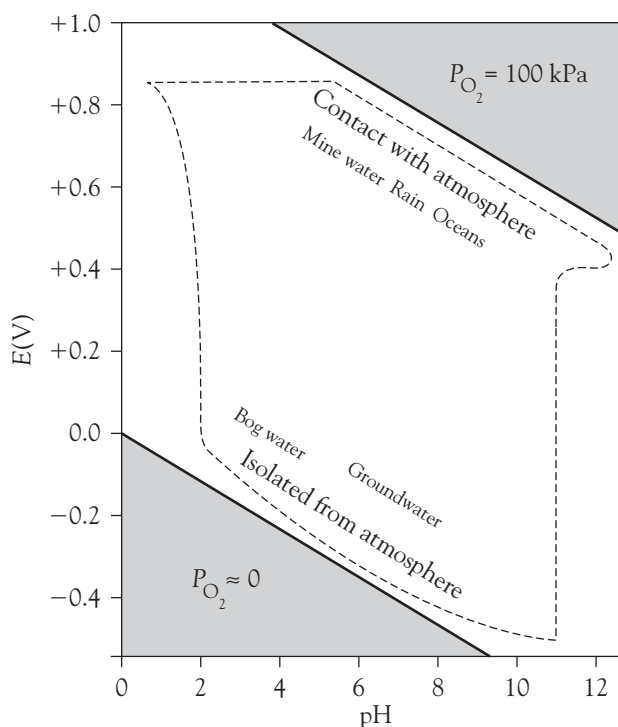
Depending on the geology of an area, the water in streams tends to be closer to neutral; seawater is slightly basic. Open water is rarely more basic than pH 9 because of the carbonate–hydrogen carbonate buffer system that is present:

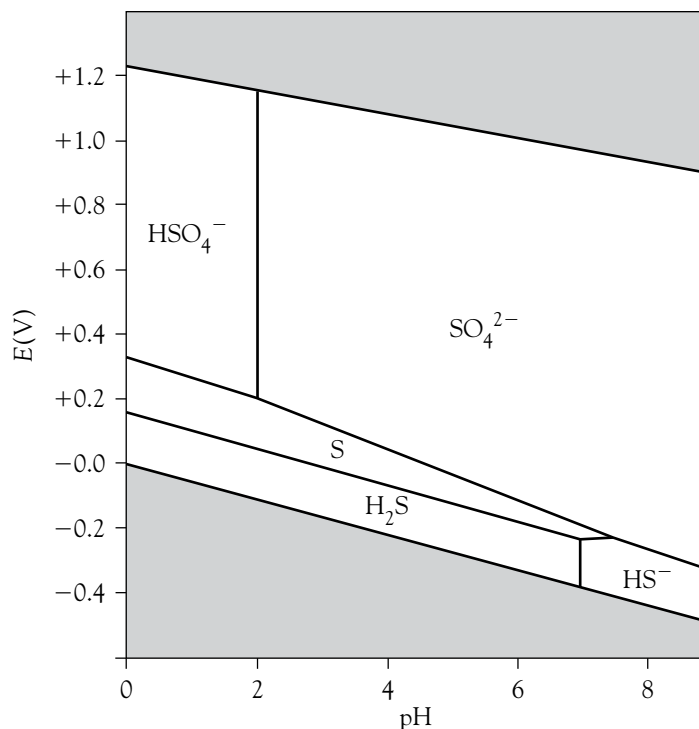


All surface waters, however, are oxidizing as a result of the high partial pressure of dissolved oxygen.

In a lake or river in which there is a high level of plant or algal growth, the level of oxygen is less. As a result, these waters have a lower potential. The lowest positive potentials occur in environments with a high biological activity and no atmospheric contact, typically bogs and stagnant lakes. Under these conditions, anaerobic bacteria flourish, the level of dissolved dioxygen will be close to 0, and

**FIGURE 8.7** Pourbaix diagram showing the limits of  $E$  and pH conditions in natural waters (dashed line). [Adapted from G. Faure, *Principles and Applications of Inorganic Geochemistry* (New York: Macmillan, 1991), p. 324.]

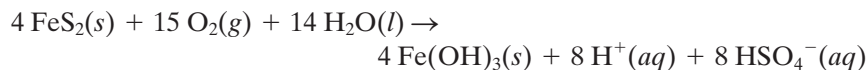




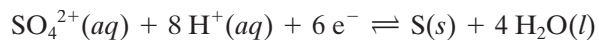
**FIGURE 8.8** Pourbaix diagram showing the thermodynamically stable sulfur species in aqueous solution as a function of potential,  $E$ , and pH. [Adapted from G. Faure, *Principles and Applications of Inorganic Geochemistry* (New York: Macmillan, 1991), p. 334.]

the environment will be highly reducing. Bogs are also often highly acidic because of the decaying vegetation they contain.

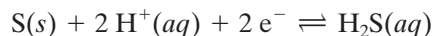
Looking at the Pourbaix diagram of sulfur species within the limits of aqueous solution (Figure 8.8), we can see that the sulfate ion is the predominant species over most of the range of pH and  $E^\ominus$ . Because the hydrogen sulfate ion is the conjugate base of a fairly strong acid, only below about pH 2 is the  $\text{HSO}_4^-$  ion preferred. Such a situation can occur in mine runoff, the acid conditions often being caused by the oxidation of iron(II) disulfide:



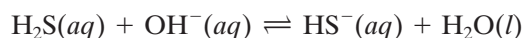
Over most of the pH range, a more reducing environment, such as in bogs, results in the conversion of sulfate ion to elemental sulfur:



In stronger reducing potentials, the sulfur is, in turn, reduced to hydrogen sulfide:



It is this gas that can sometimes be smelled in boggy areas and in many waters of volcanic origin (such as those in Yellowstone National Park). Notice that aqueous hydrogen sulfide is the predominant reduced species. The reason relates to the weakness of this acid. Only under basic conditions will the hydrogen sulfide ion predominate:



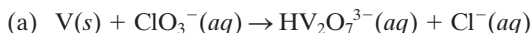
## KEY IDEAS

- Oxidation states in a compound can be derived from relative electronegativity values.
- There are periodic patterns in the common oxidation states of elements.
- Electrode potentials are thermodynamic functions.
- Redox information can be summarized by Latimer (reduction potential) diagrams.
- Frost (oxidation state) diagrams can be constructed to provide redox information in a visual manner.
- To identify the predominant species under particular potential and pH conditions, Pourbaix diagrams are used.
- Pourbaix diagrams are useful for the identification of species in aqueous environments.

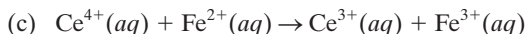
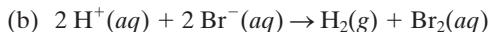
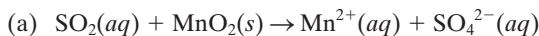
## EXERCISES

- 8.1** Define the following terms: (a) oxidizing agent; (b) Latimer diagrams.
- 8.2** Define the following terms: (a) Frost diagrams; (b) Pourbaix diagrams.
- 8.3** Using the oxidation state rules, determine the oxidation state of phosphorus in (a)  $\text{P}_4\text{O}_6$ ; (b)  $\text{H}_3\text{PO}_4$ ; (c)  $\text{Na}_3\text{P}$ ; (d)  $\text{PH}_4^+$ ; (e)  $\text{POCl}_3$ .
- 8.4** Using the oxidation state rules, determine the oxidation state of chlorine in (a)  $\text{ClF}_3$ ; (b)  $\text{Cl}_2\text{O}$ ; (c)  $\text{Cl}_2\text{O}_7$ ; (d)  $\text{HCl}$ .
- 8.5** Using electron-dot diagrams, determine the oxidation state of sulfur in each of the following compounds: (a)  $\text{H}_2\text{S}$ ; (b)  $\text{SCl}_2$ ; (c)  $\text{H}_2\text{S}_2$ ; (d)  $\text{SF}_6$ ; (e)  $\text{COS}$  (structure  $\text{O}=\text{C}=\text{S}$ ).
- 8.6** Using electron-dot diagrams, determine the formal charges and the oxidation states for each element in  $\text{SOCl}_2$ .
- 8.7** What are the likely oxidation states of iodine in its compounds?
- 8.8** What would you predict to be the highest oxidation state of xenon in its compounds? What other oxidation states are likely?
- 8.9** For each of the following compounds, deduce the oxidation state of the nonhalogen atom and identify the trend in oxidation states in the series: (a) indium(I) iodide,  $\text{InI}$ ; (b) tin(II) chloride,  $\text{SnCl}_2$ ; (c) antimony tribromide,  $\text{SbBr}_3$ ; (d) tellurium tetrachloride,  $\text{TeCl}_4$ ; (e) iodine pentafluoride,  $\text{IF}_5$ .
- 8.10** Identify the changes in oxidation states in the following equations:
- $\text{Mg}(s) + \text{FeSO}_4(aq) \rightarrow \text{Fe}(s) + \text{MgSO}_4(aq)$
  - $2 \text{HNO}_3(aq) + 3 \text{H}_2\text{S}(aq) \rightarrow 2 \text{NO}(s) + 3 \text{S}(s) + 4 \text{H}_2\text{O}(l)$
- 8.11** Identify the changes in oxidation states in the following equations:
- $\text{NiO}(s) + \text{C}(s) \rightarrow \text{Ni}(s) + \text{CO}(g)$
  - $2 \text{MnO}_4^-(aq) + 5 \text{H}_2\text{SO}_3(aq) + \text{H}^+(aq) \rightarrow 2 \text{Mn}^{2+}(aq) + 5 \text{HSO}_4^-(aq) + 3 \text{H}_2\text{O}(l)$
- 8.12** Write a half-reaction for the following reduction in acid solution:
- $$\text{H}_2\text{MoO}_4(aq) \rightarrow \text{Mo}^{3+}(aq)$$
- 8.13** Write a half-reaction for the following oxidation in acid solution:
- $$\text{NH}_4^+(aq) \rightarrow \text{NO}_3^-(aq)$$
- 8.14** Write a half-reaction for the following oxidation in basic solution:
- $$\text{S}^{2-}(aq) \rightarrow \text{SO}_4^{2-}(aq)$$
- 8.15** Write a half-reaction for the following oxidation in basic solution:
- $$\text{N}_2\text{H}_4(aq) \rightarrow \text{N}_2(g)$$
- 8.16** Balance the following redox reactions in acidic solution:
- $\text{Fe}^{3+}(aq) + \text{I}_2(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{I}^-(aq)$
  - $\text{Ag}(s) + \text{Cr}_2\text{O}_7^{2-}(aq) \rightarrow \text{Ag}^+(aq) + \text{Cr}^{3+}(aq)$
- 8.17** Balance the following redox reactions in acidic solution:
- $\text{HBr}(aq) + \text{HBrO}_3(aq) \rightarrow \text{Br}_2(aq)$
  - $\text{HNO}_3(aq) + \text{Cu}(s) \rightarrow \text{NO}_2(g) + \text{Cu}^{2+}(aq)$
- 8.18** Balance the following redox equations in basic solution:
- $\text{Ce}^{4+}(aq) + \text{I}^-(aq) \rightarrow \text{Ce}^{3+}(aq) + \text{IO}_3^-(aq)$
  - $\text{Al}(s) + \text{MnO}_4^-(aq) \rightarrow \text{MnO}_2(s) + \text{Al}(\text{OH})_4^-(aq)$

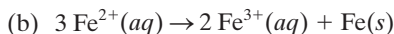
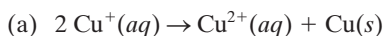
**8.19** Balance the following redox reactions in basic solution:



**8.20** Use standard reduction potentials from online Appendix 9 to determine which of the following reactions will be spontaneous under standard conditions:



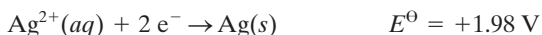
**8.21** Use standard reduction potentials from online Appendix 9 to determine which of the following disproportionation reactions will be spontaneous under standard conditions:



**8.22** Use standard reduction potentials from online Appendix 9 to suggest a chemical reagent that could be used to oxidize hydrochloric acid to chlorine gas.

**8.23** Use standard reduction potentials from online Appendix 9 to suggest a chemical reagent that could be used to reduce chromium(III) ion to chromium(II) ion.

**8.24** Silver can exist in two oxidation states, the more common silver(I) and the rarer silver(II):



(a) Is the silver(I) ion a good oxidizing agent or a good reducing agent?

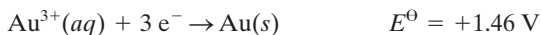
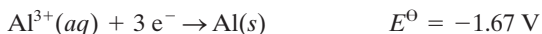
(b) Which of the following is the most feasible reagent for oxidizing silver(I) ion to silver(II) ion: difluorine, fluoride ion, diiodine, iodide ion?

(c) You are thinking of preparing silver(I) hydride, for which:



Do you think the compound is likely to be thermodynamically stable? Explain your reasoning.

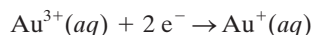
**8.25** For the two half-reactions



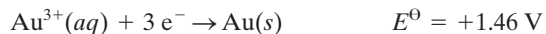
(a) Identify the half-reaction that would provide the stronger oxidizing agent.

(b) Identify the half-reaction that would provide the stronger reducing agent.

**8.26** Calculate the half-reaction potential for the reaction



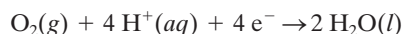
Given:



**8.27** From the standard reduction potential value in online Appendix 9, calculate the half-cell potential for the reduction of lead(II) ion to lead metal in a saturated solution of lead(II) sulfate, concentration  $1.5 \times 10^{-5}\text{ mol}\cdot\text{L}^{-1}$ .

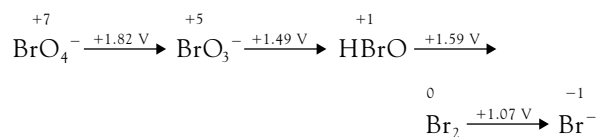
**8.28** From the standard reduction potential value in online Appendix 9, calculate the half-cell potential for the reduction of aqueous permanganate ion to solid manganese(IV) oxide at a pH of 9.00 (all other ions being at standard concentration).

**8.29** From the standard reduction potential value in online Appendix 9, calculate the potential for the reduction of oxygen gas



at pH 7.00 and normal atmospheric partial pressure of dioxygen, 20 kPa. Note that functions in logarithms should be unitless. Hence, divide the pressure value by the standard pressure of 100 kPa before inserting into the Nernst function.

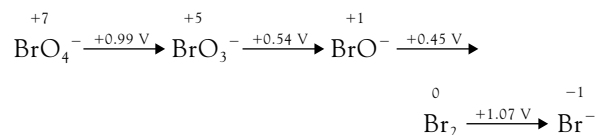
**8.30** The following Latimer potential diagram shows bromine species under acidic conditions:



(a) Identify which species are unstable with respect to disproportionation.

(b) Determine the half-potential for the reduction of the bromate ion,  $\text{BrO}_3^{2-}(aq)$ , to bromine.

**8.31** The following Latimer potential diagram shows bromine species in basic conditions:



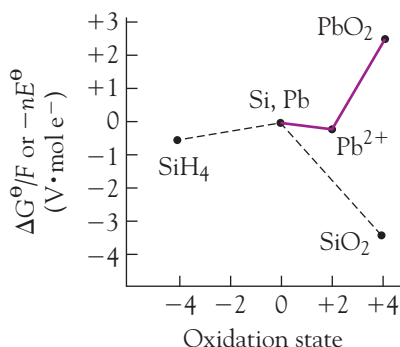
(a) Identify which species are unstable with respect to disproportionation.

(b) Determine the half-potential for the reduction of the bromate ion,  $\text{BrO}_3^-(aq)$ , to bromine.



(c) Explain why the bromine to bromide half-potential has the same value in both acidic and basic solutions.

**8.32** The following diagram below shows lead species (connected by a solid line) and silicon species (connected by a dashed line).



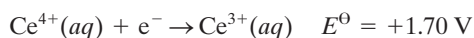
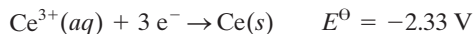
(a) Identify a strong oxidizing agent.

(b) Which is the most thermodynamically stable lead species?

(c) Which is the most thermodynamically stable silicon species?

(d) Which species could potentially disproportionate?

**8.33** Construct a Frost diagram for cerium and discuss the relative stability of the oxidation states, given



**8.34** From the Pourbaix diagram in Figure 8.7, identify the thermodynamically preferred sulfur species at a pH of 7.0 and an  $E$  of 0.0 V.

**8.35** Is the perchlorate ion a stronger oxidizing agent at pH 0.00 or at pH 14.00? Give your reasoning.

## BEYOND THE BASICS

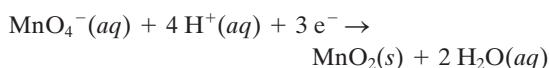
**8.36** Diarsenic trisulfide,  $\text{As}_2\text{S}_3$ , is oxidized to arsenate ion,  $\text{AsO}_4^{3-}$ , and sulfate ion by nitrate ion in acidic solution, the nitrate ion being oxidized to gaseous nitrogen monoxide. Write a balanced equation for the reaction and identify the changes in oxidation state.

**8.37** Below about  $710^{\circ}\text{C}$ , the oxidation of carbon to carbon dioxide is preferred for metal reductions, but above that temperature, the oxidation of carbon to carbon monoxide is more effective. Discuss this statement qualitatively and then use a pair of  $\Delta G^{\ominus}$  calculations to find an approximate value for the changeover temperature.

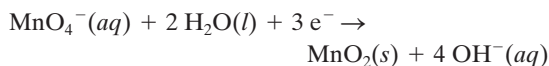
**8.38** Construct a Pourbaix diagram for the nickel system. The only four species you will need to consider are nickel metal, nickel(II) ion, nickel(II) hydroxide ( $K_{\text{sp}} = 6 \times 10^{-16}$ ), and nickel(IV) oxide. Use standard reduction potentials from online Appendix 9.

**8.39** Use the Pourbaix diagram in Figure 8.5 to suggest why, in well water containing manganese, a dark solid stain of an insoluble manganese compound forms in a toilet bowl even though the original well water is completely clear.

**8.40** Use the standard electrode potential given in online Appendix 9 for



and show that the value of  $E^{\ominus}$  obtained for a pH of 14.00 is the same as that given in the appendix for the half-reaction



Suggest why it would be meaningless to calculate the  $E^{\ominus}$  value for  $\text{MnO}_4^{-}(\text{aq}) + 8 \text{H}^{+}(\text{aq}) + 5 \text{e}^{-} \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$  at pH 14.00.

## ADDITIONAL RESOURCES

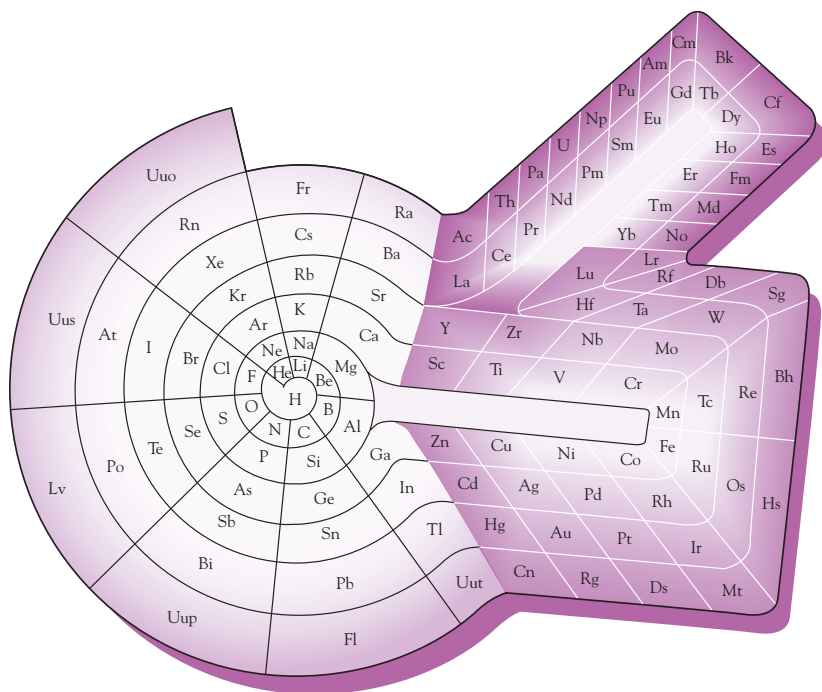
For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# PERIODIC TRENDS

## CHAPTER 9



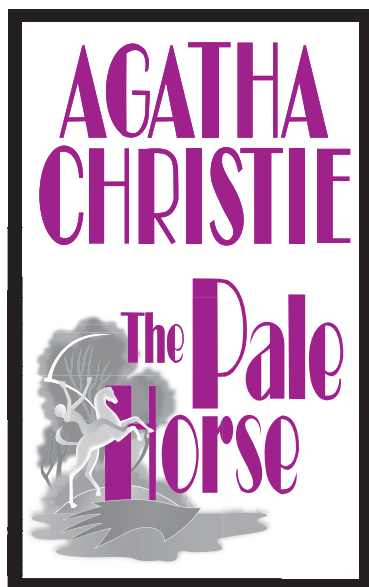
						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 9.1** Group Trends
- 9.2** Periodic Trends in Bonding
- 9.3** Isoelectronic Series in Covalent Compounds
- 9.4** The ( $n$ ) Group and ( $n + 10$ ) Group Similarities
- 9.5** Diagonal Relationships
- 9.6** The “Knight’s Move” Relationship
- 9.7** The Early Actinoid Relationships with Transition Metals
- 9.8** The Lanthanoid Relationships
- 9.9** “Combo” Elements
- 9.10** Biological Aspects

Inorganic chemistry covers the chemistry of over 100 elements. Although each element has its individual characteristics, there are patterns and trends that provide a framework of order. It therefore makes sense to compile these global features in one chapter prior to an examination of each group. This overview chapter can then be used as a starting point for the discussion of the important and unique aspects of each element in subsequent chapters.

### Context: Is the Periodic Table Only Groups and Periods?

Some years ago, a 19-month-old girl from the Middle Eastern country of Qatar was flown to England for treatment of a mysterious illness, initially suspected to be encephalitis. Despite a battery of tests, nothing specific could be found, and the girl’s condition continued to



worsen. One of her intensive care nurses, Marsha Maitland, enjoyed reading Agatha Christie murder mystery novels, and, at that time, Maitland was reading Christie's *The Pale Horse*. In this novel, the contract killer uses a tasteless, water-soluble thallium(I) salt to repeatedly commit “perfect murders.” Christie gave accurate descriptions of the symptoms of thallium(I) poisoning, and Maitland noticed how similar they were to the symptoms of the dying girl. She mentioned this fact to the attending physicians, who used a forensic pathologist to test urine samples for thallium(I). Maitland was correct: the girl had a very high level of thallium(I) in her body. The appropriate treatments were immediately administered, and after three weeks, the now-healthy girl was released from the hospital. Where had the thallium come from? Thallium(I) sulfate was used in the Middle East to kill cockroaches and rodents in drains, and it appears that the girl found some of the poison and ingested it.

In fact, the preference for many homicides-by-poison is thallium(I) sulfate. Why should thallium, an element near the bottom of Group 13, which rarely has a mention in chemistry courses, have such toxic properties in the thallium(I) oxidation state? The answer lies in the similarity of thallium(I) ion to potassium ion. How can an element in Group 13 resemble an element in Group 1? The answer is that there is much more to the periodic table than similarities within groups and periods. One element can indeed resemble elements in totally different parts of the table. The link between thallium(I) ion and potassium ion is just one of many which we will explore in this chapter.

## 9.1 Group Trends

The most significant and consistent trends in the periodic table are those within the groups. We can define the relationship as:

**Groups of elements tend to have characteristic properties. Descending a group in the periodic table, there are often smooth trends in these properties.**

There are four main groups in which those trends are most clearly defined: Groups 1 and 2 and Groups 17 and 18. For Groups 13 through 16, some of the trends are much less systematic as a result of the shift down the group from nonmetallic, through metalloid, to metallic properties. In this section, we will focus on the trends in three of the main groups: the alkali metals (Group 1), the halogens (Group 17), and the pnictogens (Group 15).

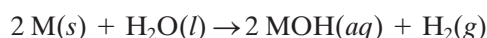
### The Alkali Metals

For the groups containing metals, such as the alkali metals, there is a decrease in melting and boiling point down the group (Table 9.1). This trend can be explained in terms of the weakening metallic bond as the atomic radius of the metal increases.

**TABLE 9.1** Melting points, boiling points, and bonding types for the Group 1 elements

Element	Melting point (°C)	Boiling point (°C)	Bonding category
Lithium	180	1330	Metallic
Sodium	98	892	Metallic
Potassium	64	759	Metallic
Rubidium	39	700	Metallic
Cesium	29	690	Metallic

Although all of the alkali metals are very reactive, reactivity increases spectacularly down the group. The best illustration is the reaction with water to give the metal hydroxide and hydrogen gas:

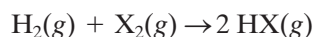


Lithium bubbles quietly to produce the hydroxide and hydrogen gas. Sodium melts, skating around on the water surface as a silvery globule, and the hydrogen that is produced usually burns. For the heavier members of the group, the reaction is extremely violent: explosions often occur when small chunks of rubidium and cesium are dropped into water. The explosions are the result of the ignition of the dihydrogen gas.

## The Halogens

For the nonmetal groups, such as the halogens, the trend in melting and boiling points is the reverse to that of Group 1, with the values increasing down the group (Table 9.2). For these elements, the explanation lies with the intermolecular forces between neighboring diatomic molecules. As we discussed in Chapter 3, Section 3.12, the dispersion forces increase in strength with the number of electrons, thus accounting for the trend.

Just as the physical properties of the halogens are in reverse order to those of the alkali metals, so are the chemical reactivities. An illustration in this case is the reaction with hydrogen:

**TABLE 9.2** Melting points, boiling points, and bonding type for the Group 17 elements

Element	Melting point (°C)	Boiling point (°C)	Bonding category
Fluorine	−219	−188	Covalent
Chlorine	−101	−34	Covalent
Bromine	−7	60	Covalent
Iodine	114	185	Covalent

**TABLE 9.3** Melting points, boiling points, and bonding types for the Group 15 elements

Element	Melting point (°C)	Boiling point (°C)	Bonding category
Nitrogen	−210	−196	Covalent
Phosphorus	44	281	Covalent
Arsenic	615(sub)		Network covalent
Antimony	631	1387	Metallic
Bismuth	271	1564	Metallic

A hydrogen and fluorine mixture is explosive. In fact, the dihydrogen-difluorine reaction was once considered as a rocket propellant. The reaction with chlorine is violent but needs catalysis by light. Reaction with bromine is slow, and that with heated iodine vapor gives an equilibrium mixture of hydrogen iodide, hydrogen, and iodine.

### The Group 15 Elements

Having seen the changes down a metallic group and then down a nonmetallic group, we will see the behavior of a group in which there is a transition from non-metallic to metallic behavior. The melting and boiling points of the Group 15 elements (Table 9.3) are illustrative of the pattern found for Groups 13 through 16.

The colorless nonmetal nitrogen,  $N_2$ , has only weak dispersion forces between neighboring diatomic molecules, accounting for its very low melting and boiling points. Phosphorus, too, is a nonmetal. The melting and boiling points listed here are for the white tetraphosphorus,  $P_4$ , allotrope. (The bonding in phosphorus allotropes is discussed in more detail in Chapter 15, Section 15.13.) With a higher number of electrons per atom and a cluster of four atoms, higher melting and boiling points are to be expected.

Arsenic, antimony, and bismuth are all gray solids with electrical and thermal conductivity increasing down the series. Arsenic has a layer structure containing network covalent bonding. These moderately strong covalent bonds must be broken to escape the solid phase. In fact, arsenic sublimates directly into the gas phase when heated strongly, converting to  $As_4$  molecular clusters analogous to those of phosphorus. Antimony and bismuth have similar solid-state structures, but there is much more interaction between layers, giving a predominantly metallic bonding type. Antimony and bismuth have the long liquid range characteristic of metals.

There is not a consistent trend in chemical reactivity descending this group. For example, diatomic nitrogen gas is unreactive, while solid white tetraphosphorus is extremely reactive. This variation makes the point that trends in element reactivity are only apparent when the members of the group share a common bonding type.

In the chemistry of the compounds, we also see a transition in behavior from typical nonmetallic to metallic. The nonmetals readily form stable oxoanions: nitrate,  $NO_3^-$ ; phosphate,  $PO_4^{3-}$ ; as does the metalloid, arsenate,  $AsO_4^{3-}$ . The

syntheses of oxoanions of the metals, antimony and bismuth, are more difficult, although they do exist, one example being the strong oxidizing agent, the bismuthate ion,  $\text{BiO}_3^-$ . Exhibiting typical metallic behavior, both antimony and bismuth form salts, such as antimony(III) sulfate,  $\text{Sb}_2(\text{SO}_4)_3$ , and bismuth(III) nitrate,  $\text{Bi}(\text{NO}_3)_3$ . The formation of cations is consistent with their metallic nature. However, the fact that these elements form oxoanions at all indicates they fit the category of weak metals.

### WORKED EXAMPLE 9.1

In Group 14, which element is most likely to have an extensive cation chemistry and readily form an oxoanion?

#### Answer

To have mostly cation chemistry, the element must have metallic character—this would be tin or lead. Formation of an oxoanion is a characteristic of a “weak” or “borderline” metal. So it is tin which would be most likely to satisfy both criteria. ■

## 9.2 Periodic Trends in Bonding

We will look first at the trends in the properties of elements across the second and third periods and relate the properties to the bonding type. We will see that element bonding trends follow the metallic-covalent side of the bond triangle (see Chapter 3, Section 3.14). Then we will examine patterns in the fluorides, oxides, and hydrides of these two periods. There are usually systematic trends in the formulas of compounds across a period. However, there are rarely smooth trends in the physical and chemical properties of the compounds since the bonding type changes from ionic, through network covalent, to small-molecule covalent (the second side of the bond triangle). Thus, our definition of trends across a period is best stated as:

**Crossing a period, we observe systematic patterns in chemical formulas of the compounds formed by the elements. In addition, there are partial trends in physical and chemical properties of the elements.**

### The Second Period Elements

The melting points of the Period 2 elements (Table 9.4) show a rapid increase in value, followed by an abrupt drop. However, the apparent trend in the

**TABLE 9.4** Melting points and bonding types of the Period 2 elements

Element	Li	Be	B	C	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne
<b>Melting point (°C)</b>	180	1287	2180	4100(sub)	−210	−229	−219	−249
<b>Bonding categories</b>	Metallic	Metallic	Network covalent	Network covalent	Covalent	Covalent	Covalent	Covalent

first part of the period masks a significant change in bonding type. Lithium and beryllium are both metals, being shiny with high electrical conductivities, yet they differ profoundly in their properties. Lithium, with only one outer electron and a comparatively large size, has weak metallic bonding resulting in a low melting point and a high chemical reactivity. Beryllium, on the other hand, has two outer electrons for metallic bonding and a much smaller radius. Hence, it has a strong metallic bond, resulting in a high melting point.

Because boron follows the trend in increasing melting points, it is tempting to think that it, too, has metallic bonding. This cannot be the case since the pure element is dark red by transmitted light and a poor electrical conductor. Instead, boron is often classified as being a metalloid. The element has a unique structure consisting of  $B_{12}$  units with the atoms joined by covalent bonds within the units and also between neighboring  $B_{12}$  units (see Chapter 13, Section 13.2). To melt boron necessitates the breaking of these linking covalent bonds, accounting for the very high melting point. The other high-melting element is carbon. Graphite, the common form of carbon, sublimates at over  $4000^{\circ}\text{C}$ . This nonmetal consists of layers of multiple-bonded carbon atoms. Thus, as with boron, very strong network covalent bonds must be broken for the melting process.

The next three members of the period—nitrogen, oxygen, and fluorine—form diatomic molecules. The pairs of atoms are held together by covalent bonds. Between neighboring molecules, there are very weak dispersion forces, accounting for the very low melting points of these elements. These second period nonmetals prefer multiple bonding when possible; thus, the dinitrogen molecule contains a triple bond and dioxygen, a double bond. Difluorine has a single bond, while the noble gas neon is monatomic.

### The Third Period Elements

In the third period (Table 9.5), the first three elements have metallic bonding. Then, like the second period, the next member, shiny blue-gray silicon, an electrical semiconductor, has network covalent bonding.

The nonmetals of the third and subsequent periods do not exhibit multiple covalent bonds in their common forms. For example, one allotrope of phosphorus is a waxy, white solid, containing groups of four atoms— $P_4$  units—bound together by single covalent bonds (see Chapter 15, Section 15.13). Similarly, yellow sulfur has  $S_8$  rings in which the constituent atoms are held

**TABLE 9.5** Melting points and bonding types of the Period 3 elements

Element	Na	Mg	Al	Si	$P_4$	$S_8$	$Cl_2$	Ar
Melting point ( $^{\circ}\text{C}$ )	98	649	660	1420	44	119	−101	−189
Bonding categories	Metallic	Metallic	Metallic	Network covalent	Covalent	Covalent	Covalent	Covalent



**TABLE 9.6** Formulas, bonding types, and phases at room temperature of the highest fluorides of the Periods 2 and 3 elements

Compound	LiF	BeF <sub>2</sub>	BF <sub>3</sub>	CF <sub>4</sub>	NF <sub>3</sub>	OF <sub>2</sub>	—
Bonding type (phase)	Ionic (solid)	Network covalent (solid)	Covalent (gas)	Covalent (gas)	Covalent (gas)	Covalent (gas)	—
Compound	NaF	MgF <sub>2</sub>	AlF <sub>3</sub>	SiF <sub>4</sub>	PF <sub>5</sub>	SF <sub>6</sub>	ClF <sub>5</sub>
Bonding type (phase)	Ionic (solid)	Ionic (solid)	Network covalent (solid)	Covalent (gas)	Covalent (gas)	Covalent (gas)	Covalent (gas)

together by single covalent bonds (see Chapter 16, Section 16.9). Chlorine, like all the halogens, is found as simple, covalently bonded diatomic molecules. It is the weakness of the dispersion forces between the small molecules that results in the low melting points of these elements. Finally, argon is a monatomic gas, like all the other noble gases, accounting for its lowest melting point of the period.

### Highest Fluorides of the Second and Third Periods

Just as the progression of the elements across the second and third periods demonstrates the transition from metallic to covalent bonding, so there is a transition in the fluorides of these elements from ionic to covalent (Table 9.6), with the network covalent region marking the borderline between the two bonding categories. We have stipulated the highest (oxidation state) fluorides since several of the nonmetals form more than one fluoride. For example, phosphorus also forms phosphorus trifluoride, PF<sub>3</sub>, and sulfur also forms sulfur tetrafluoride, SF<sub>4</sub>.

The melting point of the ionic compounds is high since the melting process involves the breaking of ionic bonds in the crystal lattice. The melting points of network covalently bonded compounds also tend to be very high since covalent bonds must be broken in the process. In contrast, the melting and boiling points of the (small molecule) covalent compounds tend to be very low since the intermolecular forces, such as dispersion and dipole-dipole, are weaker.

The trends in the formulas themselves are interesting. Crossing the second period, the formulas rise to a maximum element-fluorine ratio at carbon, then decrease again. This trend is explicable in terms of the covalent bonding of the later second period being limited to a maximum of eight electrons. For the third period elements, the oxidation number of the other element increases smoothly until sulfur. On the basis of the other fluorides and the oxidation number trend, chlorine would be expected to form chlorine heptafluoride, ClF<sub>7</sub>. The nonexistence of this compound is often attributed to the steric impossibility of fitting seven fluorine atoms around a central chlorine atom.



**TABLE 9.7** Formulas, bonding types, and phases at room temperature of the highest oxides of the Periods 2 and 3 elements

Compound	Li <sub>2</sub> O	BeO	B <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub>	N <sub>2</sub> O <sub>5</sub>	—	F <sub>2</sub> O
Bonding type (phase)	Ionic (solid)	Ionic (solid)	Network covalent (solid)	Covalent (gas)	Covalent (gas)	—	Covalent
Compound	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>10</sub>	(SO <sub>3</sub> ) <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>
Bonding type (phase)	Ionic (solid)	Ionic (solid)	Ionic (solid)	Network covalent (solid)	Covalent (solid)	Covalent (solid)	Covalent (liquid)

### Highest Oxides of the Second and Third Periods

The formulas of the highest (oxidation state) oxides, like those of the fluorides, correlate with the group number of the nonoxygen element; that is, +1 (Group 1), +2 (Group 2), +3 (Group 13), +4 (Group 14), +5 (Group 15), +6 (Group 16), and +7 (Group 17). The one exception is oxygen difluoride, the only oxide in which the other element has a higher electronegativity than oxygen. As can be seen from Table 9.7, like the fluorides, there is a diagonal band of compounds adopting network covalent structures separating the ionic and covalently bonded regions.

### Bonding Trends in the Hydrides of the Second and Third Periods

The formulas of the hydrides correlate with the lowest common oxidation state of the nonhydrogen element, that is, +1 (Group 1), +2 (Group 2), +3 (Group 13),  $\pm 4$  (Group 14),  $-3$  (Group 15),  $-2$  (Group 16), and  $-1$  (Group 17). Table 9.8 shows the patterns in bonding for the hydrides of Periods 2 and 3. The nonmetal hydrides are small-molecule covalent with very low boiling points; in fact, all are gases at room temperature except for water and hydrogen fluoride. These two particular hydrides are liquids as a result of the strong (intermolecular) hydrogen bonds (see Chapter 3, Section 3.12). Again we see the bonding pattern of ionic to network covalent to covalent on crossing the periods.

**TABLE 9.8** Formulas, bonding types, and phases at room temperature of the hydrides of the Periods 2 and 3 elements

Compound	LiH	(BeH <sub>2</sub> ) <sub>x</sub>	B <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O	HF
Bonding type (phase)	Ionic (solid)	Network covalent (solid)	Covalent (gas)	Covalent (gas)	Covalent (gas)	Covalent (liquid)	Covalent (liquid)
Compound	NaH	MgH <sub>2</sub>	(AlH <sub>3</sub> ) <sub>x</sub>	SiH <sub>4</sub>	PH <sub>3</sub>	H <sub>2</sub> S	HCl
Bonding type (phase)	Ionic (solid)	Ionic (solid)	Network covalent (solid)	Covalent (gas)	Covalent (gas)	Covalent (gas)	Covalent (gas)

**WORKED EXAMPLE 9.2**

For tellurium, Te, what is likely to be the highest formula fluoride? What is the formula of the hydride? What phase would you expect these compounds to have at room temperature?

**Answer**

Tellurium is in Group 16, thus tellurium hexafluoride should exist,  $\text{TeF}_6$  (this also follows from the pattern in Table 9.6). The hydride will be a dihydride (see Table 9.8),  $\text{TeH}_2$ . From the patterns in the periodic table (Tables 9.6 and 9.8), both of these compounds are likely to be gases. ■

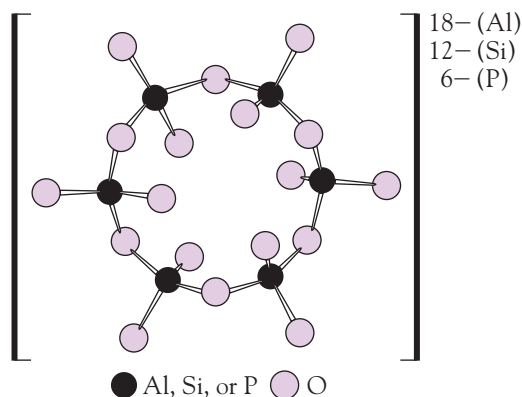
**9.3 Isoelectronic Series in Covalent Compounds**

Among the elements that form covalent compounds, we often find patterns in formulas. One example is that of the highest oxyacids of the third period:  $\text{SiO}_4^{4-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{ClO}_4^-$ . As the number of electrons on the central atom increases by one, so the charge decreases by one unit. Thus, all of these four oxyanions are *isoelectronic*. In the strict definition of isoelectronic that we use in this text:

**Isoelectronic species share the same total number of valence electrons and the same total sum of electrons.**

If species have the same number of valence electrons but different numbers of total electrons (such as  $\text{CO}_2$ ,  $\text{CS}_2$ , and  $\text{CSe}_2$ ), then we refer to them as *valence isoelectronic*.

There are numerous sets of isoelectronic species, but a particularly interesting trio is that of the cyclic ions:  $[\text{Al}_6\text{O}_{18}]^{18-}$ ,  $[\text{Si}_6\text{O}_{18}]^{12-}$  and  $[\text{P}_6\text{O}_{18}]^{6-}$  (Figure 9.1). These share a common structure, even though in the first ion, the nonoxygen element is a metal; the second, a metalloid; and the third, a nonmetal. Calcium aluminate,  $\text{Ca}_9[\text{Al}_6\text{O}_{18}]$ , is a major component of cement, while beryllium aluminum silicate,  $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$ , is the mineral and gemstone beryl.



**FIGURE 9.1** Structure of the isoelectronic  $[\text{Al}_6\text{O}_{18}]^{18-}$ ,  $[\text{Si}_6\text{O}_{18}]^{12-}$ , and  $[\text{P}_6\text{O}_{18}]^{6-}$  ions.

**TABLE 9.9** A matrix of some 14/10 diatomic species of the Period 2 elements

	Group 14	Group 15	Group 16
Group 14	$\text{C}_2^{2-}$	$\text{CN}^-$	$\text{CO}$
Group 15		$\text{N}_2$	$\text{NO}^+$
Group 16		$[\text{O}_2^{2-}]$	

**TABLE 9.10** Sequential isoelectronic series of some Period 2 oxo-species with corresponding bond angles

Electrons	Group 14	Group 15	Group 16	Bond angle
22/16	$\text{CO}_2$	$\text{NO}_2^+$		$180^\circ$
23/17	$\text{CO}_2^-$	$\text{NO}_2$	$\text{O}_3^+$	ca. $135^\circ$
24/18		$\text{NO}_2^-$	$\text{O}_3$	ca. $116^\circ$
25/19			$\text{O}_3^-$	$114^\circ$

We can construct isoelectronic matrices across sections of the periodic table; for example, Table 9.9 shows the matrix for the diatomic combinations of Period 2 elements from Groups 14, 15, and 16, having 14 total electrons and 10 valence electrons. The dioxygen dianion is in parentheses since its existence is fleeting.

Table 9.10 shows a sequential isoelectronic series, each row having one more electron than the row above it. The 22/16 electron triatomic oxo species are linear, and as the number of electrons increase, so the bond angle decreases (as predicted by valence-shell electron-pair repulsion, VSEPR, theory).

### WORKED EXAMPLE 9.3

Write the formulas of two ions which are isoelectronic with silicon tetrachloride.

#### Answer

The neighboring elements are aluminum and phosphorus. To match the number of electrons of  $\text{SiCl}_4$ , the aluminum ion will need one more electron, and phosphorus, one less. The ions will be:  $\text{AlCl}_4^-$  and  $\text{PCl}_4^+$ . ■

### WORKED EXAMPLE 9.4

The fluoride ion can substitute for the oxide ion in oxoanions. Construct the formulas of the three possible fluoro-oxosulfur compounds isoelectronic with the sulfate ion.

#### Answer

Replacing an oxide,  $\text{O}^{2-}$ , with a fluoride,  $\text{F}^-$ , in the  $\text{SO}_4^{2-}$  ion will result in a charge reduction of one unit with every replacement. The isoelectronic series will be  $\text{SO}_3\text{F}^-$ ,  $\text{SO}_2\text{F}_2$ , and  $\text{SOF}_3^+$ . ■

## 9.4 The (*n*) Group and (*n* + 10) Group Similarities

Similarities in formulas between two sets of groups, such as Groups 4 and 14, originally led Mendeleev and others to construct a simple eight-column periodic table. When chemists became aware of the importance of atomic number in determining periodic order, the resulting 18-column table had group labels 1A, 1B, etc., to continue to provide a link between the two sets. With the newer 1 to 18 numbering, the link is less apparent and is in danger of being forgotten. This chemical amnesia is regrettable, as there are some interesting parallels that actually reinforce the concept of periodicity.

The connection is predominantly between compounds and ions of the highest oxidation state of the main group elements and those of the corresponding oxidation state of the matching transition elements. A general definition for this relationship is:

**There are similarities in chemical formulas and structures of the highest oxidation state of some members of the (*n*) Group elements and of the members of the corresponding (*n* + 10) Group elements.**

One can argue on simple electron-configuration or oxidation-state grounds that there should be similarities between these two sets, but the similarities go far beyond simple formula resemblances. We find some commonality in melting points, properties, and, in a few cases, unusual corresponding structures.

### Aluminum and Scandium

Aluminum and scandium have so many similarities that the Canadian geochemist Fathi Habashi has suggested that aluminum's place in the periodic table should actually be shifted to Group 3. Certainly this makes sense from the perspective of electron configuration, for the aluminum ion has a noble gas configuration like the 3+ ions of the Group 3 elements, whereas the lower Group 13 elements have filled (*n* – 1)*d*<sup>10</sup> orbitals.

	13
3	Al
Sc	Ga
Y	In
	Tl

Group 3 ion	Electron configuration	Group 13 ion	Electron configuration
Sc <sup>3+</sup>	[Ar]	Al <sup>3+</sup>	[Ne]
		Ga <sup>3+</sup>	[Ar](3 <i>d</i> <sup>10</sup> )

The closer resemblance of aluminum to Group 3 in terms of melting point and electrode potential can be seen in Table 9.11.

In solution, both Al<sup>3+</sup> and Sc<sup>3+</sup> cations hydrolyze significantly to give acid solutions containing polymeric hydroxo species. On addition of hydroxide ion to the respective cation, the hydroxides of aluminum and scandium are both produced as gelatinous precipitates. The precipitates redissolve in excess base to give anionic species (Table 9.12). In another example, both metals form isostructural compounds of the type Na<sub>3</sub>MF<sub>6</sub>, where M = Al or Sc.

Not only does aluminum resemble scandium but also reactive aluminum metal differs significantly in its chemistry from unreactive gallium metal. Among differences in compound types, gallium, like boron, forms a gaseous

**TABLE 9.11** A comparison of some properties of Group 3 and Group 13 elements

Group 3 elements			Group 13 elements		
Element	m.p. (°C)	$E^\circ$ (V)	Element	m.p. (°C)	$E^\circ$ (V)
—	—	—	Al	660	−1.66
Sc	1540	−1.88	Ga	30	−0.53
Y	1500	−2.37	In	160	−0.34
La	920	−2.52	Tl	300	+0.72
Ac	1050	−2.6	—	—	—

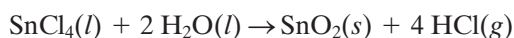
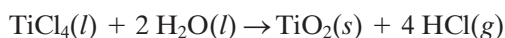
**TABLE 9.12** A comparison of aluminum and scandium species under oxidizing conditions

	Acidic	Mid-to-basic pH range	Very basic
Aluminum	$\text{Al}^{3+}(\text{aq})$	$\text{Al}(\text{OH})_3(\text{s})$	$\text{Al}(\text{OH})_4^-(\text{aq})$
Scandium	$\text{Sc}^{3+}(\text{aq})$	$\text{Sc}(\text{OH})_3(\text{s})$	$\text{Sc}(\text{OH})_4^-(\text{aq})$

hydride,  $\text{Ga}_2\text{H}_6$ . Aluminum, however, forms a polymeric white solid hydride  $(\text{AlH}_3)_x$ . Bubbling hydrogen sulfide gas through a solution of the respective cation also has a very different result. Gallium gives a precipitate of gallium sulfide,  $\text{Ga}_2\text{S}_3$ , while aluminum gives a precipitate of aluminum hydroxide,  $\text{Al}(\text{OH})_3$ . (Likewise, scandium gives a precipitate of scandium hydroxide,  $\text{Sc}(\text{OH})_3$ .) However, the structures of the aluminum halides do resemble those of gallium halides more than those of scandium halides.

### Group 14 and Titanium(IV)

Although there are similarities between titanium(IV) and silicon(IV), there is a much greater similarity between titanium(IV) and tin(IV)—a lower member of Group 14. In fact, this pair has among the closest similarities of elements in different groups. When we start with the oxides, we find that white titanium(IV) oxide and white tin(IV) oxide are isostructural and share the rare attribute of turning yellow on heating (*thermochromism*). There are very close similarities in the melting and boiling points of the chlorides: titanium(IV) chloride (m.p.  $-24^\circ\text{C}$ , b.p.  $136^\circ\text{C}$ ) and tin(IV) chloride (m.p.  $-33^\circ\text{C}$ , b.p.  $114^\circ\text{C}$ ). Both chlorides behave as Lewis acids and hydrolyze in water:



### Phosphorus(V) and Vanadium(V)

Because phosphorus is a nonmetal and vanadium a metal, there is obviously a limit to the comparisons that can be made. Nevertheless, there are some striking similarities in their +5 oxidation states. For example, the two elements form a large number of polymeric anions, including the unique matching pair of  $\text{P}_4\text{O}_{12}^{4-}$  and  $\text{V}_4\text{O}_{12}^{4-}$ . In addition, the phosphate,  $\text{PO}_4^{3-}$ , and vanadate,  $\text{VO}_4^{3-}$ , ions are

	14
4	Si
Ti	Ge
Zr	Sn
Hf	Pb

	15
5	P
V	As
Nb	Sb
Ta	Bi

**TABLE 9.13** A comparison of phosphorus(V) and vanadium(V) species under strongly oxidizing conditions

	Very Acidic	Acidic	Basic	Very Basic
Vanadium	$\text{VO}_2^+$	$\text{H}_2\text{VO}_4^-$	$\text{HVO}_4^{2-}$	$\text{VO}_4^{3-}$
Phosphorus	$\text{H}_3\text{PO}_4$	$\text{H}_2\text{PO}_4^-$	$\text{HPO}_4^{2-}$	$\text{PO}_4^{3-}$

both strong bases with parallel species across most of the pH range, except that, at low pH, vanadium forms the vanadyl ion,  $\text{VO}_2^+$  (see Chapter 20, Section 20.3), not the undissociated acid as does phosphorus (Table 9.13).

### Sulfur(VI) and Chromium(VI)

Table 9.14 shows some formula similarities between sulfur(VI) and chromium(VI). The resemblance even extends to the physical properties of some of the compounds, for example, the two oxychlorides: sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$  (m.p.  $-54^\circ\text{C}$ , b.p.  $69^\circ\text{C}$ ), and chromyl chloride,  $\text{CrO}_2\text{Cl}_2$  (m.p.  $-96^\circ\text{C}$ , b.p.  $117^\circ\text{C}$ ). These compounds resemble each other chemically, decomposing in water. However, there are major chemical differences between sulfur(VI) and chromium(VI); in particular, chromates and dichromates are strongly oxidizing and colored (chromate, yellow, and dichromate, orange), whereas the sulfates and pyrosulfates are nonoxidizing and colorless.

Whereas the vanadium(V)–phosphorus(V) oxoacids are weak acids, the chromium(VI)–sulfur(VI) oxoacids are strong, as can be seen from Table 9.15, with the sulfur(VI) oxoacid being the stronger of the two.

### Chlorine(VII) and Manganese(VII)

The oxoanions of chlorine(VII) and manganese(VII), perchlorate,  $\text{ClO}_4^-$ , and permanganate,  $\text{MnO}_4^-$ , are both strongly oxidizing and their salts are

	16
6	S
Cr	Se
Mo	Te
W	Po

	17
7	Cl
Mn	Br
Tc	I
Re	At

**TABLE 9.14** Similarities between chromium(VI) and sulfur(VI) species

Group 6		Group 16	
Formula	Systematic name	Formula	Systematic name
$\text{CrO}_3$	Chromium(VI) oxide	$\text{SO}_3$	Sulfur trioxide
$\text{CrO}_2\text{Cl}_2$	Chromyl chloride	$\text{SO}_2\text{Cl}_2$	Sulfuryl chloride
$\text{CrO}_4^{2-}$	Chromate ion	$\text{SO}_4^{2-}$	Sulfate ion
$\text{Cr}_2\text{O}_7^{2-}$	Dichromate ion	$\text{S}_2\text{O}_7^{2-}$	Pyrosulfate ion

**TABLE 9.15** A comparison of chromium(VI) and sulfur(VI) species under strongly oxidizing conditions

	Very Acidic	Acidic	Basic	Very Basic
Chromium	H <sub>2</sub> CrO <sub>4</sub>	HCrO <sub>4</sub> <sup>−</sup>	CrO <sub>4</sub> <sup>2−</sup>	
Sulfur	HSO <sub>4</sub> <sup>−</sup>	SO <sub>4</sub> <sup>2−</sup>		

**TABLE 9.16** A comparison of manganese(VII) and chlorine(VII) species under strongly oxidizing conditions

	Very Acidic	Acidic	Basic	Very Basic
Manganese	$\text{MnO}_4^-$			
Chlorine	$\text{ClO}_4^-$			

isostructural. The corresponding oxoacids are very strong acids, as apparent from Table 9.16. However, like the chromate-sulfate pair, the permanganate-perchlorate pair do differ in color: the transition metal oxoanion permanganate is deep purple, while the main group oxoanion perchlorate is colorless. Their oxides, colorless dichlorine heptaoxide,  $\text{Cl}_2\text{O}_7$ , and reddish brown manganese(VII) oxide,  $\text{Mn}_2\text{O}_7$ , are highly explosive liquids at room temperature.

Chlorine and manganese show another resemblance by forming oxides in an oxidation state that would not be predicted for either element—that of +4 ( $\text{ClO}_2$  and  $\text{MnO}_2$ ). Although chlorine dioxide is a yellow gas and manganese(IV) oxide is a black solid, it is curious why both elements should possess oxides in such an unexpected oxidation state.

**WORKED EXAMPLE 9.5**

Write the formulas of a metal compound analogous to  $\text{ClO}_3\text{F}$  and  $\text{BrO}_3\text{F}$ .

**Answer**

Using the ( $n$ ) and ( $n + 10$ ) concept, manganese of Group 7 is likely to form an analogous compound. The compound would be  $\text{MnO}_3\text{F}$ . ■

	18
8	Ar
Fe	Kr
Ru	Xe
Os	Rn

**Xenon(VIII) and Osmium(VIII)**

The next link is between lower members of Group 8 and Group 18. The chemistry of the metal osmium and of the nonmetal xenon have some fascinating parallels—particularly in the +8 oxidation state. For example, osmium forms a yellow strongly oxidizing oxide,  $\text{OsO}_4$ , while xenon forms a pale yellow explosive oxide,  $\text{XeO}_4$ . There are parallels in the formulas of oxyfluorides, too:  $\text{XeO}_2\text{F}_4$  and  $\text{OsO}_2\text{F}_4$ , and  $\text{XeO}_3\text{F}_2$  and  $\text{OsO}_3\text{F}_2$ . There are also similarities in the +6 oxidation state. The highest fluorides for both elements (formed by direct reaction of the element with fluorine) are in this oxidation state,  $\text{XeF}_6$  and  $\text{OsF}_6$ , and they both form corresponding fluoroanions:  $\text{XeF}_7^-$  and  $\text{OsF}_7^-$ .

**WORKED EXAMPLE 9.6**

Two elements with stable isotopes—one a metal, one a nonmetal—form a compound  $\text{XF}_7$ . Suggest the identity of the two elements.

**Answer**

Using the ( $n$ ) and ( $n + 10$ ) concept, the two elements are likely to be members of Group 7 and 17. For seven bonds to the central atom, the atom size must be large. Technetium, Tc, and astatine, At, are disqualified as they only

have radioactive isotopes. Thus, the two elements are likely to be rhenium and iodine, and the compounds  $\text{ReF}_7$  and  $\text{IF}_7$ . (In fact, this parallels the linkage between osmium and xenon in Groups 8 and 18, respectively.) ■

### The Alkali Metals (Group 1) and the Coinage Metals (Group 11)

Until now, we have been extolling the usefulness of the links between the Group (*n*) and (*n* + 10) elements. By contrast, there are no major similarities between the Group 1 and Group 11 elements. In fact, this pair illustrates the extremes of dissimilarity of metallic behavior! The alkali metals are reactive and all the common salts are soluble; the coinage metals are unreactive and most of their +1 oxidation state compounds are insoluble. Some examples of the major differences between the elements of the two groups are shown in Table 9.17.

### Magnesium and Zinc

Whereas Groups 1 and 11 are dissimilar, there are major similarities between magnesium (Group 2) and zinc (Group 12). The solubilities of the pairs of compounds are very similar: the chlorides and sulfates are soluble, while the carbonates are insoluble. The only major difference in chemistry is that zinc is amphoteric as might be expected of a “weak” metal close to the metalloid border. Thus, in strongly basic solution, zinc hydroxide will dissolve to form the zincate ion, which can be written as  $[\text{Zn}(\text{OH})_4]^{2-}$  (see Table 9.18.)



2	
Mg	12
Ca	Zn
Sr	Cd
Ba	Hg

**TABLE 9.17** Contrast of the alkali metals and the coinage metals

Property	Alkali metals	Coinage metals
Common oxidation numbers	Always +1	Silver +1; but copper and gold rarely +1
Chemical reactivity	Very high; increasing down the group	Very low; decreasing down the group
Density	Very low; increasing down the group (0.5 to 1.9 g·cm <sup>-3</sup> )	High; increasing down the group (9 to 19 g·cm <sup>-3</sup> )
Melting points	Very low; decreasing down the group (181°C to 29°C)	High; all about 1000°C
Aqueous redox chemistry	None	Yes (e.g., $\text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu}^+(\text{aq})$ )
Solubilities of common salts	All soluble	+1 Oxidation state compounds insoluble

**TABLE 9.18** A comparison of magnesium and zinc species under oxidizing conditions

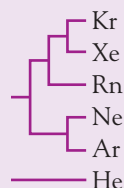
	Very Acidic	Acidic	Basic	Very Basic
Magnesium	$\text{Mg}^{2+}(\text{aq})$		$\text{Mg}(\text{OH})_2(\text{s})$	
Zinc	$\text{Zn}^{2+}(\text{aq})$		$\text{Zn}(\text{OH})_2(\text{s})$	$[\text{Zn}(\text{OH})_4]^{2-}(\text{aq})$



## Chemical Topology

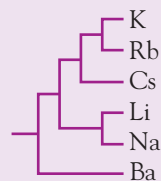
The study of patterns in chemistry is called *chemical topology*. Guillermo Restrepo and his colleagues at the Industrial University of Santander, Colombia, have applied the principles of chemical topology to the periodic table. The advantage of using a computer to analyze element patterns is that computer programs can correlate enormous amounts of data and look at degrees of matching; in this case among a total of 31 chemical and physical properties of each of the elements. The program then constructs a dendrimer diagram; that is, it produces a “tree” of similarities. Each element is represented by a “twig” on a “branch.” All the elements on a branch show similarities in their behavior. The closer the twigs, the more closely the elements are related. Of course, the limitations are that the patterns are dependent on the particular properties chosen in the comparison and the method of comparison. In fact, Restrepo has produced a total of 19 different trees, although all have remarkable similarities.

To make the tree easier to read, it is rotated through  $90^\circ$  so that the branches lie horizontal. Let us look at the branch containing the noble gases:



Thus, unreactive argon and neon are more closely related, as are the chemically reactive heavier members of the series. Helium is identified as being so different, it has its own unique branch.

The pattern for the alkali metals is similar:

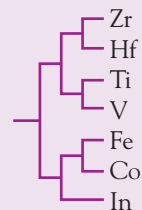


As we would expect, the alkali metals all fit on a single branch. The heavier alkali metals are closer together and more closely related, as are the two lighter ones. Of initial surprise, barium is a member of this group. However, barium is highly reactive and forms a peroxide, like the alkali metals but unlike the alkaline earth metals, so this alignment does make some sense.

An interesting branch is the one shown below, containing beryllium, aluminum, and silicon. This branch shows that there is indeed substance to the diagonal relationship since beryllium and aluminum are grouped together. It is more surprising that the metal aluminum and the metalloid silicon are part of the same branch, although aluminum does replace silicon readily in clay mineral structures:



Is chemical topology the way of the future? Certainly it provides a semiquantitative method of looking at periodic trends and patterns, and it can pick out relationships that have been overlooked in the past. For example, the main group metal indium appears to have considerable similarities with some of the transition metals, a possibility that had not been recognized before:



However, chemical topology provides just a general overview of patterns. To chemists, it is often specific similarities in reactions that are important, which need the insight of the human mind to spot.

## 9.5 Diagonal Relationships

Although chemists usually think of periodic trends vertically (down groups) or horizontally (across periods), there are, in fact, other patterns to be found in the periodic table. One of these is the *diagonal relationship*:

**There are similarities in chemical properties between an element and that to the lower right of it. This relationship is found primarily for elements in the upper-left corner of the periodic table.**

We have already seen evidence of a diagonal relationship in the bonding types of the fluorides, oxides, and hydrides, where there is a diagonal of network covalent compounds separating the ionic and covalent bonding types. The diagonal relationship is most chemically significant for three pairs of elements: lithium and magnesium, beryllium and aluminum, and boron and silicon (Figure 9.2).

Li	Be	B
	Mg	Al
		Si

**FIGURE 9.2** Elements commonly considered linked by the diagonal relationship.

### Similarities of Lithium and Magnesium

The best examples of resemblance between the chemistry of lithium and that of magnesium are:

1. The hardness of lithium metal is greater than that of the other alkali metals but similar to that of the alkaline earth metals.
2. Lithium forms a normal oxide,  $\text{Li}_2\text{O}$ , like the alkaline earth metals but unlike the other alkali metals. (Sodium forms  $\text{Na}_2\text{O}_2$ , containing the  $\text{O}_2^{2-}$  ion, while the heavier alkali metals form compounds containing the  $\text{O}_2^-$  ion, such as  $\text{KO}_2$ .)
3. Lithium is the only alkali metal to form a nitride,  $\text{Li}_3\text{N}$ , whereas the alkaline earth metals all form nitrides.
4. Three lithium salts—carbonate, phosphate, and fluoride—have very low solubilities. These anions form insoluble salts with the alkaline earth metals.
5. Lithium forms organometallic compounds similar to those of magnesium (the Grignard reagents used in organic chemistry).
6. Many lithium salts exhibit a high degree of covalency in their bonding. This bonding is similar to that of magnesium.
7. The lithium and magnesium carbonates decompose to give the appropriate metal oxide and carbon dioxide. The carbonates of the other alkali metals do not decompose when heated.

How can we explain this? An examination of the charge densities of the elements in Groups 1 and 2 (Table 9.19) reveals that the charge density of lithium is much closer to that of magnesium than to those of the other alkali metals. Hence, similarity in charge density may explain the resemblance in the chemical behaviors of lithium and magnesium.

### Similarities of Beryllium and Aluminum

Beryllium and aluminum resemble each other in three ways. Again, we can use charge density arguments to explain this diagonal relationship: that the very

**TABLE 9.19** Charge densities for the alkali metal and alkaline earth metal ions

Group 1 ion	Charge density ( $\text{C}\cdot\text{mm}^{-3}$ )	Group 2 ion	Charge density ( $\text{C}\cdot\text{mm}^{-3}$ )
$\text{Li}^+$	98	—	—
$\text{Na}^+$	24	$\text{Mg}^{2+}$	120
$\text{K}^+$	11	$\text{Ca}^{2+}$	52
$\text{Rb}^+$	8	$\text{Sr}^{2+}$	33
$\text{Cs}^+$	6	$\text{Ba}^{2+}$	23

high charge density of the beryllium  $2+$  ion is closer to that of the aluminum  $3+$  ion than it is to the larger ions of Group 2:

1. In air, both metals form tenacious oxide coatings that protect the interior of the metal sample from attack.
2. Both elements are amphoteric, forming parallel anions—tetrahydroxidoberyllates,  $[\text{Be}(\text{OH})_4]^{2-}$ , and tetrahydroxidoaluminates,  $[\text{Al}(\text{OH})_4]^-$ —in reactions with concentrated hydroxide ion.
3. Both form carbides ( $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$ ) containing the  $\text{C}^{4-}$  ion that react with water to form methane. (The other Group 2 elements form compounds containing the  $\text{C}_2^{2-}$  ion, such as  $\text{CaC}_2$ , which react with water to form ethyne.)

However, there are some differences between the chemical properties of beryllium and aluminum. One of the most apparent differences is in the formula of the hydrated ions each forms. Beryllium forms the  $[\text{Be}(\text{OH}_2)_4]^{2+}$  ion, whereas aluminum forms the  $[\text{Al}(\text{OH}_2)_6]^{3+}$  ion. The lower coordination number of the beryllium may be explained as the cation being physically too small to accommodate six surrounding water molecules at a bonding distance. For both cations, as the pH is increased, the insoluble hydroxide is formed, then, at very high pH, the precipitate redissolves to form the oxoanion (see Table 9.20).

### Similarities of Boron and Silicon

A comparison of boron and silicon is our third and final example of the diagonal relationship. This case is very different from the two other examples, for the chemistry of both elements involves covalent bonding. Thus, there can be no justification in terms of ion charge density. In fact, this relationship is not easy to understand except that both elements are on the borderline of the

**TABLE 9.20** A comparison of beryllium and aluminum species under oxidizing conditions

	Acidic	Mid-to-basic pH range	Very basic
Beryllium	$\text{Be}^{2+}(\text{aq})$	$\text{Be}(\text{OH})_2(\text{s})$	$\text{Be}(\text{OH})_4^{2-}(\text{aq})$
Aluminum	$\text{Al}^{3+}(\text{aq})$	$\text{Al}(\text{OH})_3(\text{s})$	$\text{Al}(\text{OH})_4^-(\text{aq})$

metal-nonmetal divide and have similar electronegativities. Some of the similarities are listed here:

1. Boron forms a solid acidic oxide,  $\text{B}_2\text{O}_3$ , like that of silicon,  $\text{SiO}_2$ , but unlike that of either aluminum, whose oxide is amphoteric, or carbon, whose oxide,  $\text{CO}_2$ , is acidic but gaseous.
2. Boric acid,  $\text{H}_3\text{BO}_3$ , is a very weak acid that is similar to silicic acid,  $\text{H}_4\text{SiO}_4$ , in some respects. It bears no resemblance to the amphoteric aluminum hydroxide,  $\text{Al}(\text{OH})_3$ .
3. There are numerous polymeric borates and silicates that are constructed in similar ways, using shared oxygen atoms.
4. Boron forms a range of flammable, gaseous hydrides, just as silicon does. There is only one aluminum hydride—a solid.

### WORKED EXAMPLE 9.7

Some diagonal relationships can be found elsewhere in the periodic table. Suggest the formula of a rhenium ion valence isoelectronic with that of  $[\text{Mo}_2\text{Cl}_8]^{4-}$ .

#### Answer

As rhenium has one more d electron than molybdenum, to be valence isoelectronic, the ion would have one less charge per rhenium. The ion would be  $[\text{Re}_2\text{Cl}_8]^{2-}$ . ■

## 9.6 The “Knight’s Move” Relationship

For the later main group elements, the South African chemist Michael Laing noticed a relationship between one element and the element one period down and two groups to its right. He called this pattern the “*knight’s move*” relationship from its similarity to the move in the game of chess. This relationship, apparent among the lower members of Groups 11 through 15, is defined as:

**There is a similarity between an element of Group ( $n$ ) and Period ( $m$ ) with the element in Group ( $n + 2$ ) and Period ( $m + 1$ ) in the same oxidation state. This relationship is found among elements in the lower-right portion of the periodic table.**

Here we will look at three knight’s move pairs: zinc(II) and tin(II); tin(IV) and polonium(IV); and silver(I) and thallium(I).

### Similarities of Zinc(II) and Tin(II)

In Section 9.5, we showed that there are similarities in the chemistry of magnesium ion and zinc ion through the ( $n$ ) and ( $n + 10$ ) linkage. Here we see that zinc chemistry of Group 12 is also similar to that of tin(II) of Group 14. In fact, the zinc-tin(II) linkage seems in many ways to be the stronger. For example, aqueous

Cu	Zn	Ga			
Ag	Cd	In	Sn	Sb	
		Tl	Pb	Bi	Po

solutions of their chlorides hydrolyze to give insoluble  $\text{Zn}(\text{OH})\text{Cl}$  and  $\text{Sn}(\text{OH})\text{Cl}$ , respectively. In the presence of high concentrations of chloride ions, parallel chloro-complex ions are formed:  $\text{ZnCl}_3^-$  and  $\text{SnCl}_3^-$  and  $\text{ZnCl}_4^{2-}$  and  $\text{SnCl}_4^{2-}$ .

Parallels do have their limitations. For example, zinc and tin are both amphoteric metals, dissolving in base to form zincates and stannate, respectively. However, the formulas of the ions differ, with tetrahedral  $[\text{Zn}(\text{OH})_4]^{2-}$  compared with octahedral  $[\text{Sn}(\text{OH})_6]^{4-}$  as a result of the much larger size of the tin(II) ion compared with the zinc ion.

### Similarities of Tin(IV) and Polonium(IV)

Just as tin(II) of Group 14 has a resemblance to zinc of Group 12, so tin(IV) has a resemblance to polonium(IV) of Group 16. For example, there are numerous formula correspondences between tin(IV) and polonium(IV), such as  $\text{SnCl}_4$  and  $\text{PoCl}_4$ , and the complex ions  $[\text{SnCl}_6]^{2-}$  and  $[\text{PoCl}_6]^{2-}$ . In addition, the only solid stable nitrates of both metals correspond:  $\text{Sn}(\text{NO}_3)_4$  and  $\text{Po}(\text{NO}_3)_4$ . There are matching oxides in the +4 oxidation state:  $\text{SnO}_2$  and  $\text{PoO}_2$  (and, curiously, in the +2 state:  $\text{SnO}$  and  $\text{PoO}$ ).

### Similarities of Silver(I), Thallium(I), and Potassium

As the opening Context to this chapter, we described the toxicity of thallium(I) ion of Group 13 and related the toxicity to a similarity in chemistry with potassium ion. In fact, thallium(I) ion resembles potassium ion in some ways, but also the thallium(I) knight's move match of silver(I). For example, the mineral crooksite contains either thallium(I) or silver(I) in the same lattice site:  $\text{Cu}_7(\text{Tl}, \text{Ag})\text{Se}_4$ .

So, just as zinc in Group 12 resembles tin(II) in Group 14 and magnesium in Group 2, there is a link between thallium(I) in Group 13, silver(I) in Group 11, and potassium in Group 1. Table 9.21 shows how the chemistry of thallium(I) does truly resemble potassium ion in some respects and silver(I) ion in others.

So why is thallium(I) ion so toxic? Thallium(I) accumulates in tissues with high concentrations of potassium ion. Thallium(I) invades cells so readily

Cu	Zn	Ga			
Ag	Cd	In	Sn	Sb	
		Tl	Pb	Bi	Po

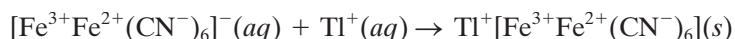
Cu	Zn	Ga			
Ag	Cd	In	Sn	Sb	
		Tl	Pb	Bi	Po

**TABLE 9.21** A comparison of the properties of thallium(I) ion to those of silver(I) and potassium ions

Properties of thallium(I)	Properties of silver(I)	Properties of potassium
Forms normal oxide, $\text{Tl}_2\text{O}$	Forms normal oxide, $\text{Ag}_2\text{O}$	Forms $\text{KO}_2$ , not normal oxide
Soluble, very basic hydroxide	Insoluble hydroxide	Soluble, very basic hydroxide
Hydroxide reacts with carbon dioxide to form carbonate	Unreactive hydroxide	Hydroxide reacts with carbon dioxide to form carbonate
Fluoride soluble, other halides insoluble	Fluoride soluble, other halides insoluble	All halides soluble
Chromate brick-red color and insoluble	Chromate brick-red color and insoluble	Chromate yellow and soluble

because it is preferred over potassium by the same cellular transport mechanism. Once in the cell, thallium(I) substitutes for potassium in potassium-activated enzymes and disrupts the functioning of the enzymes. It is also believed that thallium(I), a very soft acid (see Chapter 7, Section 7.7), combines with the soft-base sulfur of thio-amino acid groups in mitochondria, blocking oxidative phosphorylation. In this respect, thallium(I) resembles silver(I). Thallium poisoning causes degenerative changes in all cells, but particularly the nervous system and hair follicles. Unfortunately, many of its symptoms can be misdiagnosed as resulting from other illnesses.

There are two complementary treatments of thallium poisoning, each relying on one of the two linkages. First, using the principles of solution equilibrium, the administration of high levels of potassium ion can reduce the cellular concentration of thallium(I) ion. Second, potassium iron(III) hexacyanidoferrate(II),  $K^+[Fe^{3+}Fe^{2+}(CN^-)_6]$ , commonly called soluble Prussian blue (see Chapter 20, Section 20.6), is administered. The use of this nontoxic compound depends upon the similarity of thallium(I) to silver(I); that is, like silver(I), thallium(I) forms an insoluble compound with the complex ion. By this means, any thallium(I) in the gastrointestinal tract will be precipitated and excreted. In addition,



### The Inert-Pair Effect

How can the knight’s move be explained? Ions of similar charge and size (that is, similar charge densities) are likely to have similarities in their chemistry. For example, silver(I) and thallium(I) both have very low and similar charge densities. The similarity in size of the two ions of different periods is also easy to account for. With the filling of the transition metal series (and the lanthanoids), the d and f electrons are poor shielders of the outer electrons. Thus, the ion of the  $(n + 2)$  group and  $(m + 1)$  period “shrinks” to about the size of the ion of the same charge of the  $(n)$  group and the  $(m)$  period.

But this avoids the question of why such elements as thallium, tin, lead, and bismuth form compounds in a lower oxidation state than would be expected from their group number—and why that oxidation state is always less by two (for example,  $Tl^{+}$ ,  $Tl^{3+}$ ;  $Sn^{2+}$ ,  $Sn^{4+}$ ;  $Pb^{2+}$ ,  $Pb^{4+}$ ;  $Bi^{3+}$ ,  $Bi^{5+}$ ). The explanation can be found in the *inert-pair effect*. To illustrate, we will use thallium as an example. All the Group 13 elements have an outer electron configuration of  $s^2p^1$ . Thus, formation of a  $1+$  ion corresponds to the loss of the single p electron and retention of the two s electrons.

To find a reasonable explanation for the formation of these low-charge ions, we have to consider relativistic effects (mentioned in Chapter 2, Section 2.5). Using the concept of wave/particle duality, it is proposed that the velocities of electrons in outer orbitals, particularly in the 6s orbital, become close to that of light. Following from  $E = mc^2$ , the mass of these 6s electrons increases. As a result, the mean distance of the 6s electrons from the nucleus decreases: in other words, the orbital shrinks. This effect is apparent from the successive ionization energies. In Chapter 2, Section 2.6, we saw that ionization energies usually decrease down groups, but a comparison of the first three

**TABLE 9.22** Comparative ionization energies of aluminum and thallium

Element	Ionization energy ( $\text{MJ}\cdot\text{mol}^{-1}$ )		
	First (p)	Second (s)	Third (s)
<b>Aluminum</b>	0.58	1.82	2.74
<b>Thallium</b>	0.59	1.97	2.88

ionization energies of aluminum and thallium shows that the ionization energy of the outer p electron is greater, and the ionization energies of the pair of s electrons significantly greater for thallium than for aluminum (Table 9.22).

Recalling the Born-Haber cycles (Chapter 6, Section 6.3), we note that the large energy input needed to form the cation must be balanced by a high lattice energy (energy output). But the thallium(III) ion is much larger than the aluminum(III) ion; hence, the lattice energy of a thallium(III) ionic compound will be less than that of the aluminum analog. The combination of these two factors, particularly the higher ionization energy, leads to a decreased stability of the thallium(III) ionic state and, hence, the stabilizing of the thallium(I) ionic oxidation state.

### WORKED EXAMPLE 9.8

Suggest ions of other elements whose chemistry might match that of an ion of lead.

#### Answer

From the knight's move relationship, cadmium,  $\text{Cd}^{2+}$ , of Group 12 would be likely to share aspects of chemistry with the lower-oxidation state,  $\text{Pb}^{2+}$ , of Group 14. In addition, there may be similarities with calcium,  $\text{Ca}^{2+}$  of Group 2. (In fact, apart from some chemical similarities, it is of note that both cadmium and lead(II) are highly toxic. Lead(II) incorporates in bone, substituting for calcium ion.) ■

### WORKED EXAMPLE 9.9

Suggest an explanation why: (a) zinc and tin(II) have a resemblance; (b) tin(IV) and polonium(IV) have a resemblance.

#### Answer

Zinc(II) has the noble-gas core configuration of:  $[\text{Ar}]3\text{d}^{10}$ , while that of tin(II) is  $[\text{Kr}]4\text{d}^{10}5\text{s}^2$ . The two s electrons of tin act as an “inert pair,” thus stabilizing the +2 oxidation state of tin.

Tin(IV) has the noble-gas core configuration of:  $[\text{Kr}]4\text{d}^{10}5\text{s}^2$ , while that of polonium(IV) is  $[\text{Xe}]4\text{f}^{14}5\text{d}^{10}6\text{s}^2$ . The two s electrons of tin act as an “inert pair,” thus stabilizing the +4 oxidation state of polonium. ■

## 9.7 The Early Actinoid Relationships with Transition Metals

In Chapter 24, we will discuss the chemistry of the two “orphan” series, the lanthanoids and the actinoids. Curiously, although the lanthanoids have few similarities outside of their own series, there are some resemblances of actinoids to transition metals. This resemblance was so strong that, until 1944, the five actinoids then known (thorium through plutonium) were assigned as members of the fourth row of the transition series (where we place rutherfordium through hassium today) (Figure 9.3).

We can state this relationship as:

**There are similarities in chemical formulas and chemical properties between early members of the actinoid series and the corresponding members of the transition metal series.**

To illustrate, we can compare the chemistry of uranium(VI) with that of the Group 6 metals in the +6 oxidation state. The most obvious similarity is provided by the oxoanions: the yellow diuranate ion,  $\text{U}_2\text{O}_7^{2-}$ , with the orange dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$ . Uranium forms a uranyl chloride,  $\text{UO}_2\text{Cl}_2$ , matching those of chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , and molybdenyl chloride,  $\text{MoO}_2\text{Cl}_2$ . In general, as we might expect, uranium bears the closest similarity to tungsten. For example, uranium and tungsten (but not molybdenum and chromium) form stable hexachlorides,  $\text{UCl}_6$  and  $\text{WCl}_6$ , respectively. Just as uranium resembles the Group 6 elements, so protactinium resembles the Group 5 elements, and thorium resembles the Group 4 elements.

The resemblance in properties results from similarities in outer electron configurations, as can be seen from comparisons of molybdenum, tungsten, uranium, and seaborgium, the next “true” member of Group 6.

Atom	Electron configuration	Ion	Electron configuration
Mo	$[\text{Kr}]5s^24d^4$	$\text{Mo}^{6+}$	$[\text{Kr}]$
W	$[\text{Xe}]6s^2(4f^{14})5d^4$	$\text{W}^{6+}$	$[\text{Xe}](4f^{14})$
U	$[\text{Rn}]7s^25f^36d^1$	$\text{U}^{6+}$	$[\text{Rn}]$
Sg	$[\text{Rn}]7s^2(5f^{14})6d^4$	$\text{Sg}^{6+}$	$[\text{Rn}](5f^{14})$

Whereas the f orbitals in tungsten and seaborgium are “buried,” those of uranium are part of the valence shell. In fact, the partial occupancy of 5f and 6d orbitals in uranium suggests that they are of similar energies. Thus, uranium readily attains a +6 oxidation state like the members of the Group 6 elements.

Ti	V	Cr
Zr	Nb	Mo
Hf	Ta	W
Th	Pa	U

**FIGURE 9.3** The relationship between the early actinoid elements and those of the corresponding transition metal groups.

## 9.8 The Lanthanoid Relationships

In terms of relationships, the lanthanoids have to be among the most similar of the elements. This might seem surprising, considering that the progression of the elements along the series corresponds to the successive filling of the 4f orbitals.



Cerium(IV) behaves like zirconium(IV) and hafnium(IV) of Group 4 and like thorium(IV) of the corresponding actinoids. For example, all four of these

**TABLE 9.23** A comparison of hafnium, cerium, and thorium species under strongly oxidizing conditions

	Very Acidic	Acidic	Basic	Very Basic
Hafnium	$\text{Hf}^{4+}(\text{aq})$		$\text{HfO}_2(\text{s})$	
Cerium	$\text{Ce}^{4+}(\text{aq})$		$\text{CeO}_2(\text{s})$	
Thorium	$\text{Th}^{4+}(\text{aq})$		$\text{ThO}_2(\text{s})$	

ions form insoluble fluorides and phosphates. The similarity can be seen from a comparison of acid-base behavior under strongly oxidizing conditions of hafnium, cerium and thorium (Table 9.23).

There are particularly strong similarities in the chemistry of cerium(IV) and thorium(IV). Cerium(IV) oxide (used in self-cleaning ovens) and thorium(IV) oxide both adopt the fluorite structure. They form isostructural nitrates,  $\text{M}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , where M is Ce or Th, and both form hexanitrate-complex ions  $[\text{M}(\text{NO}_3)_6]^{2-}$ . The major difference between the two elements in this oxidation state is that thorium(IV) is the thermodynamically stable form of that element while cerium(IV) is strongly oxidizing. It is because of the high redox potential of cerium that ammonium hexanitratocerate(IV),  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ , is used in redox titrations:



## 9.9 “Combo” Elements

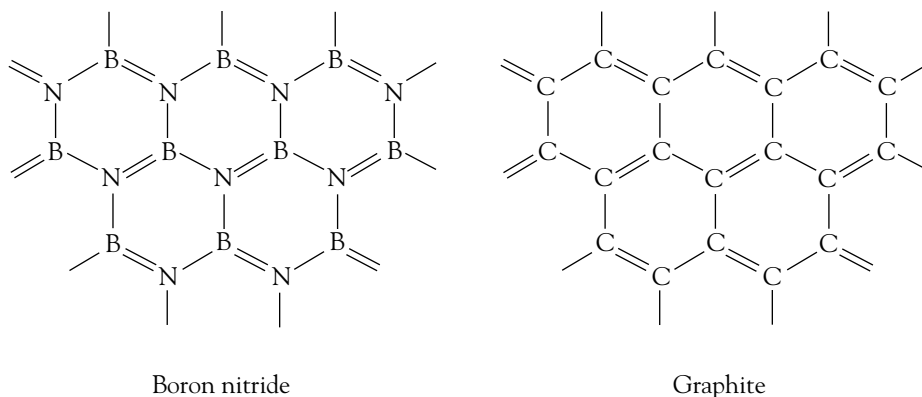
The compound carbon monoxide has several similarities to dinitrogen,  $\text{N}_2$ . For example, they are both triply-bonded molecules with similar boiling points:  $-196^\circ\text{C}$  ( $\text{N}_2$ ) and  $-190^\circ\text{C}$  ( $\text{CO}$ ). A major reason for the parallel behavior is that the dinitrogen molecule and the carbon monoxide molecule are isoelectronic. This similarity extends to the chemistry of the two molecules. In particular, there are several transition metal compounds where dinitrogen can substitute for a carbon monoxide entity. For example, it is possible to replace one or two carbon monoxides bonded to chromium in  $\text{Cr}(\text{CO})_6$  to give isoelectronic  $\text{Cr}(\text{CO})_5(\text{N}_2)$  and  $\text{Cr}(\text{CO})_4(\text{N}_2)_2$ .

The “combo” elements are a subset of isoelectronic behavior in which the sum of the valence electrons of a pair of atoms of one element matches the sum of the valence electrons of two horizontal neighboring elements:

**A combo element can be defined as the combination of an  $(n - x)$  group element with an  $(n + x)$  group element to form compounds that parallel those of the  $(n)$  group element.**

### Boron-Nitrogen Analogs of Carbon Species

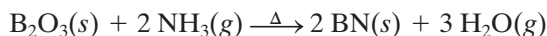
The best example of a combo element is that of the boron and nitrogen combination. Boron has one less valence electron than carbon, and nitrogen has one



**FIGURE 9.5** Comparative layer structures of boron nitride and graphite.

more. For many years, chemists have tried to make analogs of carbon compounds that contain alternating boron and nitrogen atoms. Included in their successes have been analogs of the pure forms of carbon. The two common allotropes of carbon are graphite, the lubricant, and diamond, the hardest naturally occurring substance known.

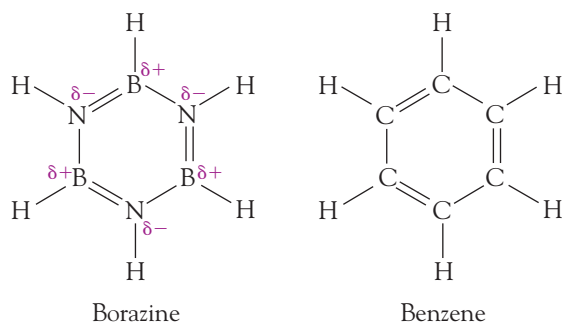
Unfortunately, both carbon allotropes burn when heated to give carbon dioxide gas, thus precluding the use of either of these substances in high-temperature applications. Boron nitride, BN, however, is the ideal substitute. The simplest method of synthesis involves heating diboron trioxide with ammonia at about 1000°C:



The product has a graphite-like structure (Figure 9.5) and is an excellent high-temperature, chemically resistant lubricant.

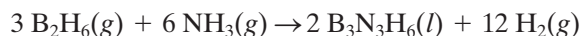
Unlike graphite, boron nitride is a white solid that does not conduct electricity. This distinction is probably a result of the different way the layers in the two crystals are stacked. The layers in the graphite-like form of boron nitride are almost exactly the same distance apart as those in graphite, but the boron nitride layers are organized so that the nitrogen atoms in one layer are situated directly over boron atoms in the layers above and below, and vice versa. This arrangement is logical, because the partially positive boron atoms and partially negative nitrogen atoms are likely to be electrostatically attracted to each other. By contrast, the carbon atoms in one layer of graphite are directly over the center of the carbon rings in the layers above and below. An alternative reason for the lack of electrical conductivity is the weaker aromaticity in the layers due to the differing electronegativities of boron and nitrogen.

In a further analogy to carbon, application of high pressures and high temperatures converts the graphite-like allotrope of boron nitride to a diamond-like form called *borazon*. This allotrope of boron nitride is similar to diamond in terms of hardness and is far superior in terms of chemical inertness at high temperatures. Hence, borazon is often used in preference to diamond as a grinding agent.



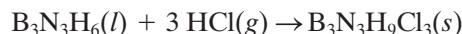
**FIGURE 9.6** Comparison of the structures of borazine and benzene.

There is another similarity between boron-nitrogen and carbon compounds. The reaction between diborane,  $\text{B}_2\text{H}_6$ , and ammonia gives borazine,  $\text{B}_3\text{N}_3\text{H}_6$ , a cyclic molecule analogous to benzene,  $\text{C}_6\text{H}_6$ :



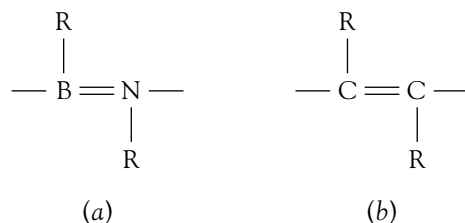
In fact, borazine is sometimes called “inorganic benzene” (Figure 9.6). This compound is a useful reagent for synthesizing other boron-nitrogen analogs of carbon compounds, but at this time it has no commercial applications. Note that, as one would expect from their comparative electronegativities, the boron atoms bear a slight positive charge and the nitrogen atoms, a slight negative charge. This assignment is confirmed from the way that electrophilic (electron-loving) reagents bond preferentially to the nitrogen atoms.

Despite similarities in boiling points, densities, and surface tensions, the polarity of the boron-nitrogen bond means that borazine exhibits less aromaticity than benzene. Hence, borazine is much more prone to chemical attack than is the homogeneous ring of carbon atoms in benzene. For example, hydrogen chloride reacts with borazine to give  $\text{B}_3\text{N}_3\text{H}_9\text{Cl}_3$ , in which the chlorine atoms bond to the more electropositive boron atoms:



This compound can be reduced by sodium tetrahydridoborate,  $\text{NaBH}_4$ , to give  $\text{B}_3\text{N}_3\text{H}_{12}$ , an analog of cyclohexane,  $\text{C}_6\text{H}_{12}$ . In fact, like cyclohexane,  $\text{B}_3\text{N}_3\text{H}_{12}$  adopts the chair conformation. Another parallel is that of polyimino-borane shown in Figure 9.7a with isoelectronic polyacetylene (Figure 9.7b).

Although isoelectronic, ammonia borane,  $\text{H}_3\text{NBH}_3$ , has few similarities with ethane,  $\text{H}_3\text{CCH}_3$ , except for structure. Whereas ethane is a gas at room



**FIGURE 9.7** The repeating units of (a) the polyimino-boranes and (b) polyacetylene.

temperature, ammonia borane is a solid with a melting point of 104°C, a difference that can be ascribed to the very polar nature of the boron-nitrogen bond, giving rise to strong dipole-dipole attractions between neighboring molecules and hence a high melting point.

### Combo Elements and Semiconductors

The combo element concept is important in the context of semiconductors. Materials scientists realized that by using isoelectronic combinations to match semiconducting elements, it was possible to make semiconductors with desired properties.

A particular focus of interest is the Period 4 elements centered on germanium. Germanium adopts the diamond structure, which is the same as the sphalerite structure (see Chapter 5, Section 5.3), one of the two packing arrangements of zinc sulfide, but with all of the atoms being identical and occupying both anion and cation sites in the lattice. Examples of compounds (combo elements) adopting this same sphalerite crystal structure are gallium arsenide, GaAs; zinc selenide, ZnSe; and copper(I) bromide, CuBr. Although these common combo examples are truly isoelectronic, the two elements do not necessarily have to come from the same period; thus, more generally, we can say the sum of the valence electrons must add up to eight. This electron relationship is known as the *Zintl principle*. Figure 9.8 shows the combinations of elements that can result in this series of Zintl solids.

In Chapter 4, Section 4.2, we saw that for metals, there was an overlap between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). It is this overlap that enables electrical conductivity to occur throughout the metal structure. In the case of insulators, the gap between the two energy levels is very large, whereas for semiconductors, the gap is small enough that it is feasible for electrons to be excited to the higher energy state. We can see the trend in Table 9.24 using a family of Zintl (isoelectronic) solids.

It is quite remarkable that the length of side of a unit cell is essentially constant (within experimental error) throughout the series, even though there is a change in bonding from pure covalent (Ge) through polar covalent (GaAs) to substantially ionic (ZnSe, CuBr). The increased polarity of the bond causes a decrease in the conductivity of the solid. Thus, germanium and

		B	C	N	O	F
		Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
Au	Hg	Tl	Pb	Bi	Po	At

**FIGURE 9.8** A portion of the periodic table showing the combination of elements that will provide compounds that are isoelectronic with each of the Group 14 elements. Such possible pairs are shown in identical shading.

**TABLE 9.24** The properties of a series of isoelectronic solids

Solid	Unit-cell dimension (pm)	Electronegativity difference	Energy gap (kJ·mol <sup>-1</sup> )
Ge	566	0.0	64
GaAs	565	0.4	137
ZnSe	567	0.8	261
CuBr	569	0.9	281

gallium arsenide are semiconductors, while zinc selenide and copper(I) bromide are insulators.

But there is more to the study of this simple series than scientific curiosity. These band gaps allow us to construct light-emitting diodes (LEDs), devices that have been used for many years as indicator lights but that are now finding uses as energy-efficient vehicle taillights, traffic lights, and night lights and as replacements for halogen lamps in household lighting. To obtain the chosen color, specific band gaps are needed. These band gaps can be adjusted by substituting proportions of one element for another in a Zintl solid. A particularly useful series is that of  $\text{GaP}_x\text{As}_{(1-x)}$ , where  $x$  has a value between zero and one. Gallium phosphide, GaP, itself has a band gap of  $222 \text{ kJ}\cdot\text{mol}^{-1}$ , while as we saw above, that of gallium arsenide is  $137 \text{ kJ}\cdot\text{mol}^{-1}$ . In between combinations have corresponding intermediate band gaps; for example,  $\text{GaP}_{0.5}\text{As}_{0.5}$  has a band gap of about  $200 \text{ kJ}\cdot\text{mol}^{-1}$ .

The most exciting combo-element pair is gallium and nitrogen, an analog of silicon. This diagonal pair around silicon provides a semiconducting material that is already changing our lives. Gallium nitride is a tough material that can be used in LEDs to generate blue-violet and—with added indium nitride—green light. Using GaN/InN for the green color, if every traffic light around the world were converted from conventional bulbs to LEDs, the energy saving would be enormous. The intensely deep blue GaN LEDs are used on the fronts of some types of city buses, such as those in Toronto, Canada, so that an approaching bus can be seen from a long distance away.

## 9.10 Biological Aspects

In this chapter, we have been looking at patterns in the periodic table. Therefore, our example of a biological application relates to such patterns; in this case, the importance of the group relationship of strontium to calcium.

### Strontium

Bone and teeth consist of crystals of hydroxyapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  and the fibrous protein collagen. Two of the reasons why nature chooses hydroxyapatite as a biological structural material are the insolubility of calcium phosphates and the high availability of the calcium ion. Nature might have used strontium instead of calcium except that strontium is about 100 times less abundant in nature than calcium.

When nuclear weapons were first being tested, it was thought that the hazards were localized and of little danger. The 1951 atmospheric tests in Nevada changed that view. Among the fission products was strontium-90, which, as might be expected, substitutes for calcium ion. In fact, strontium is preferentially absorbed over calcium. As a highly radioactive isotope (half-life 29 years), the strontium-90 irradiates the bone marrow critical to reproduction of cells that mediate immune function. Baby teeth are a convenient way of measuring strontium-90 levels since they are naturally lost and provide

measures of strontium-90 levels over the child's lifetime. There are no natural sources of strontium-90. Measurements of strontium-90 in baby teeth in St. Louis showed levels increasing steadily until 1964, when there was a ban on atmospheric weapons tests. Children, with their rapid bone growth, readily absorb strontium-90, and strontium-90 levels have correlated with increases in childhood leukemia rates.

Although atmospheric nuclear testing has long been ended, research indicates a possible link between radioactive emissions from commercial nuclear power plants and abnormally high levels of childhood leukemia (and other radiation-related diseases) in certain parts of the United States. Thus, concerns about this hazardous isotope still exist.

However, radioactive strontium-85 is used to treat extreme bone pain, often resulting from bone cancer. Like the other isotopes of strontium, highly radioactive strontium-85 accumulates in the bones of these patients, the radiation specifically deadening the surrounding nerves that are causing the severe pain.

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## KEY IDEAS

- Group trends are particularly systematic at the left and right ends of the table.
- Periodic trends tend to show a transition in bonding type from ionic through network covalent to small-molecule covalent.
- There are similarities in the highest oxidation state between many pairs of ( $n$ ) and ( $n + 10$ ) elements.
- A diagonal relationship exists for elements in the extreme top-left portion of the table.
- Some elements in the lower-right segment of the table are linked by the knight's move relationship.

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## EXERCISES

- 9.1** Explain what is meant by (a) the Zintl principle; (b) the diagonal relationship.
- 9.2** Explain what is meant by (a) the knight's move relationship; (b) ( $n$ ) group and ( $n + 10$ ) group similarities.
- 9.3** What are the common features of an alum?
- 9.4** Explain the trends in melting point for (a) the Group 2 elements; (b) the Group 17 elements; (c) the Group 14 elements.
- 9.5** Write the formulas for the Period 4 main group metal fluorides. Suggest the bonding type in each case.
- 9.6** Write the formulas for the Period 4 main group metal hydrides. Suggest the bonding type in each case.
- 9.7** If calcium hydride is melted and electrolyzed, what would you expect will be the products at the (a) anode; (b) cathode?
- 9.8** Compare and contrast the chemistry of (a) manganese(VII) and chlorine(VII); (b) silver(I) and rubidium.
- 9.9** There is the following trend in melting points of Period 2 metal oxides:  $\text{MgO}$ ,  $2800^\circ\text{C}$ ;  $\text{CaO}$ ,  $1728^\circ\text{C}$ ;  $\text{SrO}$ ,  $1635^\circ\text{C}$ ;  $\text{BaO}$ ,  $1475^\circ\text{C}$ . Suggest a reason for this trend.
- 9.10** Draw structures for the boron-nitrogen combo analog of (a) naphthalene,  $\text{C}_{10}\text{H}_8$ ; (b) biphenyl,  $\text{C}_{12}\text{H}_{10}$ .
- 9.11** Which metal hydroxide is isostructural with aluminum hydroxide?
- 9.12** Write a chemical equation for the reaction of water with liquid silicon tetrachloride and titanium(IV) chloride.
- 9.13** Write a chemical equation for the reaction of water with solid sulfur trioxide and with chromium(VI) oxide.
- 9.14** What are the formulas of the highest oxidation state oxide of chlorine and manganese? What other oxides of the two elements resemble each other in formula?



- 9.15** (a) Write the formulas of aluminum oxide and scandium oxide.  
(b) Write formulas for the oxyanions of phosphorus and vanadium in their highest oxidation states.
- 9.16** Explain briefly why aluminum might be considered a member of Group 3 instead of Group 13.
- 9.17** Titanium(IV) nitrate shares many properties, including identical crystal structure, with a metal of a different group. Suggest the identity of the metal.
- 9.18** Phosphorus forms an oxychloride of formula  $\text{POCl}_3$ . Which transition metal is likely to form an oxychloride of matching formula?
- 9.19** In Table 9.4, the melting point of neon is significantly less than that of nitrogen, oxygen, or fluorine. Suggest an explanation.
- 9.20** One source of scandium is the ore sterrite,  $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$ . This ore is isostructural with an ore of a main group metal. Write the formula of that ore.
- 9.21** Suggest an explanation in terms of orbital occupancy why the oxidation state of +2 is found for the element europium.
- 9.22** Suggest an explanation in terms of orbital occupancy why the oxidation state of +4 is found for the element cerium.
- 9.23** Knight's move relationships exist when both elements are in the same oxidation states. Which oxidation states would be shared by (a) copper and indium; (b) cadmium and lead?
- 9.24** Knight's move relationships exist when both elements are in the same oxidation states. Which oxidation states would be shared by (a) indium and bismuth; (b) zinc and tin?
- 9.25** Silver bromide has a melting point of  $430^\circ\text{C}$ . Which bromide would you expect to have a similar melting point? Check data tables and confirm your answer.
- 9.26** Write the formulas of two oxoanions that seaborgium (Sg) might form.
- 9.27** Carbon and nitrogen form the cyanide ion:  $(\text{C}\equiv\text{N})^-$ . Write the formulas of the corresponding isoelectronic species of (a) carbon with oxygen; (b) carbon with carbon.
- 9.28** Sodium is the only alkali metal for which the dioxide(2-),  $\text{Na}_2\text{O}_2$ , is the most stable oxide species. Using Table 9.20, deduce the alkaline earth metal that also forms a stable dioxide(2-) compound.
- 9.29** Monazite, the lanthanoid phosphate ore,  $\text{MPO}_4$ , also typically contains about 3 percent of a Group 3 metal ion. Suggest the identity of this ion.

## BEYOND THE BASICS

- 9.30** Write a chemical equation for the reaction of silane,  $\text{SiH}_4$ , with dioxygen.
- 9.31** If silane,  $\text{SiH}_4$ , has a positive free energy of formation, why does it exist at all?
- 9.32** Magnesium and zinc have similar chemistries as a result of the  $(n)$  and  $(n + 10)$  relationship. They can be considered related in a different way if the "true" transition metals, Groups 3 to 10, are removed. What would be another way of considering their relationship?
- 9.33** You have a solution containing either magnesium ion or zinc ion. Suggest a reaction that you could use to identify the cation.
- 9.34** Moisture/density gauges are used by construction companies to determine the properties of the soil on which they are building. These gauges use two radioactive sources, cesium-137 and americium-241, in their functioning. Many are stolen in the United States, as there is a large black market demand for them; probably because the gauges are so expensive that unethical contractors can get them cheaply this way. Some are abandoned and/or broken open when the thieves discover they contain radioactive materials. Suggest why the cesium-137 could be a particular hazard.
- 9.35** A compound  $\text{Zn}_x[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$  has a similar crystal structure to that of the mineral sodalite,  $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$ . The total number of valence electrons in the aluminosilicate ion and the phosphonitride ion is the same.  
(a) Calculate the charge on the phosphonitride ion.  
(b) Calculate  $x$ , the number of zinc ions in the zinc phosphonitride.
- 9.36** Predict the formula for the highest fluoride of iodine. Research whether this compound exists. Suggest why its atom ratio is different from the highest fluoride of chlorine.
- 9.37** Calculate the oxidation numbers of the other element for each fluoride in Table 9.8 and identify the pattern in these numbers.
- 9.38** Calculate the oxidation numbers of the other element for each hydride in Table 9.9 and identify the pattern in these numbers.



**9.39** Research the formulas of the highest oxides as the Group 8 elements are descended. Calculate the oxidation numbers of the Group 8 element in each case. What do you note about the highest value?

**9.40** In the following matrix of 22/16-electron isoelectronic series, certain known species have been deliberately omitted with the spaces marked by X. Write the formulas for the missing species.

	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17
Group 14		$\text{BC}_2^{5-}$	X	$\text{C}_2\text{N}^-$		
Group 15		X	X	X	$\text{N}_2\text{O}$	$\text{N}_2\text{F}^+$
Group 16	$\text{BeO}_2^{2-}$	X	$\text{CO}_2$	$\text{NO}_2^+$		
Group 17	X					

**9.41** In the accompanying matrix of linear triatomic 22/16-electron isoelectronic series, certain known species have been deliberately omitted with the spaces marked by X. Write the formulas for the missing species.

	Group 15	Group 16	Group 17
Group 15	$\text{CN}_2^{2-}$	X	FCN
Group 16	X	$\text{CO}_2$	X

## ADDITIONAL RESOURCES

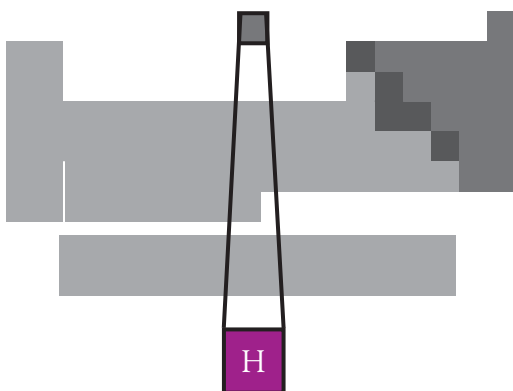
For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# HYDROGEN

## CHAPTER 10



						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

### 10.1 Isotopes of Hydrogen

### 10.2 Nuclear Magnetic Resonance

### 10.3 Properties of Hydrogen

### 10.4 The Trihydrogen Ion

### 10.5 Hydrides

### 10.6 Water and Hydrogen Bonding

### 10.7 Clathrates

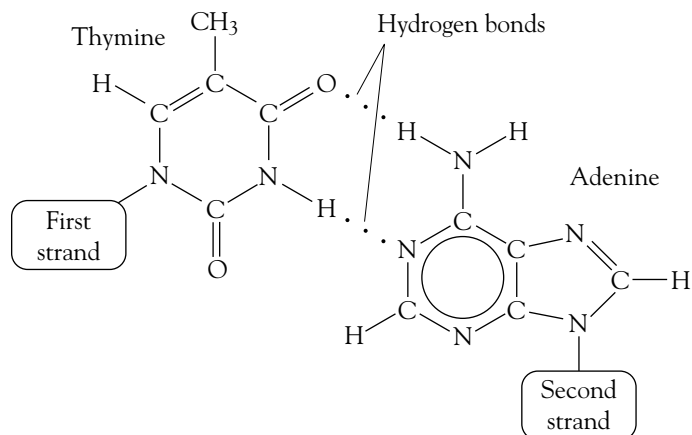
### 10.8 Element Reaction Flowchart

Only one element in the periodic table does not belong to any particular group—hydrogen. This element has a unique chemistry. Furthermore, its three isotopes differ so much in their molar masses that the physical and chemical properties of the isotopes are measurably different.

## Context: Hydrogen Bond—the Real “Special Agent”

The existence of life depends on two particular properties of hydrogen: the closeness of the electronegativities of carbon and hydrogen and the ability of hydrogen to form hydrogen bonds when covalently bonded to nitrogen or oxygen. The low polarity of the carbon-hydrogen bond contributes to the stability of organic compounds in our chemically reactive world. Biological processes also rely on both polar and nonpolar surfaces, with the best example of the latter being the lipids. It is important to realize that nonpolar sections of biological molecules, usually containing just carbon and hydrogen atoms, are just as significant as their polar regions.

Hydrogen bonding is a vital part of all biomolecules. Proteins are held in shape by hydrogen bonds that form cross-links between chains. The strands of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), the genetic material, are held together by hydrogen bonds as well. But more than that, the hydrogen bonds in the double helices are not random: they form between specific pairs of organic bases. These pairs are preferentially hydrogen bonded because the two components



Hydrogen bond interaction between thymine and adenine fragments of the two strands in a DNA molecule.

fit together to give particularly close approaches of the hydrogen atoms involved in the hydrogen bonding. This bonding is illustrated below for the interaction between two particular base units, thymine and adenine. It is the specific matching that results in the precise ordering of the components in the DNA and RNA chains, a system that allows those molecules to reproduce themselves almost completely error-free.

## 10.1 Isotopes of Hydrogen

The isotopes of hydrogen are particularly important in chemistry. Because the relative mass differences between hydrogen's isotopes are so large, there is a significant dissimilarity in physical properties and, to a lesser extent, in chemical behavior among them. Natural hydrogen contains three isotopes: protium, or “common” hydrogen, which contains zero neutrons (abundance 99.985 percent); deuterium, which contains one neutron (abundance 0.015 percent); and radioactive tritium, which contains two neutrons (abundance  $10^{-15}$  percent). In fact, this is the only set of isotopes for which special symbols are used: H for protium, D for deuterium, and T for tritium. As the molar mass of the isotopes increases, there is a significant increase in both the boiling point and the bond energy (Table 10.1).

**TABLE 10.1** Physical properties of the isotopes of hydrogen

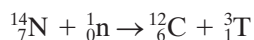
Isotope	Molar mass ( $\text{g}\cdot\text{mol}^{-1}$ )	Boiling point (K)	Bond energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\text{H}_2$	2.02	20.6	436
$\text{D}_2$	4.03	23.9	443
$\text{T}_2$	6.03	25.2	447

## Deuterium

The covalent bonds of deuterium (and tritium) with other elements are stronger than those of common hydrogen. For example, when water is electrolyzed to give hydrogen gas and oxygen gas, it is the O—H covalent bonds that are broken more readily than O—D bonds. As a result, the remaining liquid contains a higher and higher proportion of “heavy” water, deuterium oxide. When 30 L of water is electrolyzed down to a volume of 1 mL, the remaining liquid is about 99 percent pure deuterium oxide. Normal water and heavy water, D<sub>2</sub>O, differ in all their physical properties; for example, deuterium oxide melts at 3.8°C and boils at 101.4°C. The density of deuterium oxide is about 10 percent higher than that of protium oxide at all temperatures. As a result, heavy water ice cubes will sink in “light” water at 0°C. Deuterium oxide is used widely as a solvent so that the hydrogen atoms in solute molecules can be studied without their properties being “swamped” by those in the aqueous solvent. Reaction pathways involving hydrogen atoms also can be studied by using deuterium-substituted compounds.

## Tritium

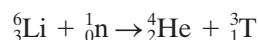
Tritium is a radioactive isotope with a half-life of about 12 years. With such a short half-life, we might expect that none survives naturally; in fact, tritium is continuously being formed by the impact of cosmic rays on atoms in the upper atmosphere. One pathway for its production involves the impact of a neutron on a nitrogen atom:



The isotope decays to give the rare isotope of helium, helium-3:



There is a significant demand for tritium. It is sought for medical purposes, where it is useful as a tracer. In its radioactive decay, the isotope emits low-energy electrons ( $\beta$ -rays) but no harmful  $\gamma$ -rays. The electrons can be tracked by a counter and cause minimal tissue damage. The most significant consumers of tritium are the military forces of the countries possessing hydrogen (more accurately, tritium) bombs. To extract the traces of tritium that occur in water would require the processing of massive quantities of water. An easier synthetic route entails the bombardment of lithium-6 by neutrons in a nuclear reactor:



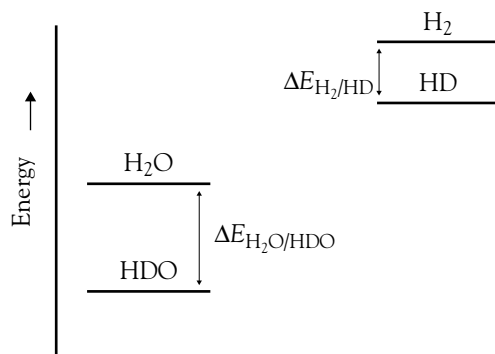
Tritium's short half-life creates a problem for military scientists of nuclear power because, over time, the tritium content of nuclear warheads diminishes until it is below the critical mass needed for fusion. Hence, warheads have to be periodically “topped up” with tritium if they are to remain usable.

## Hydrogen Isotopes in Chemistry

In our discussions of the chemistry of elements, we rarely mention the effects of isotopes on chemical reactions, yet such effects are of considerable importance,

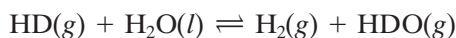
Four other isotopes of hydrogen have been synthesized: hydrogen-4, hydrogen-5, hydrogen-6, and hydrogen-7. Each has a half-life of about  $10^{-22}$  s.

**FIGURE 10.1** A plot of relative energies for the hydrogen gas–water equilibrium for the hydrogen and deuterium isotopes.



particularly for hydrogen, where isotopic mass differences are so large. The difference in isotope masses can affect reaction rates and the position of equilibria.

We have a better understanding of the role of isotopes as a result of the Bigeleisen-Mayer formulation. This relationship showed that bonds to light isotopes are easier to break than those to heavier isotopes. Thus, the heavy isotope of an element will favor chemical species in which it is bound more strongly. We find, for example, that in the environment, the heavier isotope of sulfur, sulfur-34, is slightly more abundant as sulfate (where sulfur has strong covalent bonds to four oxygen atoms) than as sulfide. It is possible to separate isotopes by means of chemical equilibria. A good example of an isotope effect in a chemical reaction is:



The plots of energy wells are shown for the four species in Figure 10.1. It can be seen that deuterium forms a proportionally stronger bond with oxygen than with hydrogen. Thus, there is an energy preference for the HDO/H<sub>2</sub> combination; in other words, the equilibrium lies to the right and it is the water that is enriched in deuterium. It is by means of a series of such equilibria that pure D<sub>2</sub>O can be produced.

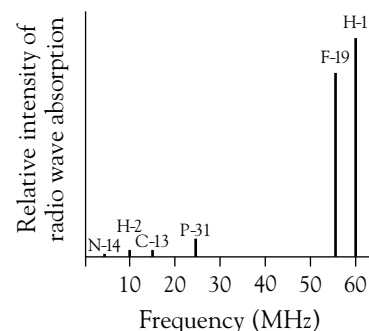
## 10.2 Nuclear Magnetic Resonance

One of the most useful tools for studying molecular structure is nuclear magnetic resonance (NMR). This technique involves the study of nuclear spin. As discussed in Chapter 2, Section 2.3, like electrons, protons and neutrons have spins of  $\pm\frac{1}{2}$ . In an atom, there are four possible permutations of nuclear particles: even numbers of both protons and neutrons, odd number of protons and even number of neutrons, even number of protons and odd number of neutrons, and odd numbers of both protons and neutrons. The last three categories, then, will have unpaired nucleons. This condition might be expected to occur in an enormous number of nuclei, but, with spin pairing being a major driving force for the stability of nuclei, only 4 of the 273 stable nuclei have odd numbers of both protons and neutrons.

Normally, for the unpaired nucleons, each spin state ( $+\frac{1}{2}$  or  $-\frac{1}{2}$ ) has the same energy. However, in a magnetic field, the spin can be either parallel with the field or opposed to it, and the parallel arrangement has lower energy. The splitting of (difference between) the two energy levels is very small and corresponds to the radio frequency range of the electromagnetic spectrum. When we focus a radio wave source on the sample with unpaired nucleons and adjust the frequency of radio waves to the energy level of the splitting, electromagnetic radiation is absorbed by the sample as unpaired nucleons reverse their spins to oppose the field; that is, they move to the higher energy level. In a field of 15 000 gauss, absorption happens at 63.9 MHz (or  $6.39 \times 10^7 \text{ s}^{-1}$ ) for an isolated proton.

The relative intensity of the absorption depends very much on the identity of the nucleus. As it happens, hydrogen-1 gives the most intense absorption among the nuclei (Figure 10.2). This is fortunate because hydrogen is the most common element in the universe and therefore readily available for study. Even today, years after the discovery of NMR, hydrogen is the element most studied by this technique.

If this were all that NMR could do, it would not be a particularly useful technique. However, the electrons surrounding a nucleus affect the actual magnetic field experienced by the nucleus. Because the magnetic field for each environment differs from that applied by a magnet, the splitting of the energy levels and the frequency of radiation absorbed are unique for each species. Thus, absorption frequency reflects the atomic environment. The difference in frequency absorbed (called the chemical shift, or simply, shift) is very small—about  $10^{-6}$  of the signal itself. Hence, we report the shifts in terms of parts per million (ppm). In addition, splitting of the transition levels can occur through interaction with neighboring odd-spin nuclei. Thus, the relative locations of atoms can often be identified by NMR. This technique is a great aid to chemists, particularly organic chemists, both for the identification of a compound and for the study of electron distributions within molecules. It is also used extensively in the health field under the name of magnetic resonance imaging (MRI).



**FIGURE 10.2** Relative intensities of the unique absorption by common isotopes in a magnetic field of 14 000 gauss.

### 10.3 Properties of Hydrogen

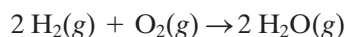
As stated earlier, hydrogen is a unique element, not belonging to any of the other groups in the periodic table. Some versions of the periodic table place it as a member of the alkali metals, some as a member of the halogens, others place it in both locations, and a few place it on its own. The basic reasons for and against placement of hydrogen in either Group 1 or Group 17 are summarized in Table 10.2. Throughout this book, hydrogen has a place in the periodic table all its own, emphasizing the uniqueness of this element. In particular, since hydrogen has an electronegativity higher than those of the alkali metals and lower than those of the halogens, it makes sense to place hydrogen midway between the two groups.

**TABLE 10.2** Reasons for and against placing hydrogen in Group 1 or 17

	Argument for placement	Argument against placement
<b>Alkali metal group</b>	Forms monopositive ion, $\text{H}^+$ ( $\text{H}_3\text{O}^+$ )	Is not a metal
<b>Halogen group</b>	Has a single s electron	Does not react with water
	Is a nonmetal	Rarely forms mononegative ion, $\text{H}^-$
	Forms a diatomic molecule	Is comparatively nonreactive

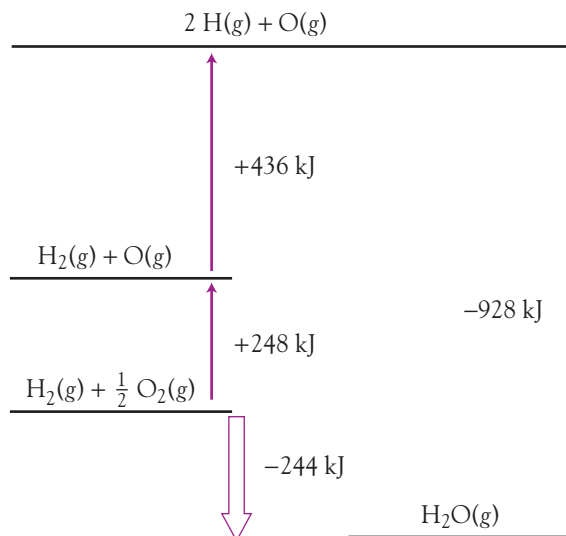
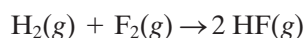
### Reactions of Hydrogen Gas

Dihydrogen is a colorless, odorless gas that liquefies at  $-253^\circ\text{C}$  and solidifies at  $-259^\circ\text{C}$ . Hydrogen gas is not very reactive, partly because of the high H—H covalent bond energy ( $436 \text{ kJ}\cdot\text{mol}^{-1}$ ). Dihydrogen does react with dioxygen. If hydrogen gas and oxygen gas are mixed and sparked, the reaction is explosive:



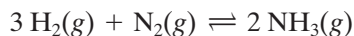
The reaction has to be enthalpy driven because there is a decrease in entropy resulting from the 3 moles of gaseous reactants to 2 moles of gaseous products (see Chapter 6, Section 6.1). If we add the bond energies, we see that the strong O—H bond ( $464 \text{ kJ}\cdot\text{mol}^{-1}$ ) makes the reaction thermodynamically feasible (Figure 10.3).

Dihydrogen reacts with the halogens, with the rate of reaction decreasing down the group. It has a violent reaction with difluorine to give hydrogen fluoride:



**FIGURE 10.3** Theoretical enthalpy cycle for the formation of water.

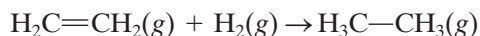
The reaction of dihydrogen with dinitrogen (discussed more fully in Chapter 15, Section 15.5) is very slow in the absence of a catalyst:



At high temperatures, dihydrogen reduces many metal oxides to the metallic element. For example, copper(II) oxide is reduced to copper metal:



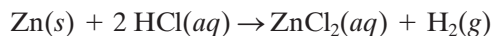
In the presence of a catalyst (usually powdered palladium or platinum), dihydrogen will reduce carbon-carbon double and triple bonds to single bonds. For example, ethene,  $\text{C}_2\text{H}_4$ , is reduced to ethane,  $\text{C}_2\text{H}_6$ :



The reduction with dihydrogen is used to convert unsaturated liquid fats (edible oils), which have numerous carbon-carbon double bonds, to higher melting, partially saturated solid fats (margarines), which contain fewer carbon-carbon double bonds.

### Synthesis of Hydrogen Gas

In the laboratory, hydrogen gas can be generated by the action of dilute acids on many metals. A particularly convenient reaction is that between zinc and dilute hydrochloric acid:



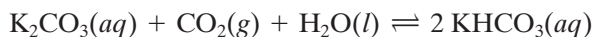
There are several different routes of industrial synthesis, one of these being the *steam re-forming process*. In the first step of this process, the endothermic reaction of natural gas (methane) with steam at high temperatures gives carbon monoxide and hydrogen gas. It is difficult to separate the two products because the mixture must be cooled below  $-205^\circ\text{C}$  before the carbon monoxide will condense. To overcome this problem and to increase the yield of hydrogen gas, the mixture is cooled, additional steam is injected, and the combination is passed over a different catalyst system. Under these conditions, the carbon monoxide is oxidized in an exothermic reaction to carbon dioxide, and the added water is reduced to hydrogen:



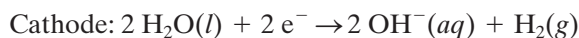
The carbon dioxide can be separated from hydrogen gas in several ways. One is to cool the products below the condensation temperature of carbon dioxide ( $-78^\circ\text{C}$ ), which is much higher than that of dihydrogen ( $-253^\circ\text{C}$ ). However, this process still requires large-scale refrigeration systems. Another route involves passage of the gas mixture through a solution of potassium carbonate. Carbon dioxide is an acid oxide, unlike carbon monoxide, which is neutral. One mole of carbon dioxide reacts with an excess of carbonate ion and water to give 2 moles of the hydrogen carbonate ion. When reaction is complete, the



potassium hydrogen carbonate solution can be removed and heated to regenerate the potassium carbonate, while the pure carbon dioxide gas can be collected and pressurized:



For most purposes, the purity of the dihydrogen (molecular hydrogen) obtained from thermochemical processes is satisfactory. However, very pure hydrogen gas (at least 99.9 percent) is generated by an electrochemical route: the electrolysis of a sodium hydroxide or potassium hydroxide solution. The reaction produces oxygen gas at the anode and hydrogen gas at the cathode:

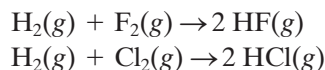


### WORKED EXAMPLE 10.1

Using data in Appendix 3, explain why the reaction of hydrogen with fluorine is much more exothermic than the reaction of hydrogen with chlorine.

#### Answer

The two chemical equations are:



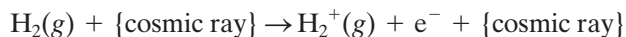
According to the bond energy data, the F—F bond is weaker ( $155 \text{ kJ}\cdot\text{mol}^{-1}$ ) than the Cl—Cl bond ( $240 \text{ kJ}\cdot\text{mol}^{-1}$ ). On the product side of the equations, the H—F bond is stronger ( $565 \text{ kJ}\cdot\text{mol}^{-1}$ ) than the H—Cl bond ( $428 \text{ kJ}\cdot\text{mol}^{-1}$ ).

Thus, two factors cause the first reaction to be more exothermic. The dissociation of fluorine molecules requires less energy than the dissociation of chlorine molecules. On the product side, the formation of the hydrogen-fluorine bond releases more energy than the formation of the hydrogen-chlorine bond. ■

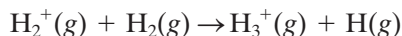
## 10.4 The Trihydrogen Ion

We think of chemistry in terms of what occurs at about 100 kPa and  $25^\circ\text{C}$ , the conditions on the surface of this planet. But stable chemical species can be very different in other parts of the universe. One of the most interesting species is the trihydrogen cation,  $\text{H}_3^+$ . This ion is prevalent throughout the Interstellar Medium (ISM), and it plays the most important role in interstellar gas-phase chemistry. The Central Molecular Zone of our galaxy contains the trihydrogen ion at concentrations of over one million times that of the ISM.

The formation of the trihydrogen ion is a two-step process. First, a high-energy cosmic ray impacts a dihydrogen molecule, with a small fraction of the ray's energy being sufficient to cause ionization:



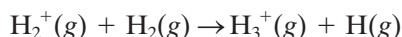
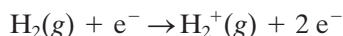
The collision of a dihydrogen ion with a dihydrogen molecule produces the trihydrogen ion:



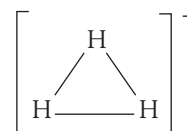
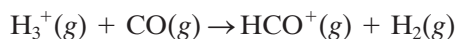
The ion consists of an equilateral triangle of hydrogen atoms with H—H bond lengths of 87 pm (see Figure 10.4).

The bonding in  $\text{H}_3^+$  is the simplest example of a three-center two-electron bond. This bond can be illustrated by the molecular orbital diagram in Figure 10.5. A correct depiction would involve a three-dimensional diagram. As paper and normal computer screens are two-dimensional, Figure 10.5 shows the two contributing hydrogen atoms to the left and the additional hydrogen ion to the right. From three atomic orbitals, three molecular orbitals are formed: a bonding orbital, a nonbonding orbital, and an antibonding orbital. The two electrons fill the bonding orbital; thus the molecule has a single bond shared between the three atoms.

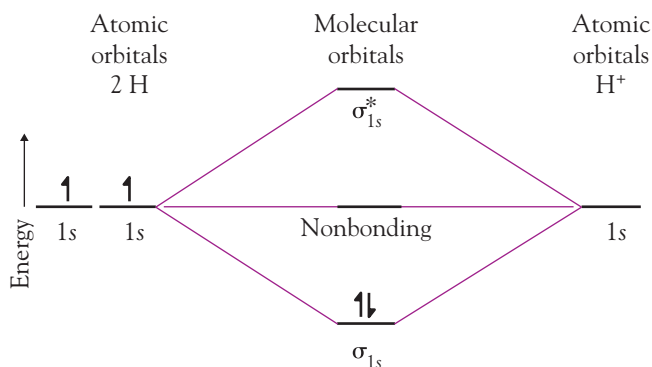
The trihydrogen ion is also present in the upper levels of planetary atmospheres, especially those of the outer planets Jupiter, Saturn, Neptune, and Uranus. The trihydrogen ion is formed in these gas giants by the collision of solar wind and other sources of high-energy electrons with hydrogen molecules:



In the ISM, the destruction of the trihydrogen ion occurs mostly by collision with carbon monoxide molecules, the second most common molecular species (dihydrogen being the most common):



**FIGURE 10.4** The shape of the trihydrogen ion.



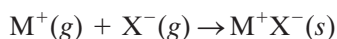
**FIGURE 10.5** A simplified molecular orbital diagram of the bonding in the  $\text{H}_3^+$  ion.

## 10.5 Hydrides

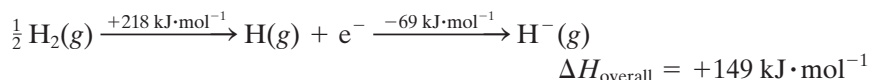
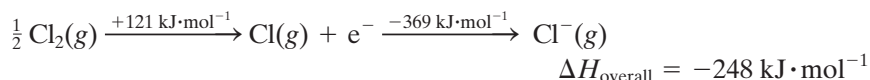
Binary compounds of hydrogen are given the generic name of hydrides. Hydrogen, which forms binary compounds with most elements, has an electronegativity only slightly above the median value of all the elements in the periodic table. As a result, it behaves as a weakly electronegative nonmetal, forming ionic compounds with very electropositive metals and covalent compounds with nonmetals, as we discussed in Chapter 9, Section 9.2. In addition, it forms metallic hydrides with some of the transition metals. The distribution of the three major types of hydrides is shown in Figure 10.6.

### Ionic Hydrides

All the ionic hydrides are very reactive white solids and are formed only by the most electropositive metals. We can see the reason by contrasting the formation of an ionic metal chloride with an ionic metal hydride. The formation of a crystal lattice (gas to solid) will result in a negative entropy change:



Thus, it is the enthalpy of formation of the crystal lattice which has to be the driving force for the reaction. The ionization energy of a metal cation is always positive. It is in the theoretical enthalpy change of formation of chloride ion with that of hydride ion where the crucial difference arises:



With the H—H bond being much stronger than the Cl—Cl bond and a much lower electron affinity of hydrogen than chlorine, anion formation for the hydride ion is significantly positive, whereas that for chloride is very negative. For that reason, only a cation with a very low ionization energy (such as those

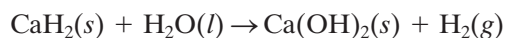
**FIGURE 10.6** Three common types of hydrides: ionic, covalent, and metallic. Only the main and transition groups are shown. A few lanthanoids and actinoids also form metallic hydrides (not shown). For unshaded elements, hydrides are either unknown or poorly characterized.

<div><div></div> Ionic</div>																		He
<div><div></div> Metallic</div>																		
<div><div></div> Covalent</div>																		
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo	

Ionic  
 Metallic  
 Covalent

of the alkali metals) will enable the net enthalpy change for the hydride formation to be negative.

The hydride ion is a strong reducing agent. For example, it will reduce water to hydrogen gas. The reaction of calcium hydride with water is sometimes used in organic chemistry as a means to chemically dry organic solvents:



## Covalent Hydrides

Hydrogen forms compounds containing covalent bonds with all the nonmetals (except the noble gases) and with very weakly electropositive metals such as gallium and tin. Almost all the simple covalent hydrides are gases at room temperature. There are three subcategories of covalent hydrides:

Those in which the hydrogen atom is nearly neutral

Those in which the hydrogen atom is substantially positive

Those in which the hydrogen atom is slightly negative, including the electron-deficient boron compounds

For the first category, because of their low polarity, the sole intermolecular force between neighboring hydride molecules is dispersion; as a result, these covalent hydrides are gases with low boiling points. Typical examples of these hydrides are hydrogen selenide,  $\text{H}_2\text{Se}$  (b.p.  $-60^\circ\text{C}$ ), and phosphine,  $\text{PH}_3$  (b.p.  $-90^\circ\text{C}$ ).

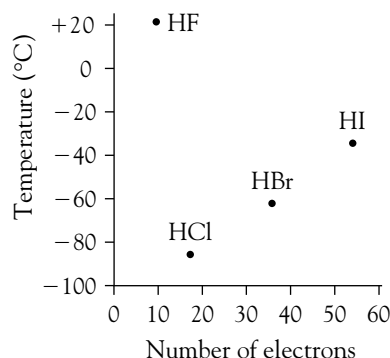
The largest group of near-neutral covalent hydrides contains carbon—the hydrocarbons—and comprises the alkanes, the alkenes, the alkynes, and the aromatic hydrocarbons. Many of the hydrocarbons are large molecules in which the intermolecular forces are strong enough to allow them to be liquids or solids at room temperature. All the hydrocarbons are thermodynamically unstable toward oxidation. For example, methane reacts spontaneously with dioxygen to give carbon dioxide and water:



The process is very slow unless the mixture is ignited; that is, the reaction has a high activation energy.

Ammonia, water, and hydrogen fluoride belong to the second category of covalent hydrides—hydrogen compounds containing positively charged hydrogen atoms. These compounds differ from the other covalent hydrides in their abnormally high melting and boiling points. This property is illustrated by the boiling points of the Group 17 hydrides (Figure 10.7).

The positively charged hydrogen in these compounds is attracted by an electron pair on another atom to form a weak bond. Although the attraction is commonly known as a hydrogen bond (discussed in Chapter 3, Section 3.11), it is more accurately called a *protonic bridge*. Even though, as an intermolecular force, protonic bridging is very strong, it is still weak compared to a covalent bond. For example, the  $\text{H}_2\text{O} \cdots \text{HOH}$  protonic bridge has a bond energy of  $22 \text{ kJ} \cdot \text{mol}^{-1}$  compared to  $464 \text{ kJ} \cdot \text{mol}^{-1}$  or the  $\text{O}-\text{H}$  covalent bond.

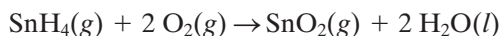


**FIGURE 10.7** Boiling points of the Group 17 hydrides.

In introductory chemistry texts, protonic bridges are regarded as very strong dipole-dipole interactions occurring as a result of the very polar covalent bonds in the bridged molecules. However, according to this concept of electrostatic attraction, hydrogen chloride should also show this effect, and it does not (to any significant extent).

Hydrogen bonds can also be described in terms of a covalent model using molecular orbital theory. This model utilizes the overlap of a  $\sigma$  orbital on one water molecule with a  $\sigma$  orbital on another molecule. The interaction of these two orbitals results in a bonding/nonbonding pair occupied by one electron pair (in the bonding set). The observation that hydrogen bond lengths are usually much shorter than the sum of the van der Waals radii of the two atoms supports this model. Furthermore, we find that the stronger the protonic bridge, the weaker the O—H covalent bond. Thus, the two bonds are strongly interrelated.

The third category of hydrides in which the hydrogen atom is slightly negative includes diborane,  $B_2H_6$ , silane,  $SiH_4$ , germane,  $GeH_4$ , and stannane (systematic name: tin(IV) hydride),  $SnH_4$ . These monomeric hydrides containing negatively charged hydrogen react violently with oxygen. For example, stannane burns to give tin(IV) oxide and water:



A partially negative hydrogen (a *hydridic hydrogen*) is thus much more reactive than a partially positive hydrogen atom. The bonding in boranes is particularly unusual, and we will discuss that topic in Chapter 13, Section 13.4. In addition, a few hydrides have polymeric structures with hydrogen atoms bridging between the metal atoms. It is the “weak” metals—beryllium, magnesium, aluminum, copper, and zinc—that form these structures.

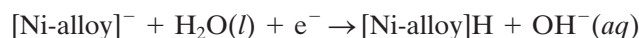
### Metallic (d-Block) Hydrides

Some transition metals form a third class of hydrides, the metallic hydrides. These compounds are often nonstoichiometric; for example, the highest hydrogen titanium ratio is found in a compound with the formula  $TiH_{1.9}$ . The nature of these compounds is complex. Thus, the titanium hydride mentioned previously

is now believed to consist of  $(\text{Ti}^{4+})(\text{H}^-)_{1.9}(\text{e}^-)_{2.1}$ . It is the free electrons that account for the metallic luster and high electrical conductivity of these compounds. The density of the metal hydride is often less than that of the pure metal because of structural changes in the metallic crystal lattice, and the compounds are usually brittle. The electrical conductivity of the metallic hydrides is generally lower than that of the parent metal as well.

Most metallic hydrides can be prepared by warming the metal with hydrogen under high pressure. At high temperatures, the hydrogen is released as dihydrogen gas again. Many alloys (for example,  $\text{Ni}_5\text{La}$ ) can absorb and release copious quantities of hydrogen. Their proton densities exceed that of liquid hydrogen, a property that makes them of great interest as a means of hydrogen storage for use in hydrogen-powered vehicles.

A major use of a metal hydride is in the nickel metal hydride batteries that are used in portable computers, cordless vacuum cleaners, cellular phones, and many other cordless electrical devices. The first essential for such a battery is to find a metal alloy that reversibly absorbs and releases hydrogen at ambient temperatures. These hydrogen-absorbing alloys combine a metal, A, whose hydride formation is exothermic with another metal, B, whose hydride formation is endothermic. The alloys exist as four possible ratios: AB (e.g.,  $\text{TiFe}$ ),  $\text{AB}_2$  (e.g.,  $\text{ZnMn}_2$ ),  $\text{AB}_5$  (e.g.,  $\text{LaNi}_5$ ), and  $\text{A}_2\text{B}$  (e.g.,  $\text{Mg}_2\text{Ni}$ ). Stoichiometries of these intermetallic compounds (see Chapter 4, Section 4.5) are sought that give an essentially energy-neutral hydride formation. It is the combinations  $\text{TiNi}_2$  and  $\text{LaNi}_5$  that have proved best suited for the function. In the cells, at the anode, nickel(II) hydroxide is oxidized to nickel(III) oxide hydroxide, while at the cathode, water is reduced to hydrogen atoms, which are absorbed into the metal alloy:

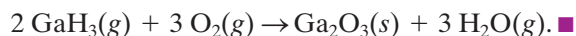


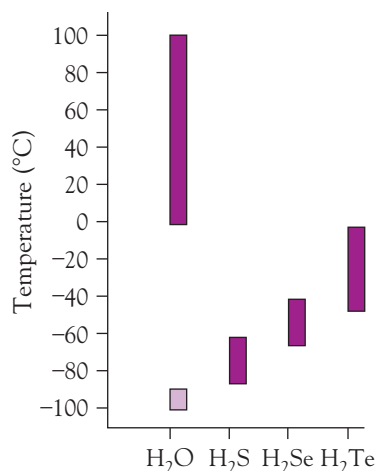
### WORKED EXAMPLE 10.2

What is the likely formula of the compound of gallium and hydrogen? Using Allred-Rochow (A-R) electronegativity values (Chapter 3, Section 3.11), what classification and subclassification would you expect for the compound? Write a balanced equation for the reaction with oxygen.

#### Answer

Gallium is a main-group element of Group 13. It has an A-R of 1.82 compared with 2.20 for hydrogen. Thus, the probable formula of the compound will be  $\text{GaH}_3$ . It should be a covalent hydride with slightly negative hydrogen atoms. These usually gaseous hydrides are highly reactive and so it should burn in air to form the solid ionic element oxide:





**FIGURE 10.8** The liquid ranges of the Group 16 hydrides. If water molecules were not bound to one another by hydrogen bonds, then water's liquid range would be between  $-90^{\circ}\text{C}$  and  $-100^{\circ}\text{C}$  (shaded rectangle). [From G. Rayner-Canham et al., *Chemistry: A Second Course* (Don Mills, ON, Canada: Addison-Wesley, 1989), p. 164.]

### WORKED EXAMPLE 10.3

What is the likely formula of the compound of arsenic and hydrogen? Using Allred-Rochow (A-R) electronegativity values (Chapter 3, Section 3.11), what classification and subclassification would you expect for the compound?

#### Answer

Arsenic is a main-group element of Group 15. It has an A-R of 2.20 compared with 2.20 for hydrogen. As elements have their lower oxidation state with hydrogen (Chapter 9, Section 9.2), thus the probable formula of the compound will be  $\text{AsH}_3$ . It should be a covalent hydride with essentially neutral hydrogen atoms. ■

### WORKED EXAMPLE 10.4

What is the likely formula of the compound of strontium and hydrogen? Using Allred-Rochow (A-R) electronegativity values (Chapter 3, Section 3.11), what classification would you expect for the compound? Write a balanced equation for the reaction with oxygen.

#### Answer

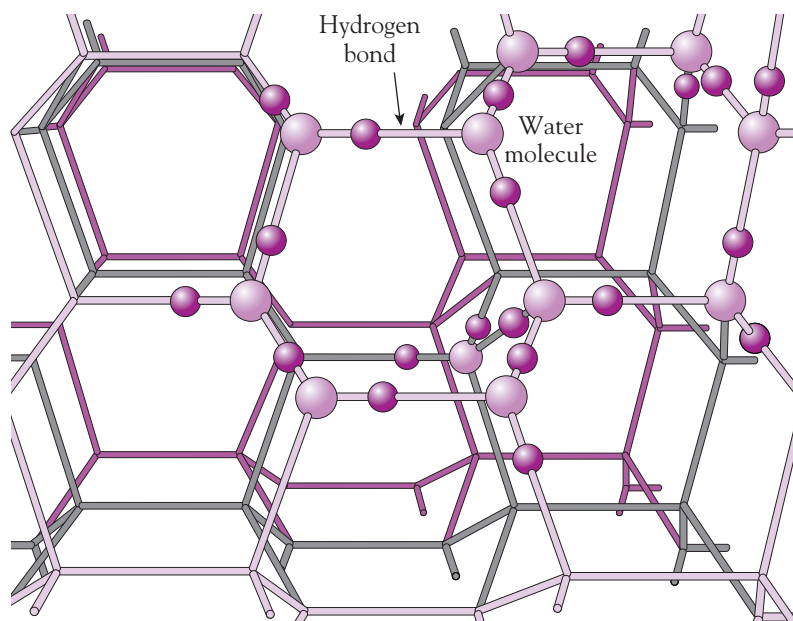
Strontium is a main-group metal of Group 2. Thus the formula of the compound should be  $\text{SrH}_2$ . Strontium has an A-R of 0.97 compared with 2.20 for hydrogen. Thus, the bonding will be highly ionic. Reaction with water should give the metal hydroxide and hydrogen gas.



## 10.6 Water and Hydrogen Bonding

Water is the only common liquid on this planet. Without water as a solvent for our chemical and biochemical reactions, life would be impossible. Yet a comparison of water to the other hydrides of Group 16 would lead us to expect it to be a gas at the common range of temperatures found on Earth. In fact, on the basis of a comparison with the other Group 16 hydrides, we would expect water to melt at about  $-100^{\circ}\text{C}$  and boil at about  $-90^{\circ}\text{C}$  (Figure 10.8). The deviation from the trend, as discussed in the Context of this chapter, is the hydrogen bonding between neighboring water molecules.

Hydrogen bonding results in another very unusual property of water—the liquid phase is denser than the solid phase. In the solid phase, the water molecules are held in a rigid structure with open holes between the network of covalent and hydrogen bonds (Figure 10.9). On the melting of ice, some



**FIGURE 10.9** A representation of part of the ice structure, showing the open framework. The larger circles represent the oxygen atoms. [From G. Rayner-Canham et al., *Chemistry: A Second Course* (Don Mills, ON, Canada: Addison-Wesley, 1989), p. 165.]

of these hydrogen bonds are broken and the open structure partially collapses. This change increases the liquid's density. The density reaches a maximum at 4°C, at which point the increase in density due to the collapsing of the hydrogen-bonded clusters of water molecules is overtaken by the decrease in density due to the increasing molecular motion resulting from the rise in temperature.

## 10.7 Clathrates

Until a few years ago, clathrates were a laboratory curiosity. Now the methane and carbon dioxide clathrates in particular are becoming of major environmental interest. A clathrate is defined as a substance in which molecules or atoms are trapped within the crystalline framework of other molecules. The name is derived from the Latin word *clathratus*, which means “enclosed behind bars.” In our discussion here we will focus on the gas clathrates of water, sometimes called *gas hydrates*. Although the latter term is widely used, it is not strictly correct, since the term *hydrate* usually implies some intermolecular attraction between the substance and the surrounding water molecules as, for example, in hydrated metal ions.

The noble gas clathrates used to be the classic example of a clathrate. Until 1962, no chemical compounds of the noble gases were known, and clathrates provided the only chemistry of those elements. For example, when



## Water: The New Wonder Solvent

In this century of green chemistry, one of the most crucial problems in industry is solvent use. Many solvents, particularly those used in organic synthesis, are toxic to humans and are potential environmental pollutants. One of the best replacements turns out to be our most common solvent, water. Traditionally, water was avoided for organic synthesis because it has a low to near-zero solubility for the low and nonpolar solutes that make up much of organic chemistry. However, at high pressure and temperature, the properties of water change remarkably.

For all substances which can exist in the liquid and gas phases, above a high-enough temperature and pressure, the two phases become indistinguishable. To express this phenomenon another way: in a tube containing liquid and gas taken above this point, the meniscus will cease to exist. For water, the critical point is at a temperature of 374°C and a pressure of 22 MPa.

Under near-critical conditions, water is a more benign solvent and can be used for synthesis rather than decomposition. One of the important differences between normal water and subcritical water is the dielectric constant (a measure of the polarity of the solvent). The increase in pressure and temperature leads to a substantial decrease in the dielectric constant, reducing its polarity to a value close to that of acetone. For example, heptane is  $10^5$  times more soluble in near-critical water, while toluene is miscible. Thus, water becomes an excellent solvent for low and nonpolar reactants.

Also, near-critical water is autoionized about  $10^3$  times more than ordinary water. With the much greater concentrations of hydronium and hydroxide ions, acid- or base-catalyzed reactions can be performed without the need for adding an actual acid or base to the reactants. A wide variety of organic reactions have been shown to proceed in near-critical water cleanly and without need for a catalyst.

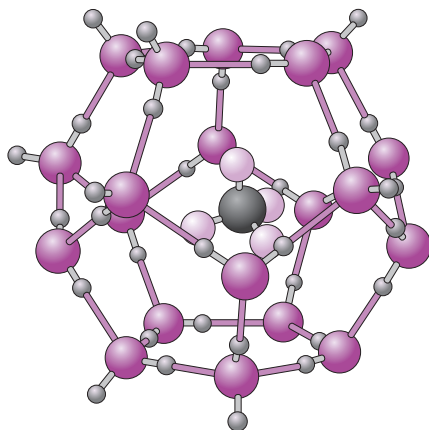
In industrial processes, between 50 and 80 percent of capital and operating costs are committed to the separation of the products. Reducing the pressure on a near-critical water reaction causes the water dielectric constant to increase. In turn, this renders the organic products insoluble and easily (and cheaply) separable.

If near-critical water processes are so wonderful, why are they not yet widely used? To produce the near-critical conditions, thick, expensive, stainless-steel pressure vessels must be used. With some reactions, the more chemically resistant (but extremely expensive) titanium has to be used as a reaction container. Also, there needs to be more research on optimizing conditions before large-scale investment is undertaken. Nevertheless, commercial organic synthesis using near-critical water solvent offers strong advantages, such as the avoidance of organic solvent systems, elimination of undesirable catalysts, avoidance of unwanted by-products, and improved reaction selectivity. Its time has come.

xenon dissolves in water under pressure and the solution is cooled below 0°C, crystals with the approximate composition of  $\text{Xe} \cdot 6\text{H}_2\text{O}$  are formed. Warming the crystals causes immediate release of the gas. There is no chemical interaction between the noble gas and the water molecule; the gas atoms are simply locked into cavities in the hydrogen-bonded ice structure. As the ice melts, the cavity structure collapses and the gas atoms are released. However, a significant point is that the presence of a “guest” within the ice structure stabilizes the crystal lattice and raises the melting point of the ice to several degrees above 0°C.

### Methane Clathrates

It was the discovery of methane hydrates (Figure 10.10) on the seafloor that turned clathrates into an issue of major importance. We are now aware that



**FIGURE 10.10** A representation of part of the methane clathrate structure.

large areas of the ocean floors have thick layers of methane clathrates just beneath the top layer of sediment. It is probable these clathrate layers have formed over eons by the interaction of rising methane from leaking subsurface gas deposits with near-freezing water percolating down through the sediment layers. Provided the water is at a temperature and pressure below those of the melting point of the clathrate, the clathrate will form. Each cubic centimeter of hydrate contains about  $175 \text{ cm}^3$  of methane gas measured at standard ambient temperature and pressure (SATP) (298 K and 100 kPa). The methane content of the clathrate is sufficient that the “ice” will actually burn. It is believed that the total carbon in the methane clathrate deposits in the world oceans is twice that of the sum of all coal, oil, and natural gas deposits on land.

Because the stability of methane clathrates is so temperature and pressure dependent, there is concern that the warming of oceans may lead to the melting of clathrate deposits, releasing large volumes of methane into the atmosphere. There are also extensive methane clathrate deposits in the permafrosts of northern Canada and northern Russia. The released methane would then have a significant effect on climate because methane is a potent greenhouse gas (see Chapter 14, Section 14.11). It has been argued that some sudden past changes of climate were triggered by methane release from clathrates. For example, the lowering of water levels during ice ages would have reduced the pressure on seabed deposits, possibly liberating large volumes of gas. The increased methane levels would then have caused global warming, terminating the ice age.

### Carbon Dioxide Clathrates

Carbon dioxide is another molecule which can fit in the ice structure. One proposed method of storing waste carbon dioxide is as the clathrate. Pumping carbon dioxide into the deep ocean results in a clathrate of high stability; for example, at a depth of 250 m, where the pressure is about 2.7 MPa, the clathrate is stable up to  $+5^\circ\text{C}$ . Whereas “normal” ice is less dense than liquid

## Is There Life Elsewhere in Our Solar System?

It is difficult for a chemist or biochemist to visualize any life-form that does not depend on water. Water is an ideal solvent, and it is hydrogen bonds that allow protein and DNA molecules to form their complex structures. This raises the question of where there is liquid water, is there life? We are now aware of extremophile bacteria that can thrive in the most unlikely environments. In fact, living bacteria have been found in ice layers nearly 4 km beneath the Antarctic ice sheet and just above Lake Vostok, which is under the ice sheet itself.

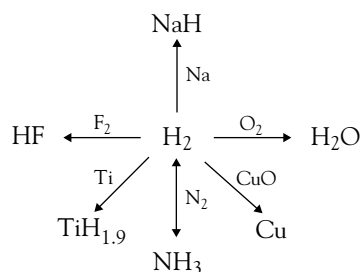
Until recently, this seemed to be a theoretical question. Although Mars certainly had rivers and lakes in the past, there is no evidence of any current surface liquid water. It was traditionally believed that the other moons in the solar system would be like our own—rocky, dust covered, lifeless—covered by craters, mainly formed by impacts of asteroids over the entire geological timescale. From photos sent back by space probes, we now know that the moons of Jupiter and

Saturn show some incredible differences in surfaces. Now our attention is focusing on one of Jupiter's moons, Europa.

In the search for living organisms beyond the Earth, Europa is the moon of greatest interest to astrochemists. Europa is the smoothest surfaced celestial body ever discovered. As Europa also has a very low average density, the surface is thought to consist of ice. The surface must have been liquid in the geologically recent past to “freeze over” meteor impact sites.

This raises the question as to whether there is still liquid water beneath the surface ice of Europa. After all, ice is a good insulator (even though the surface is at  $-160^{\circ}\text{C}$ ), and the tidal friction from Jupiter may well provide an energy source. From that question follows another: if there is liquid water, has any life developed in it? A few years ago, this question would have raised laughter, but no more. Evidence of recent melting, dissolved ionic solutes—and maybe embedded simple organisms—would be exciting.

water, the carbon dioxide clathrate has a density of about  $1.1\text{ g}\cdot\text{cm}^{-3}$  and sinks to the ocean floor. It has been proposed that megatonnes of excess carbon dioxide could be disposed of in this way. There are three major concerns with this concept. First and most important, the layer of carbon dioxide clathrate will smother the many organisms of the deep oceans. Second, experiments have already shown that fishes exhibit respiratory distress when they approach the acidic carbon dioxide-saturated water around experimental clathrate deposits. Third, over an extended period—perhaps hundreds of thousands of years—the clathrates will probably release their captive carbon dioxide to the surrounding waters, causing a pH decrease of the oceans. The pH change would obviously have an effect on the ecological balance of marine life.



## 10.8 Element Reaction Flowchart

In each chapter discussing chemical elements, a flowchart will be used to display the key reactions of that element. See the flowchart for hydrogen in the margin.

## KEY IDEAS

- Dihydrogen is a reactive, gaseous element.
- Three classes of hydrides are known: ionic, covalent (three subcategories), and metallic.
- Hydrogen bonding plays a major role in determining the physical properties of water.

## EXERCISES

**10.1** Define the following terms: (a) protonic bridge; (b) hydridic bridge.

**10.2** Define the following terms: (a) clathrate; (b) phase diagram.

**10.3** An ice cube at 0°C is placed in some liquid water at 0°C. The ice cube sinks. Suggest an explanation.

**10.4** Which of the following isotopes can be studied by nuclear magnetic resonance: carbon-12, oxygen-16, oxygen-17?

**10.5** When we study the NMR spectrum of a compound, why are the absorption frequencies expressed as ppm?

**10.6** Explain why hydrogen is not placed with the alkali metals in the periodic table.

**10.7** Explain why hydrogen is not placed with the halogens in the periodic table.

**10.8** Explain why hydrogen gas is comparatively unreactive.

**10.9** Is the reaction of dihydrogen with dinitrogen to produce ammonia entropy or enthalpy driven? Do not consult data tables. Explain your reasoning.

**10.10** Write chemical equations for the reaction between  
(a) tungsten(VI) oxide,  $\text{WO}_3$ , and dihydrogen with heating  
(b) hydrogen gas and chlorine gas  
(c) aluminum metal and dilute hydrochloric acid

**10.11** Write chemical equations for the reaction of  
(a) potassium hydrogen carbonate on heating  
(b) ethyne,  $\text{HC}\equiv\text{CH}$ , with dihydrogen  
(c) lead(IV) oxide with hydrogen gas on heating  
(d) calcium hydride and water

**10.12** Show that the combustion of methane,  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ , is indeed spontaneous by calculating the standard molar enthalpy, entropy, free energy

of combustion from enthalpy of formation, and absolute entropy values. Use the data tables in Appendix 1.

■ Clathrates (methane and carbon dioxide) have become of increasing environmental interest.

of combustion from enthalpy of formation, and absolute entropy values. Use the data tables in Appendix 1.

**10.13** Construct a theoretical enthalpy cycle (similar to that of Figure 10.3) for the formation of ammonia from its elements. Obtain bond energy information and the standard enthalpy of formation of ammonia from the data tables in Appendices 1 and 3. Compare your diagram to that in Figure 10.3 and comment on the differences.

**10.14** What is the major difference between ionic and covalent hydrides in terms of physical properties?

**10.15** Discuss the three types of covalent hydrides.

**10.16** Which of the following elements is likely to form an ionic, metallic, or covalent hydride or no stable hydride: (a) chromium; (b) silver; (c) phosphorus; (d) potassium?

**10.17** Write the expected formulas for the hydrides of the Period 4 main group elements from potassium to bromine. What is the trend in the formulas? In what way are the first two members of the series different from the others?

**10.18** Construct a plot of the enthalpies of formation of carbon, silicon, and tin hydrides (see Appendix 1) against the element-hydrogen electronegativity difference for each hydride. Suggest an explanation for the general trend.

**10.19** Predict which of the following hydrides is a gas or a solid: (a)  $\text{HCl}$ ; (b)  $\text{NaH}$ . Give your reason in each case.

**10.20** If the hydrogen bond between a pair of hydrogen and fluorine atoms is the strongest hydrogen bond, why does water have a much higher melting point than hydrogen fluoride?

**10.21** What are the two properties of hydrogen that are crucial to the existence of life?

**10.22** Write balanced chemical equations corresponding to each transformation in the element reaction flowchart for hydrogen (page 260).

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**BEYOND THE BASICS**

**10.23** Predict which of the following hydrides is likely to be strongly hydrogen bonded and so deduce the likely phases of each of the hydrides at room temperature: (a)  $\text{H}_2\text{O}_2$ ; (b)  $\text{P}_2\text{H}_4$ ; (c)  $\text{N}_2\text{H}_4$ ; (d)  $\text{B}_2\text{H}_6$ .

**10.24** Write balanced chemical equations for the air oxidation of (a)  $\text{B}_2\text{H}_6$ ; (b)  $\text{PbH}_4$ ; (c)  $\text{BiH}_3$ .

**10.25** The hydride ion is sometimes considered similar to a halide ion; for example, the lattice energies of sodium hydride and sodium chloride are  $-808 \text{ kJ}\cdot\text{mol}^{-1}$  and  $-788 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. However, the enthalpy of formation of sodium hydride is much less than that of a sodium halide, such as sodium chloride. Use the data tables in the appendices to calculate enthalpy of formation values for the two compounds and identify the factor(s) that cause the values to be so different.

**10.26** Explain why

- (a) interstitial hydrides have a lower density than that of the parent metal
- (b) ionic hydrides are more dense than the parent metal

**10.27** Hydrogen gas has been proposed as the best fuel for the twenty-first century. However, a company in Florida has developed AquaFuel as an alternative. This gas mixture is formed by passing a high current through water using carbon electrodes. What are the likely gaseous products of electrolysis? Write a balanced molecular equation for the process. Write a balanced molecular equation for the combustion of the mixture. Calculate the energy released per mole of gas mixture and compare it to the energy released per mole of hydrogen gas combustion.

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**ADDITIONAL RESOURCES**

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

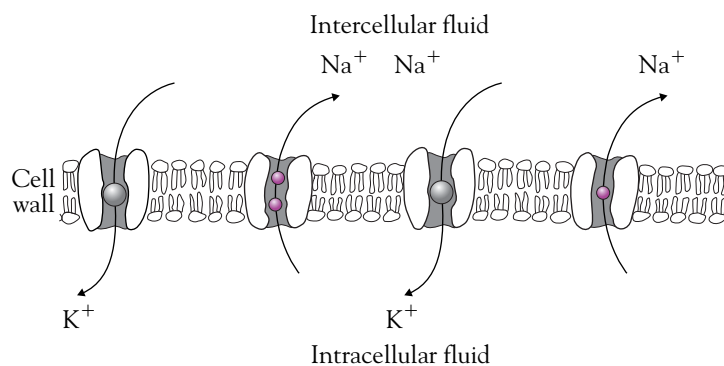


For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



concentration gradient of potassium across cell membranes is responsible for the electrode potential that allows nerves and muscles to function. Sodium is predominantly found outside cells in extracellular fluid (approximately  $10 \text{ mmol}\cdot\text{L}^{-1}$  inside cells,  $145 \text{ mmol}\cdot\text{L}^{-1}$  outside cells), whereas potassium is found inside cells, in intracellular fluid (approximately  $90 \text{ mmol}\cdot\text{L}^{-1}$  inside cells,  $10 \text{ mmol}\cdot\text{L}^{-1}$  outside cells).

Without an active chemical process, the concentrations of each of the two ions would be the same inside and outside the cells. The energy for the ion pump comes from the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP), a process which provides our Context for Chapter 15. But how do the cells distinguish which is a sodium ion to be pumped out, and the potassium ions to be pumped in? The answer comes, in large part, from the ion size. The “naked” sodium ion has a radius of 116 pm, while that of the “naked” potassium ion is 165 pm. There are separate channels, smaller ones through which sodium ions are transported, and larger ones, which convey the potassium ions (see the following figure). For every two potassium ions pumped into the cell, three sodium ions are pumped out, so there is a potential difference across the cell wall.



The sodium-potassium pump in a cell wall.

In the sodium channels, each sodium cation is electrostatically attracted to up to six partially negative oxygen atoms of surrounding protein molecules. Similarly, in the potassium channels, each large potassium cation is electrostatically attracted to up to eight partially negative oxygen atoms of surrounding protein molecules. There is another crucial factor in the functioning of the channels: the enthalpy of hydration of the alkali metal ions. We introduced the concept in Chapter 6, Section 6.4, and now in Section 11.2, we show that the large, alkali metals have correspondingly low hydration enthalpies. For the hydrated ions in solution, the very first step of the transport process through the cell wall is the removal of the hydration sphere so that the naked ions can move through the channels. Although the energy is regained by the rehydration upon exit from the channel, nevertheless, it is the simple physical properties of these two alkali metal ions which make cell functioning possible.

## 11.1 Group Trends

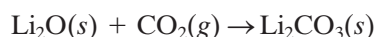
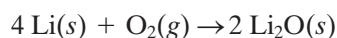
All of the alkali metals are shiny, silver-colored metals. Like the other metals, they have high electrical and thermal conductivities. But in other respects, they are very atypical. For example, the alkali metals are very soft, and they become softer progressing down the group. For example, lithium can be cut with a knife, whereas potassium can be “squashed” like soft butter.

### Physical Properties

Most metals have high melting points, but those of the alkali metals are very low and become lower descending Group 1, with cesium melting just above room temperature. In fact, the combination of high thermal conductivity and low melting point makes sodium useful as a heat transfer material in some nuclear reactors. The softness and low melting points of the alkali metals can be attributed to the very weak metallic bonding in these elements. For a “typical” metal, the enthalpy of atomization is in the range of 400 to 600  $\text{kJ}\cdot\text{mol}^{-1}$ , but as can be seen from Table 11.1, those of the alkali metals are much lower. Even more atypical are the densities of the alkali metals. Most metals have densities between 5 and 15  $\text{g}\cdot\text{cm}^{-3}$ , but those of the alkali metals are far less. In fact, lithium has a density one-half that of water!

### Chemical Reactivity

With such a low density, lithium would be ideal for making unsinkable (although soft!) ships, except for one other property of the alkali metals—their high chemical reactivity. The metals are usually stored under oil because when they are exposed to air, a thick coating of oxidation products covers the lustrous surface of each metal very rapidly. For example, lithium is oxidized to lithium oxide, which in turn reacts with carbon dioxide to give lithium carbonate:



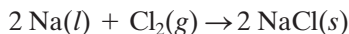
The alkali metals react with most nonmetals. For example, every molten alkali metal burns in chlorine gas to give off a white smoke of the metal chloride. The reaction of sodium with dichlorine really typifies the wonder of

**TABLE 11.1** Melting points and densities of the alkali metals

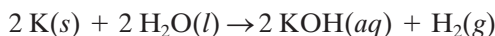
Element	Melting point ( $^{\circ}\text{C}$ )	Density ( $\text{g}\cdot\text{cm}^{-3}$ )
Li	180	0.53
Na	98	0.97
K	64	0.86
Rb	39	1.53
Cs	29	1.87



chemistry—that a highly reactive, dangerous metal reacts with a poisonous gas to produce a compound that is essential to life.



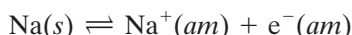
As discussed in Chapter 9, Section 9.1, the reactions of the alkali metals with water are very dramatic, with reactivity increasing down the group. The equation for the reaction of water with potassium is



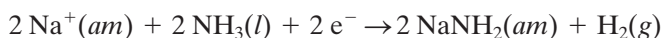
Because they are so much more reactive than the “average” metal, the alkali metals are sometimes referred to as the supermetals.

### Reaction with Ammonia

The alkali metals themselves have the unusual property of dissolving in liquid ammonia to yield solutions that are deep blue when dilute. These solutions conduct current electrolytically, and the main current carrier in the solution is thought to be the ammonia-solvated electron,  $e^-(am)$ , which is a product of the ionization of the sodium atoms:



When concentrated by evaporation, the solutions have a bronze color and behave like a liquid metal. On long standing, or more rapidly in the presence of a transition metal catalyst, the solutions decompose to yield the amide salt,  $\text{NaNH}_2$ , and hydrogen gas:



#### WORKED EXAMPLE 11.1

Estimate the mass (in kg) of a soccer-ball sized piece of cesium (radius of a soccer ball = 12.5 cm; density Cs =  $1.87 \text{ g}\cdot\text{cm}^{-3}$ ).

#### Answer

The volume of a soccer ball would therefore be  $\frac{4}{3}\pi(12.5)^3 = 8.18 \times 10^3 \text{ cm}^3$ . Therefore, the mass of the football would be  $8.18 \times 10^3 \text{ cm}^3 \times 1.87 \text{ g}\cdot\text{cm}^{-3} = 1.53 \times 10^4 \text{ g}$  or 15.3 kg. ■

## 11.2 Features of Alkali Metal Compounds

All the Group 1 elements are metals. As a result, all the members of the group have common features. The alkali metal ions always have an oxidation number of +1 and they exist as the free ion across the whole pH range (see Table 11.2).

Most of the alkali metal compounds are stable, ionic solids. The compounds are colorless unless they contain a colored anion such as chromate or

**TABLE 11.2** A comparison of lithium, sodium, and potassium species under oxidizing conditions

	Very Acidic	Acidic	Basic	Very Basic
<b>Lithium</b>	$\text{Li}^+(aq)$			
<b>Sodium</b>	$\text{Na}^+(aq)$			
<b>Potassium</b>	$\text{K}^+(aq)$			

permanganate. Even for these highly electropositive elements, the bonds in their compounds with nonmetals have a small covalent component.

### Stabilization of Large Anions

Because the cations of the alkali metals (except for that of lithium) have among the largest sizes and hence the lowest charge densities, they are able to stabilize large low-charge anions (see Chapter 6, Section 6.5). For example, the ions of sodium through cesium are the only cations that form solid hydrogen carbonate salts.

### Ion Hydration

All ions are hydrated when dissolved in water. However, this is not always true in the solid phase. Hydration in the crystalline solid depends on the balance of lattice energy and ion hydration energies. The lattice energy results from the electrostatic attraction between the cations and anions: the higher the charge density of the ions, the larger the lattice energy. Thus, the lattice energy term favors the loss of an ion's hydration sphere on crystallization to give the small (higher-charge density) anhydrous ion. But the hydration energy depends on the attraction between the ion and the surrounding polar water molecules. A major factor contributing to the strength of the ion-dipole attraction is the charge density of the ions. In this ionic tug-of-war, we find that high-charge density usually favors retention of all or part of the hydration sphere in the solid phase, while salts of low-charge ions tend to be anhydrous.

As we mentioned earlier, the alkali metals have very low-charge densities compared to those of other metals. Thus, we would expect—and find—that the majority of solid alkali metal salts are anhydrous. The charge densities of lithium and sodium ions are high enough to favor the formation of a few hydrated salts. With the lowest charge densities of all metals, very few potassium, rubidium, and cesium salts are hydrated.

The low-charge densities are reflected in the trend in hydration enthalpy among the alkali metals (Table 11.3). The values are very low (for comparison, that of the  $\text{Mg}^{2+}$  ion is  $1920 \text{ kJ}\cdot\text{mol}^{-1}$ ), and the values decrease as the radius increases down the group.

**TABLE 11.3** Hydration enthalpies of the alkali metal ions

Ion	Hydration enthalpy ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\text{Li}^+$	519
$\text{Na}^+$	406
$\text{K}^+$	322
$\text{Rb}^+$	301
$\text{Cs}^+$	276

**TABLE 11.4** Alkali metals and their flame colors

Metal	Color
Lithium	Crimson
Sodium	Yellow
Potassium	Lilac
Rubidium	Red-violet
Cesium	Blue

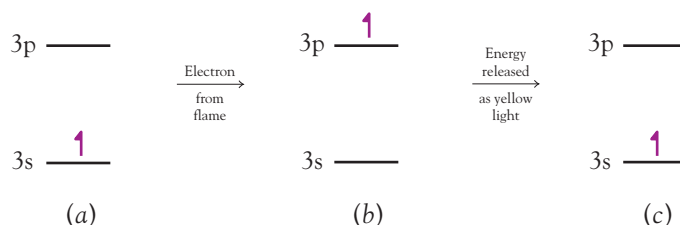
### Flame Colors



Each of the alkali metals produces a characteristic flame color when a sample of an alkali metal salt is placed in a flame (Table 11.4). In the process, energy from the combustion reactions of the fuel is transferred to the metal salt that is placed in the flame. This transfer causes electrons in the alkali metal atoms to be raised to excited states. The energy is released in the form of visible radiation as the electron returns to the ground state. Each alkali metal undergoes its own unique electron transitions. For example, the yellow color of sodium is a result of the energy (photon) emitted when an electron drops from the  $3p^1$  orbital to the  $3s^1$  orbital of a neutral sodium atom, the ion having acquired its valence electron from the combustion reactions in the flame (Figure 11.1). The production of these colors is put to good use in fireworks.

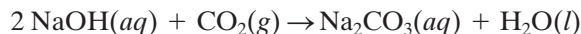
### Alkali Metal Hydroxides

The solid hydroxides are white, translucent solids that absorb moisture from the air until they dissolve in the excess water—a process known as *deliquescence*. The one exception is lithium hydroxide, which forms the stable octahydrate,  $\text{LiOH}\cdot 8\text{H}_2\text{O}$ . Alkali metal hydroxides are all extremely hazardous because the hydroxide ion reacts with skin protein to destroy the skin surface. Sodium hydroxide and potassium hydroxide are supplied as pellets, and these



**FIGURE 11.1** In a flame, the sodium ion (a) acquires an electron in the 3p orbital (b). As the electron drops from the excited 3p state to the ground 3s state (c), the energy is released as yellow light.

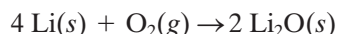
are produced by filling molds with the molten compound. As solids or in solution, they also absorb carbon dioxide from the atmosphere:



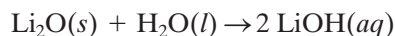
The alkali metal hydroxides are convenient sources of the hydroxide ion because they are very water soluble. When hydroxide ion is needed as a reagent, its source is chosen on the basis of either cost or solubility. In inorganic chemistry, sodium hydroxide (caustic soda) is most commonly used as the source of hydroxide ion because it is the least expensive metal hydroxide. Potassium hydroxide (caustic potash) is preferred in organic chemistry because it has a higher solubility in organic solvents than does sodium hydroxide.

### 11.3 Trends in Alkali Metal Oxides

Most metals in the periodic table react with dioxygen gas to form oxides containing the oxide ion,  $\text{O}^{2-}$ . However, of the alkali metals, only lithium forms a normal oxide when it reacts with oxygen:

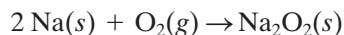


Lithium oxide reacts with water to form lithium hydroxide:



#### Sodium Dioxide(2−)

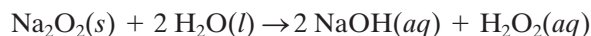
Sodium reacts with dioxygen to give sodium dioxide(2−),  $\text{Na}_2\text{O}_2$  (commonly called *sodium peroxide*), containing the dioxide(2−) ion,  $\text{O}_2^{2-}$  (often called the *peroxide ion*):

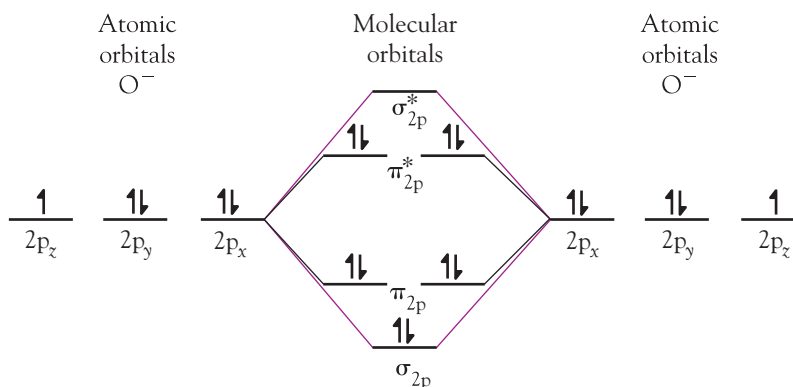


The notation “2−” simply indicates the charge on the ion, and it avoids the need for learning the many prefixes that used to be employed for that purpose. We are now using parenthetical Arabic numbers to name species whenever there is more than one possible anionic charge. This is a method recommended by the American Chemical Society.

Sodium dioxide(2−) is diamagnetic, and the oxygen-oxygen bond length is about 149 pm, much longer than the 121 pm in the dioxygen molecule. We can explain the diamagnetism and the weaker bond by constructing the part of the molecular orbital diagram derived from the 2p atomic orbitals (Figure 11.2). This diagram shows that three bonding orbitals and two antibonding orbitals are occupied. All the electrons are paired and the net bond order is 1 rather than 2, which is the bond order in the dioxygen molecule (see Chapter 3, Section 3.4).

Sodium dioxide(2−) reacts rapidly and exothermically with water to form sodium hydroxide and hydrogen peroxide:

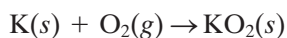




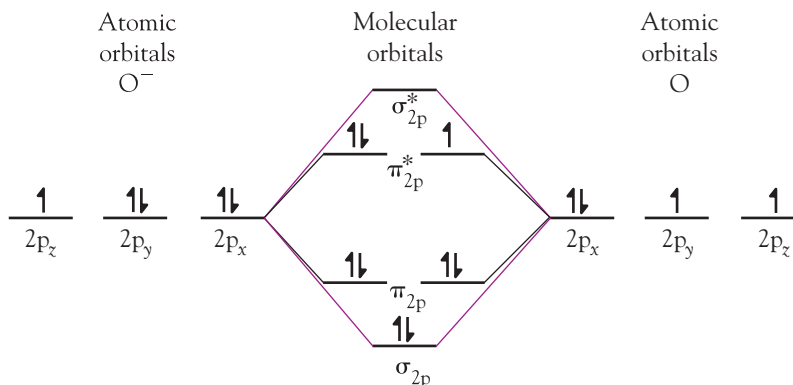
**FIGURE 11.2** Filling of the molecular orbitals derived from the 2p orbitals for the dioxide(1−) ion (commonly called the peroxide ion).

### Potassium Dioxide(1−)

Potassium (and rubidium and cesium) reacts with an excess of dioxygen to form a dioxide(1−) (traditionally named *superoxide*) containing the paramagnetic dioxide(1−) ion,  $\text{O}_2^-$ :



The oxygen-oxygen bond length in the dioxide(1−) ion (133 pm) is less than that in the dioxide(2−) but slightly greater than that in dioxygen itself. We can also explain these different bond lengths in terms of the molecular orbital filling (Figure 11.3). The dioxide(1−) ion possesses three bonding pairs and one and one-half antibonding pairs. The net bond order in a dioxygen(1−) ion is  $1\frac{1}{2}$ , between the bond order of 1 in the dioxide(2−) ion and the bond order of 2 in the dioxygen molecule. We can explain the ready formation of both the dioxide(1−) and the dioxide(2−) ions by postulating that the least polarizing cations (those with low-charge density) stabilize these large polarizable anions.

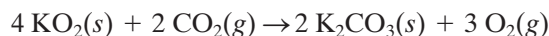


**FIGURE 11.3** Filling of the molecular orbitals derived from the 2p orbitals for the dioxide(1−) ion (commonly called the superoxide ion).

Reaction of potassium dioxide(1–) with water produces potassium hydroxide, hydrogen peroxide, and oxygen gas:



Potassium dioxide(1–) is used in space capsules, submarines, and some types of self-contained breathing equipment because it absorbs exhaled carbon dioxide (and moisture) and releases dioxygen gas:



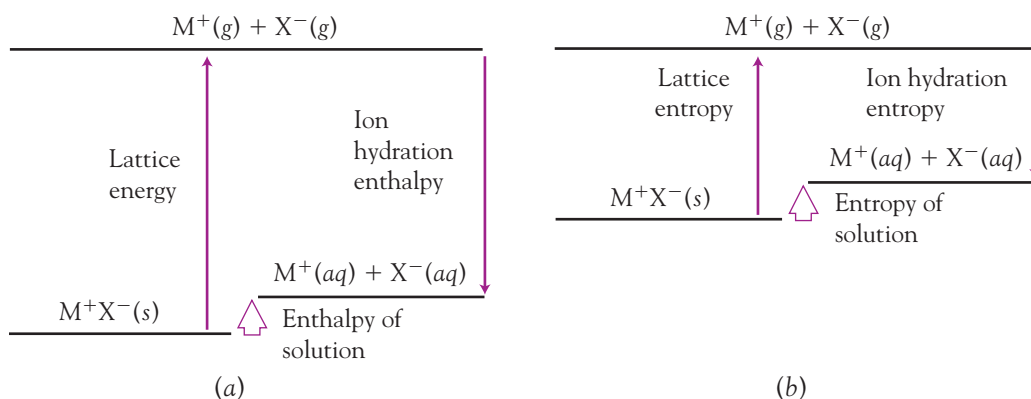
## 11.4 Solubility of Alkali Metal Salts

It is the solubility of all the common alkali metal salts that makes them so useful as reagents in the chemistry laboratory. Whether it is a nitrate, a phosphate, or a fluoride anion that we need, we can almost always count on the alkali metal salt to enable us to make a solution of the required anion. Yet the solubilities cover a wide range of values. For example, a saturated solution of lithium chloride has a concentration of  $14 \text{ mol}\cdot\text{L}^{-1}$ , whereas a saturated solution of lithium carbonate has a concentration of only  $0.18 \text{ mol}\cdot\text{L}^{-1}$ . This variability is illustrated by the solubilities of the sodium halides (Table 11.5).

To explain this solubility trend, we need to look at the energy cycle involved in the formation of a solution from the solid. As we discussed in Chapter 6, Section 6.4, the solubility of a compound is dependent on the enthalpy changes (the lattice energy and the enthalpy of hydration of the cation and anion) together with the corresponding entropy changes. These are shown in Figure 11.4. For the salt to be appreciably soluble, the free energy,  $\Delta G^\ominus$ , should be negative, where  $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ .

**TABLE 11.5** Solubilities of the sodium halides at 25°C

Compound	Solubility ( $\text{mol}\cdot\text{L}^{-1}$ )
NaF	0.99
NaCl	6.2
NaBr	9.2
NaI	12.3



**FIGURE 11.4** Enthalpy cycle (a) and entropy cycle (b) for the solution of an ionic compound.  $M^+$  is the alkali metal ion and  $X^-$  is the anion.

**TABLE 11.6** Enthalpy factors in the solution process for the sodium halides

Compound	Lattice energy (kJ·mol <sup>-1</sup> )	Hydration enthalpy (kJ·mol <sup>-1</sup> )	Net enthalpy change (kJ·mol <sup>-1</sup> )
NaF	+930	-929	+1
NaCl	+788	-784	+4
NaBr	+752	-753	-1
NaI	+704	-713	-9

**TABLE 11.7** Entropy factors in the solution process for the sodium halides, expressed as  $T\Delta S$  values

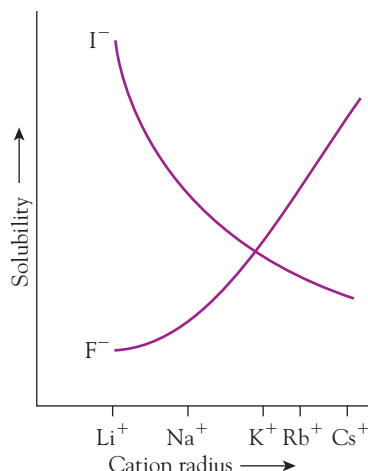
Compound	Lattice entropy (kJ·mol <sup>-1</sup> )	Hydration entropy (kJ·mol <sup>-1</sup> )	Net entropy change (kJ·mol <sup>-1</sup> )
NaF	+72	-74	-2
NaCl	+68	-55	+13
NaBr	+68	-50	+18
NaI	+68	-45	+23

If we look at the enthalpy terms (Table 11.6), we see that for each sodium halide, the lattice energy is almost exactly balanced by the sum of the cation and anion hydration enthalpies. In fact, the error in these experimental values is larger than the calculated differences. As a result, we can only say that the lattice energy and hydration enthalpy terms are essentially equal.

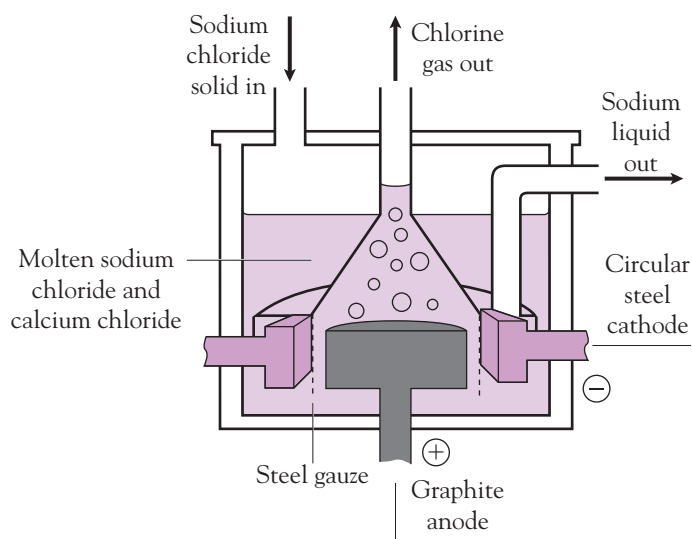
When we calculate the entropy changes (Table 11.7), we find that for all the salts except sodium fluoride, the entropy gained by the ions as they are freed from the crystal lattice is numerically larger than the entropy lost when these gaseous ions are hydrated in solution. To obtain the free energy change for the solution process, we combine these two very small net changes in enthalpy and entropy. Amazingly, the calculated free energies provide a trend parallel to that of the measured solubilities (Table 11.8). Furthermore,

**TABLE 11.8** Calculated free energy change for the solution process for the sodium halides

Compound	Enthalpy change (kJ·mol <sup>-1</sup> )	Entropy change (kJ·mol <sup>-1</sup> )	Free energy change (kJ·mol <sup>-1</sup> )
NaF	+1	-2	+3
NaCl	+4	+13	-9
NaBr	-1	+18	-19
NaI	-9	+23	-32



**FIGURE 11.5** Solubility of alkali metal fluorides and iodides as a function of alkali metal ion radius.



**FIGURE 11.6** A Downs cell.

if we plot the solubilities of the salts one anion forms with different alkali metal cations as a function of the ionic radius of the alkali metal ions, in most cases we get a smooth curve. This curve may have a positive or negative slope (or in some cases reach a minimum in the middle of the series). To illustrate such trends, the solubilities of alkali metal fluorides and iodides are shown in Figure 11.5.

We can understand the different curves in Figure 11.6 by focusing on the lattice energies. Although there is a strong dependence of lattice energy on ionic charge, there is a secondary relationship to the cation/anion radius ratio; that is, a significant mismatch in ionic sizes will lead to a lower than expected lattice energy. Table 11.9 shows the ionic radii of the cations, lithium and cesium, and the anions, fluoride and iodide. Thus, lithium iodide, the ions of which have very different sizes, is much more soluble than lithium fluoride, the ions of which have similar sizes. Conversely, cesium iodide, the ions of which have similar sizes, is much less soluble than cesium fluoride, in which there is a large mismatch in ionic size.

**TABLE 11.9** Selected ionic radii

Cation	Radius (pm)	Anion	Radius (pm)
$\text{Li}^+$	73	$\text{F}^-$	119
$\text{Cs}^+$	181	$\text{I}^-$	206



## Mono Lake

This California lake, nestled against the Sierra Nevada, is unique in the world, and this uniqueness derives from its chemistry. Surrounded by mountains and volcanic hills, the lake has no outlet, so water loss is by evaporation. The lake is estimated to be among the oldest in North America—at least 760 000 years old. During that time, soluble salts have been leached out of the surrounding rocks by surface waters and underground springs, accumulating in this lake of surface area about 180 km<sup>2</sup> (70 mi<sup>2</sup>) with an average depth of about 20 m (60 ft). It has been calculated that the lake contains about  $2.8 \times 10^8$  tonnes of dissolved salts.

Whereas the Great Salt Lake in Utah contains mostly sodium chloride, Mono Lake contains a fascinating mix of soluble sodium and potassium salts, including chloride, sulfate, hydrogen carbonate, carbonate, borate, and a trace of fluoride, iodide, arsenate, and tungstate ions. Among the other metal ions in the lake are calcium, magnesium, and strontium. As a result of the high HCO<sub>3</sub><sup>−</sup> and CO<sub>3</sub><sup>2−</sup> concentrations, the pH of the lake is about 10. Although the bulk composition of the lake is known, there is still much to discover about the ion interactions and the variation in composition with depth and season.

The tufa towers are the most characteristic feature of the lake. They are mainly formed when underwater springs rich in calcium ion mix with the carbonate ion of the lake waters. Hence, the towers identify the location of underwater springs. The water is so saturated in these two ions that calcium carbonate deposits form over the lake bottom, over discarded soft-drink cans and any other debris. The towers only form underwater; thus, those visible today result from a drop in water level since

1941, when feed water was diverted to agricultural and consumable use elsewhere in the state.

Not only is the chemistry of the lake unique, so is its ecology. With the high pH and high soluble salt concentrations, the only water life is algae, brine shrimp, and black alkali flies. These algae-feeding flies swarm around the lake, spending two of their three life stages entirely underwater. The flies are rich in fat and protein, making them an excellent source of food for migrating birds “refueling” for their long journeys. In fact, the lake is one of the most productive ecosystems in the world.

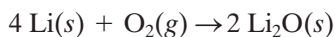
As more and more of the water was diverted, the water level dropped, reaching a minimum of about 50 percent of its 1941 volume in 1982. Had the level dropped by much more, the ion concentration would have become too high even for the brine shrimp and alkali flies, killing all life in the lake and the birds that depended on it. Fortunately, the lake has been designated as an Outstanding National Resource Water. This means that the lake volume must be restored to about 70 percent of its former volume (at present, the figure is about 60 percent), and the volume, allowing for winter-summer variation, must be maintained forever at about that value.

Mono Lake is now of interest to NASA scientists studying Martian chemistry. There are many old Martian lake beds, and it is believed that the lakes may have had similar compositions to that of Mono Lake and perhaps supported related life-forms. The astrochemists are eager to obtain ultra-high-resolution photos of the Martian lake beds to see if they, too, have tufa towers, which would be an indication of parallel chemical processes.

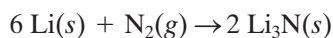
## 11.5 Lithium

Lithium, having a density of about half that of water, is the least dense of all metals. Its very low density makes lithium attractive for use in aerospace alloys. For example, alloy LA 141, which consists of 14 percent lithium, 1 percent aluminum, and 85 percent magnesium, has a density of only 1.35 g·cm<sup>−3</sup>, almost exactly half that of aluminum, the most commonly used low-density metal.

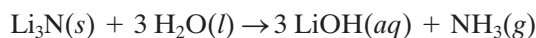
The metal has a bright silvery appearance, but when a surface is exposed to moist air, it very rapidly turns black. Like the other alkali metals, lithium reacts with the dioxygen in air:



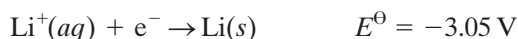
It is the only alkali metal, and one of a very few elements in the entire periodic table, to react with dinitrogen (see Chapter 9, Section 9.5). Breaking the triple bond in the dinitrogen molecule requires an energy input of  $945 \text{ kJ} \cdot \text{mol}^{-1}$ . To balance this energy uptake, the lattice energy of the product must be very high. Of the alkali metals, only the lithium ion, which has the greatest charge density of the group, forms a nitride with sufficiently high lattice energy:



The nitride is reactive, however, forming ammonia when added to water:



Liquid lithium is the most corrosive material known. For example, if a sample of lithium is melted in a glass container, it reacts spontaneously with the glass to produce a hole in the container, the reaction being accompanied by the emission of an intense, greenish white light. In addition, the lithium ion has the most negative standard reduction potential of any element:



That is, the metal itself releases more energy than any other element when it is oxidized to its ion (+3.05 V).

Yet, of the alkali metals, it has the least spectacular reaction with water. As discussed in Chapter 6, Section 6.6, we must not confuse thermodynamic spontaneity, which depends on the free energy change, with rate of reaction, which is controlled by the height of the activation energy barrier. In this particular case, we must assume that the activation energy for the reaction with water is greater for lithium than for the other alkali metals. Because lithium metal has the greatest lattice energy of the alkali metals and because escape from the lattice must be involved in any oxidation/hydration pathway, it is not really surprising that the activation energy is higher.

### WORKED EXAMPLE 11.2

Use the Kapustinskii equation from Chapter 6, Section 6.1, to estimate the lattice energy of lithium nitride,  $\text{Li}_3\text{N}$ , given the ionic radii of  $\text{Li}^+$  and  $\text{N}^{3-}$  are 73 pm and 146 pm, respectively.

#### Answer

The Kapustinskii equation is

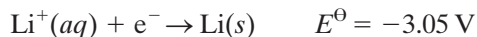
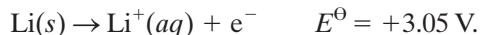
$$U = \frac{1.202 \times 10^5 v z^+ z^-}{r_0} \left( 1 - \frac{34.5}{r_0} \right) \text{ kJ} \cdot \text{mol}^{-1}.$$

For  $\text{Li}_3\text{N}$ ,

$$U = \frac{1.202 \times 10^5 \times 4 \times 1 \times 3}{219} \left( 1 - \frac{34.5}{219} \right) \text{ kJ} \cdot \text{mol}^{-1} = 5549 \text{ kJ} \cdot \text{mol}^{-1}. \blacksquare$$

**WORKED EXAMPLE 11.3**

Calculate the energy produced on oxidation of one mole of lithium to lithium ions at 25°C.

**Answer**

We can use  $\Delta G^\ominus = -nFE^\ominus$  to calculate the energy released during this oxidation process.

$$\begin{aligned} \Delta G^\ominus &= -1 \times 9.648 \times 10^4 \text{ C} \cdot \text{mol}^{-1} \times 3.05 \text{ V} \\ &= -2.96 \times 10^5 \text{ C} \cdot \text{V} \cdot \text{mol}^{-1} = -2.96 \times 10^5 \text{ J} \cdot \text{mol}^{-1}. \blacksquare \end{aligned}$$

**Uses of Lithium**

The largest industrial use of lithium is in lithium greases—in fact, more than 60 percent of all automotive greases contain lithium. The compound used is lithium stearate,  $\text{C}_{17}\text{H}_{35}\text{COOLi}$ , which is mixed with oil to give a water-resistant, greaselike material that does not harden at cold temperatures yet is stable at high temperatures.

The comparatively high-charge density of the lithium ion is responsible for several other important ways in which lithium's chemistry differs from that of the rest of the alkali metals. In particular, there is an extensive organometallic chemistry of lithium in which the bonding is definitely covalent (see Chapter 23, Section 22.5). Even for common salts, such as lithium chloride, their high solubilities in many solvents of low polarity, particularly ethanol and acetone, indicate a high degree of covalency in the bonding. One specific organometallic compound, butyllithium,  $\text{LiC}_4\text{H}_9$ , is a useful reagent in organic chemistry. It can be prepared by treating lithium metal with chlorobutane,  $\text{C}_4\text{H}_9\text{Cl}$ , in a hydrocarbon solvent such as hexane,  $\text{C}_6\text{H}_{12}$ :

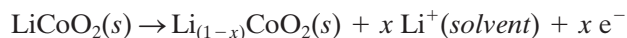


After the lithium chloride is separated by filtration, the solvent can be removed by distillation; liquid butyllithium remains in the distillation vessel. This compound has to be handled carefully because it spontaneously burns when exposed to the dioxygen in air.

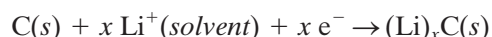
**Lithium Batteries**

Lithium is the most common anode material in new battery technology. With its high reduction potential and very low mass per unit of stored energy, it is currently used in compact high-voltage cells. Because lithium has a density  $\frac{1}{20}$  that of lead, substantial mass savings are possible once the very challenging task of devising an inexpensive reversible (rechargeable) lithium cycle is perfected. Thus, the lithium battery is strongly favored to replace the lead-acid battery for electric vehicle propulsion.

Lithium batteries are now becoming commonplace, but there are, in fact, many types of them. The lithium ion rechargeable battery is used in portable computers and cell phones. The anode consists of lithium cobalt(III) oxide,  $\text{LiCoO}_2$ , the cathode is graphite, and an organic liquid is used as the electrolyte. In the charging cycle, at the cathode, lithium ions are released into the solution as electrons are removed from the electrode. Charge balance is maintained by one cobalt(III) ion being oxidized to cobalt(IV) for each lithium ion released:



At the anode, lithium ions enter between the graphite layers and are reduced to lithium metal. This insertion of a “guest” atom into a “host” solid, a process accompanied by only small, reversible changes in structure, is known as *intercalation*, and the resulting product is called an *intercalation compound*:



The discharge of the cell corresponds to the reverse reactions.

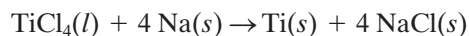
There are many other lithium batteries using different electrode materials. Some of the electrode materials and the battery codes are as follows: manganese(IV) oxide (CR), polycarbonmonofluoride (BR), vanadium(V) oxide (VL), and manganese oxide with lithium-aluminum cathode (ML). In most of these cells, the transition metal serves as part of the redox system, oscillating between two oxidation states, (IV)  $\leftrightarrow$  (III) for manganese and (V)  $\leftrightarrow$  (IV) for vanadium.

## 11.6 Sodium

Sodium is the alkali metal for which there is the highest industrial demand. Like all the alkali metals, the pure element does not exist naturally because of its very high reactivity.

### Uses of Sodium

Sodium metal is required for the synthesis of a large number of sodium compounds, but it is also used in the extraction of other metals. The easiest way to obtain many of the rarer metals such as thorium, zirconium, tantalum, and titanium is by the reduction of their compounds with sodium. For example, titanium can be obtained by reducing titanium(IV) chloride with sodium metal:



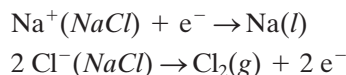
The sodium chloride can then be washed away from the pure titanium metal.

### The Industrial Extraction of Sodium

The silvery metal is manufactured by the Downs process, in which sodium chloride (m.p.  $801^\circ\text{C}$ ) is electrolyzed in the molten state. The electrolysis is done in a cylindrical cell with a central graphite anode and a surrounding steel cathode (Figure 11.6). A mixture of calcium chloride and sodium chloride is

used to reduce the melting point and hence lower the temperature at which the cell needs to be operated. Although calcium chloride itself has a melting point of 772°C, a mixture of 33 percent sodium chloride and 67 percent calcium chloride has a melting point of about 580°C. It is the lower melting point of the mixture that makes the process commercially feasible.

The two electrodes are separated by a cylindrical steel gauze diaphragm so that the molten sodium, which floats to the top of the cathode compartment, will be kept away from the gaseous chlorine formed at the anode:

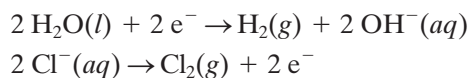


The sodium metal produced contains about 0.2 percent calcium metal. Cooling the metal mixture to 110°C allows the calcium impurity (m.p. 842°C) to solidify and sink into the melt. The pure sodium (m.p. 98°C) remains liquid and can be pumped into cooled molds, where it solidifies.

## 11.7 Sodium Hydroxide

### The Industrial Synthesis of Sodium Hydroxide

Sodium hydroxide is the sixth most important inorganic chemical in terms of quantity produced. It is prepared by the electrolysis of brine (aqueous sodium chloride). The diaphragm cell is used to produce commercial sodium hydroxide. In this cell, water is reduced to hydrogen gas and hydroxide ion at the cathode, and chloride ion is oxidized to chlorine gas at the anode (although some water is oxidized to oxygen gas as well):

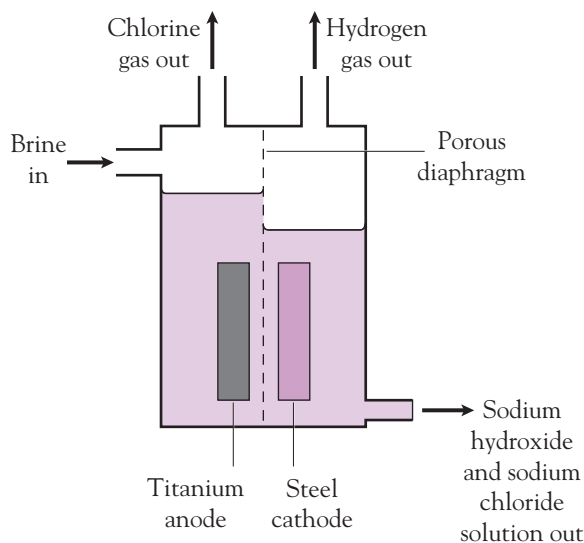


The essential design feature (Figure 11.7) is the diaphragm or separator, which prevents the hydroxide ion produced at the cathode from coming into contact with the chlorine gas produced at the anode. This separator, which has pores that are large enough to allow the brine to pass through, used to be made of asbestos but is now made of a Teflon mesh. The cells use prodigious quantities of electricity, typically between 30 000 and 150 000 Å.

During the electrolysis, the cathode solution, which consists of a mixture of 11 percent sodium hydroxide and 16 percent sodium chloride, is removed continuously. The harvested solution is evaporated, a process that causes the less soluble sodium chloride to crystallize. The final product is a solution of 50 percent sodium hydroxide and about 1 percent sodium chloride. This composition is quite acceptable for most industrial purposes.

### Commercial Uses of Sodium Hydroxide

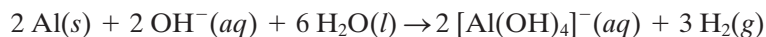
About 30 percent of sodium hydroxide production is used as a reagent in inorganic chemical plants, and about 20 percent is used for the synthesis of other



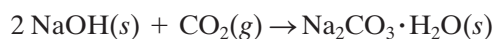
**FIGURE 11.7** A diaphragm cell.

inorganic chemicals. Another 20 percent is consumed in the pulp and paper industry, and the remaining 30 percent is used in hundreds of other ways.

Sodium hydroxide is the most important base in the chemistry laboratory. It also has a number of household uses, where it is commonly referred to as lye. The most direct application takes advantage of its reaction with greases, particularly those in ovens (such as Easy-Off Oven Cleaner<sup>®</sup>) or those clogging drains (such as Drano<sup>®</sup>). In some commercial drain-treatment products, aluminum metal is mixed with the sodium hydroxide. When added to water, the following chemical reaction occurs, producing the aluminate ion and hydrogen gas. The hydrogen gas bubbles cause the liquid to churn vigorously, enhancing the contact of grease with fresh sodium hydroxide solution, an action that dissolves the plug more quickly:



Sodium hydroxide is also used in the food industry, mainly to provide hydroxide ion for breaking down proteins. For example, potatoes are sprayed with sodium hydroxide solution to soften and remove the skins before processing. (Of course, they are washed thoroughly before the next processing step!) Olives have to be soaked in sodium hydroxide solution to soften the flesh enough to make them edible. Grits, too, are processed with sodium hydroxide solution. The most unusual application is in the manufacture of pretzels. The dough is coated with a thin layer of sodium hydroxide solution before salt crystals are applied. The sodium hydroxide appears to function as a cement, attaching the salt crystals firmly to the dough surface. In the baking process, carbon dioxide is released, thereby converting the sodium hydroxide to harmless sodium carbonate monohydrate:



Salt was one of the earliest commodities to be traded, and 2000 years ago, Roman soldiers were partially paid in salt (*sal*)—hence our term *salary* for pay.

## 11.8 Sodium Chloride

Seawater is a 3 percent solution of sodium chloride, together with many other minerals. It has been calculated that the sea contains 19 million m<sup>3</sup> of salt—about one and a half times the volume of all North America above sea level. The salt produced by using the Sun's energy to evaporate seawater used to be a major source of income for some Third World countries, such as the Turks and Caicos Islands. Unfortunately, production of salt by this method is no longer economically competitive, and the ensuing loss of income and employment has caused serious economic problems for these countries.

Even today, salt is a vital commodity. More sodium chloride is used for chemical manufacture than any other mineral, with world consumption exceeding 150 million tonnes per year. Today, almost all commercially produced sodium chloride is extracted from vast underground deposits, often hundreds of meters thick. These beds were produced when large lakes evaporated to dryness hundreds of millions of years ago. About 40 percent of the rock salt is mined like coal, and the remainder is extracted by pumping water into the deposits and pumping out the saturated brine solution.

## 11.9 Sodium Carbonate and Sodium Hydrogen Carbonate

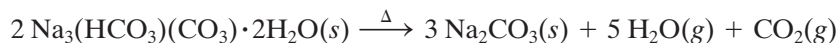
The alkali metals (and ammonium ion) form the only soluble carbonates. Sodium carbonate, the most important of the alkali metal carbonates, exists in the anhydrous state (soda ash), as a monohydrate, Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O, and most commonly as the decahydrate, Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O (washing soda). The large transparent crystals of the decahydrate *effloresce* (lose water of crystallization) in dry air to form a powdery deposit of the monohydrate:



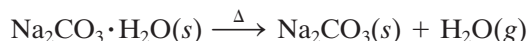
### The Industrial Extraction of Sodium Carbonate

Sodium carbonate is the ninth most important inorganic compound in terms of quantity used. In North America, the compound is obtained from the mineral *trona*, which contains about 90 percent of a mixed carbonate–hydrogen carbonate, Na<sub>2</sub>CO<sub>3</sub>·NaHCO<sub>3</sub>·2H<sub>2</sub>O, commonly called sodium sesquicarbonate. *Sesqui* means “one and one-half,” and it is the number of sodium ions per carbonate unit in the mineral. Sodium sesquicarbonate is not a mixture of the two compounds but a single compound in which the crystal lattice contains alternating carbonate and hydrogen carbonate ions interspersed with sodium ions and water molecules in a 1:1:3:2 ratio; that is, Na<sub>3</sub>(HCO<sub>3</sub>)(CO<sub>3</sub>)·2H<sub>2</sub>O. By far the largest quantity of trona in the world, 4.5 × 10<sup>10</sup> tonnes, is found in Wyoming.

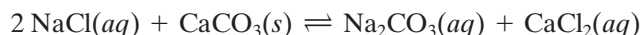
In the monohydrate process of extraction, trona is mined like coal about 400 m underground, crushed, and then heated (calcined) in rotary kilns. This treatment converts the sesquicarbonate to carbonate:



The resulting sodium carbonate is dissolved in water and the insoluble impurities are filtered off. The sodium carbonate solution is then evaporated to dryness, thereby producing sodium carbonate monohydrate. Heating this product in a rotary kiln gives the anhydrous sodium carbonate:



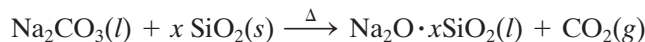
Elsewhere in the world, sodium hydrogen carbonate (and from it, the carbonate) is made by the *Solvay*, or ammonia-soda, *process*. This process involves the reaction of sodium chloride with calcium carbonate:



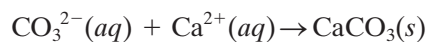
However, the equilibrium position for this reaction lies far to the left. With the use of aqueous ammonia, through a series of ingenious reaction steps, the above overall reaction can be accomplished. The problem with the Solvay process is the amount of the by-product calcium chloride that is produced: the demand for calcium chloride is much less than the supply from this reaction. Furthermore, the process is quite energy intensive, making it more expensive than the simple method of extraction from trona.

### Commercial Uses of Sodium Carbonate

About 50 percent of the U.S. production of sodium carbonate is used in glass manufacture. In the process, the sodium carbonate is reacted with silicon dioxide (sand) and other components at about 1500°C. The actual formula of the product depends on the stoichiometric ratio of reactants (the process is discussed in more detail in Chapter 14, Section 14.14). The key reaction is the formation of a sodium silicate and carbon dioxide:



Sodium carbonate is also used to remove alkaline earth metal ions from water supplies by converting them to their insoluble carbonates, a process called water “softening.” The most common ion that needs to be removed is calcium. Very high concentrations of this ion are found in water supplies that have come from limestone or chalk geological formations:



### Sodium Hydrogen Carbonate

The alkali metals, except for lithium, form the only solid hydrogen carbonates (commonly called bicarbonates). Once again, the notion that low-charge-density cations stabilize large low-charge anions can be used to explain the existence of these hydrogen carbonates. Sodium hydrogen carbonate is less



water-soluble than sodium carbonate. Thus, it can be prepared by bubbling carbon dioxide through a saturated solution of the carbonate:

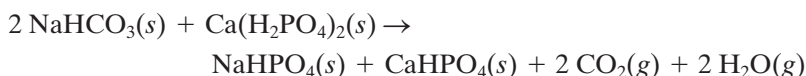


Heating sodium hydrogen carbonate causes it to decompose back to sodium carbonate:



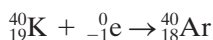
This reaction provides one application of sodium hydrogen carbonate, the major component in dry powder fire extinguishers. The sodium hydrogen carbonate powder itself smothers the fire, but in addition, the solid decomposes to give carbon dioxide and water vapor, themselves fire-extinguishing gases.

The main use of sodium hydrogen carbonate is in the food industry to cause bakery products to rise. It is commonly used as *baking powder*, a mixture of sodium hydrogen carbonate and calcium dihydrogen phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , with some starch added as a filler. The calcium dihydrogen phosphate is acidic and, when moistened, reacts with the sodium hydrogen carbonate to generate carbon dioxide:



## 11.10 Potassium

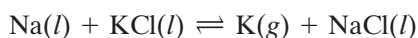
The potassium found in the natural environment is slightly radioactive because it contains about 0.012 percent of the radioactive isotope potassium-40. In fact, a significant proportion of the radiation generated within our bodies comes from this isotope, which has a half-life of  $1.3 \times 10^9$  years. Approximately 89 percent of the potassium atoms decay by emitting an electron, while the other 11 percent decay by capturing an electron (evidence that electron density does penetrate the nucleus):



The ratio of potassium-40 to argon-40 is one way of dating rocks in that once the magma solidifies, the argon formed will be trapped within the rock structure.

### The Industrial Extraction of Potassium

Potassium metal is produced commercially by chemical means. Extraction in an electrolytic cell would be too hazardous because of the extreme reactivity of the metal. The chemical process involves the reaction of sodium metal with molten potassium chloride at 850°C:

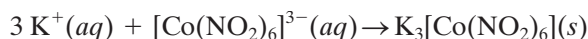


Although the equilibrium lies to the left, at this temperature potassium is a gas (b.p. 766°C; b.p. for sodium is 890°C)! Thus, the Le Châtelier principle can be

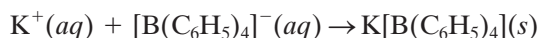
used to drive the reaction to the right by pumping the green potassium gas from the mixture as it is formed.

### Insoluble Potassium Compounds

We have already mentioned that alkali metal salts exhibit a wide range of solubilities. In particular, the least soluble are those with the greatest similarity in ion size. Thus, a very large anion would form the least soluble salts with the larger cations of Group 1. This concept holds for the very large hexanitritocobaltate(III) anion,  $[\text{Co}(\text{NO}_2)_6]^{3-}$ . Its salts with lithium and sodium are soluble, whereas those with potassium, rubidium, and cesium are insoluble. Thus, if a solution is believed to contain either sodium or potassium ion, addition of the hexanitritocobaltate(III) ion can be used as a test. A bright yellow precipitate indicates the presence of potassium ion:



Another very large anion that can be used in a precipitation test with the larger alkali metals is the tetraphenylborate ion,  $[\text{B}(\text{C}_6\text{H}_5)_4]^-$ :



## 11.11 Potassium Chloride

Like sodium chloride, potassium chloride (commonly called *potash*) is recovered from ancient dried lake deposits, many of which are now deep underground. About half of the world's reserves of potassium chloride lie under the Canadian provinces of Saskatchewan, Manitoba, and New Brunswick. As the ancient lakes dried, all their soluble salts crystallized. Hence, the deposits are not of pure potassium chloride but also contain crystals of sodium chloride; potassium magnesium chloride hexahydrate,  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ; magnesium sulfate monohydrate,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ; and many other salts.

To separate the components, several different routes are used. One employs the differences in solubility: the mixture is dissolved in water and then the salts crystallize out in sequence as the water evaporates. However, this process requires considerable amounts of energy to vaporize the water. A second route involves adding the mixture of crystals to saturated brine. When air is blown through the slurry, the potassium chloride crystals adhere to the bubbles. The potassium chloride froth is then skimmed off the surface. The sodium chloride crystals sink to the bottom and can be dredged out.

The third route is most unusual, because it is an electrostatic process. The solid is ground to a powder, and an electric charge is imparted to the crystals by a friction process. The potassium chloride crystals acquire a charge that is the opposite of that of the other minerals. The powder is then poured down a tower containing two highly charged drums. The potassium chloride adheres to one drum, from which it is continuously removed, and the other salts adhere to the oppositely charged drum. Unfortunately, the reject minerals from potash processing have little use, and their disposal is a significant problem.

There is just one use for all this potassium chloride—as fertilizer. Potassium ion is one of the three essential elements for plant growth (nitrogen and phosphorus being the other two), and about  $4.5 \times 10^7$  tonnes of potassium chloride are used worldwide for this purpose every year, so it is a major chemical product.

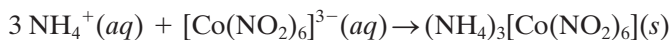
### 11.12 Ammonium Ion as a Pseudo-Alkali Metal Ion

Some polyatomic ions resemble element ions in their behavior, and, in a few cases, there is a molecule that corresponds to the matching element. We can define this unusual category as:

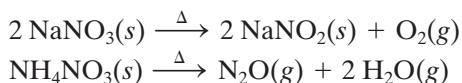
**A polyatomic ion whose behavior in many ways mimics that of an ion of an element or of a group of elements.**

Even though the ammonium ion is a polyatomic cation containing two non-metals, it behaves in many respects like an alkali metal ion. The similarity results from the ammonium ion being a large low-charge cation just like the cations of the alkali metals. In fact, the radius of the ammonium ion (151 pm) is very close to that of the potassium ion (152 pm). However, the chemistry of ammonium salts more resembles that of rubidium or cesium ions, perhaps because the ammonium ion is not spherical and its realistic radius is larger than its measured value. The similarity to the heavier alkali metals is particularly true of the crystal structures. Ammonium chloride, like rubidium and cesium chloride, has a CsCl structure at high temperatures and a NaCl structure at low temperatures.

The ammonium ion resembles an alkali metal ion in its precipitation reactions. Although all simple sodium compounds are water soluble, there are insoluble compounds of the heavier alkali metal ions with very large anions. We find that the ammonium ion gives precipitates with solutions of these same anions. A good example is the hexanitritocobaltate(III) ion,  $[\text{Co}(\text{NO}_2)_6]^{3-}$ , which is commonly used as a test in qualitative analysis for the heavier alkali metals. A bright yellow precipitate is obtained with the ammonium ion analogously to potassium, rubidium, and cesium ions:



However, the similarity does not extend to all chemical reactions that these ions undergo. For example, gentle heating of alkali metal nitrates gives the corresponding nitrite and oxygen gas, but heating ammonium nitrate results in decomposition of the cation and anion to give dinitrogen oxide and water:



A major weakness of the parallel between ammonium ion and the heavier alkali metal ions is that the parent pseudo-element of the ammonium ion, “ $\text{NH}_4$ ,” cannot be isolated.

## 11.13 Biological Aspects

### Lithium and Mental Health

Lithium is used as a treatment of bipolar disorder (commonly called *manic depression*). Biochemists have shown that lithium ion functions in part by substituting for magnesium in an enzyme process, possibly as a result of the diagonal relationship between the two ions (see Chapter 9, Section 9.5). About 1 percent of the population suffers from this debilitating illness, in which one's moods oscillate from euphoria and hyperactivity to depression and lethargy. Lithium ion is a mood-stabilizing drug.

Lithium's benefits were discovered through a combination of accident (serendipity) and observation. In 1938, an Australian psychiatrist, J. Cade, was studying the effects of a large organic anion on animals. To increase the dosage, he needed a more soluble salt. For large anions, the solubilities of the alkali metal ions increase as their radius decreases; hence, he chose the lithium salt. However, when he administered this compound, the animals started to show behavioral changes. He realized that the lithium ion itself must have altered the workings of the brain. Further studies showed that the lithium ion had a profound effect on bipolar disorder patients.

Ironically, the discovery of the health effects of lithium could have been made much earlier because it had been well known in folk medicine that water from certain lithium-rich British springs helped alleviate the disorder. More recently, a study in Texas has shown that areas having lower levels of hospital admissions with bipolar disorder correlated with higher levels of lithium ion in the local drinking water.

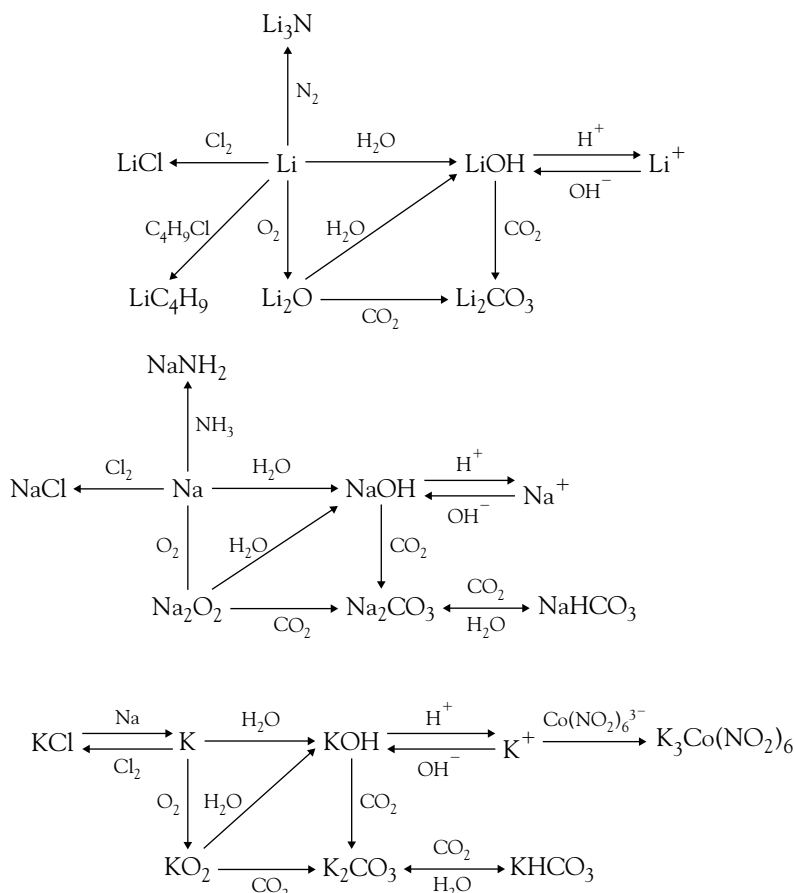
It is a particular imbalance of neurotransmitters that gives rise to the bipolar disorder symptoms. This imbalance can be traced back to the enzyme inositol-monophosphatase (abbreviated IMPase). IMPase converts the monophosphates of inositol, a sugar-like molecule, to free inositol, a process requiring the participation of two magnesium ions. It appears that lithium will readily substitute for one of the magnesium ions in the enzyme pathway, slowing down the process. This alleviates the mood swings, a preferable solution compared to using drug combinations that will subdue the manic phase or counter depressive episodes.

Lithium therapy does have its problems. Side effects include excessive thirst, memory problems, and hand tremor. Additionally, Bertrand's rule curve (see Chapter 2, Context) is very narrow; that is, there is only a very small range between therapeutic and toxic doses. Despite its problems, lithium therapy has restored the health of enormous numbers of individuals.

## 11.14 Element Reaction Flowcharts

The three most important elements of this group are lithium, sodium, and potassium; flowcharts are shown for these three elements. Remember, only

interrelated reactions are shown in these flowcharts, not all of the important reactions.



## KEY IDEAS

- As metals, the Group 1 elements have very low densities, melting points, and boiling points.
- The alkali metals have a very high chemical reactivity.
- The large alkali metal cations (lithium is the exception) stabilize large, low-charge anions.
- Group 1 ion salts are soluble except the heavier metal ions (potassium through cesium) with very large anions.
- Reaction of the metals with oxygen leads to different products, depending on the cation size.
- In many ways, the ammonium ion behaves like an alkali metal ion.

## EXERCISES

**11.1** Write balanced chemical equations for each of the following reactions:

- sodium metal with water
- rubidium metal with dioxygen
- solid potassium hydroxide with carbon dioxide
- heating solid sodium nitrate

**11.2** Write balanced chemical equations for each of the following reactions:

- lithium metal with dinitrogen
- solid cesium dioxide(1-) with water
- heating solid sodium hydrogen carbonate
- heating solid ammonium nitrate

**11.3** In what ways do the alkali metals resemble “typical” metals? In what ways are they very different?

**11.4** Which is the least reactive alkali metal? Why is this unexpected on the basis of standard oxidation potentials? What explanation can be provided?

**11.5** Describe three of the common features of the chemistry of the alkali metals.

**11.6** An alkali metal, designated as M, forms a hydrated sulfate,  $M_2SO_4 \cdot 10H_2O$ . Is the metal more likely to be sodium or potassium? Explain your reasoning.

**11.7** Suggest a possible reason why sodium hydroxide is much more water-soluble than sodium chloride.

**11.8** In the Downs cell for the preparation of sodium metal,

- (a) why can't the electrolysis be performed in aqueous solution?
- (b) why is calcium chloride added?

**11.9** Why is it important to use a temperature of about  $850^\circ\text{C}$  in the extraction of potassium metal?

**11.10** Describe the advantages and disadvantages of the diaphragm cell for the production of sodium hydroxide.

**11.11** Several of the alkali metal compounds have common names. Give the systematic name corresponding to (a) caustic soda; (b) soda ash; (c) washing soda.

**11.12** Several of the alkali metal compounds have common names. Give the systematic name corresponding to (a) caustic potash; (b) trona; (c) lye.

**11.13** Explain what is meant by (a) efflorescence; (b) intercalation.

**11.14** Explain what is meant by (a) supermetals; (b) deliquescent.

**11.15** Write the chemical equations for the reactions involved in the Solvay synthesis of sodium carbonate. What are the two major problems with this process?

**11.16** Explain briefly why only the alkali metals form solid, stable hydrogen carbonate salts.

**11.17** Explain briefly why the ammonium ion is often referred to as a pseudo-alkali metal.

**11.18** Construct an approximate molecular orbital diagram to depict the bonding in the gaseous lithium hydride molecule.

**11.19** Suggest two reasons why potassium dioxide(1–), not cesium dioxide(1–), is used in spacecraft air recirculation systems.

**11.20** Suggest which of the following anions is likely to give a precipitate with the ammonium ion: phosphate,  $\text{PO}_4^{3-}$ , or tetraphenylborate,  $[\text{B}(\text{C}_6\text{H}_5)_4]^-$ . Give your reason.

**11.21** Of the alkali metals, the ammonium ion most closely resembles the rubidium or cesium ion. Explain.

**11.22** Where are the sodium ions and potassium ions located with respect to living cells?

**11.23** Write balanced chemical equations corresponding to each transformation in the element reaction flowcharts for lithium, sodium, and potassium (page 286).

## BEYOND THE BASICS

**11.24** In this chapter, we have ignored the radioactive member of Group 1, francium. On the basis of group trends, suggest the key properties of francium and its compounds.

**11.25** What minimum current at 7.0 V, assuming 100 percent efficiency, would be needed in a Downs cell to produce 1.00 tonne of sodium metal per day? (Passage of 1 mol of electrons requires  $9.65 \times 10^4 \text{ A}\cdot\text{s}^{-1}$ ; that is, 1 Faraday of electricity.)

**11.26** Platinum hexafluoride,  $\text{PtF}_6$ , has an extremely high electron affinity ( $772 \text{ kJ}\cdot\text{mol}^{-1}$ ). Yet, when lithium metal is reacted with platinum hexafluoride, it is lithium fluoride,  $\text{Li}^+\text{F}^-$ , not  $\text{Li}^+\text{PtF}_6^-$ , that is formed. Suggest a reason.

**11.27** Suggest an explanation why  $\Delta_f H^\ominus$  becomes less negative along the series  $\text{LiF}$ ,  $\text{NaF}$ ,  $\text{KF}$ ,  $\text{RbF}$ ,  $\text{CsF}$ , while it becomes more negative along the series  $\text{LiI}$ ,  $\text{NaI}$ ,  $\text{KI}$ ,  $\text{RbI}$ ,  $\text{CsI}$ .

**11.28** The atomic mass of lithium is listed as  $6.941 \text{ g}\cdot\text{mol}^{-1}$ . However, lithium compounds are not used as primary analytical standards since the atomic mass of the lithium is often about  $6.97 \text{ g}\cdot\text{mol}^{-1}$ . Suggest an explanation for this.

**11.29** Which compound, sodium fluoride or sodium tetrafluoroborate,  $\text{Na}[\text{BF}_4]$ , is likely to be the more soluble in water? Give your reasoning.

**11.30** Determine whether the theoretical cesium(II) fluoride,  $\text{CsF}_2$ , will spontaneously decompose into cesium fluoride:



given that the lattice energy of  $\text{CsF}_2$  is  $2250 \text{ kJ}\cdot\text{mol}^{-1}$ . The second ionization energy of cesium is  $2.430 \text{ MJ}\cdot\text{mol}^{-1}$ . Obtain all additional data from the appendices. This calcu-

lation will only provide the enthalpy change. For spontaneity we need to find the free energy change from the entropy and enthalpy data. Will the entropy change also favor decomposition? Give your explanation.

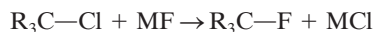
**11.31** From lattice dimension, the hydride ion appears to have a radius of 130 pm in lithium hydride but 154 pm in cesium hydride. Suggest a reason for the difference in the two values.

**11.32** Solid cesium chloride will react with hydrogen chloride gas to give a compound containing a polyatomic anion. Write the formula of the anion. Lithium chloride does not react with hydrogen chloride. Suggest a reason why this reaction does not occur.

**11.33** A solution containing equimolar concentrations of the ions  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{F}^-$ , and  $\text{I}^-$  is evaporated to dryness. Which

salts will crystallize out,  $\text{LiF}$  and  $\text{KI}$  or  $\text{LiI}$  and  $\text{KF}$ ? Check your answer by working out the energetically preferred lattice energies (use the Kapustinskii equation—Chapter 6, Section 6.1).

**11.34** In the high-temperature/pressure organic substitution reaction of a carbon-chlorine bond with a carbon-fluorine bond using an alkali metal fluoride,  $\text{MF}$ :



Why is the use of potassium fluoride preferred to that of sodium fluoride?

**11.35** Suggest why the decay of potassium-40 should most likely lead to the formation of calcium-40.

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

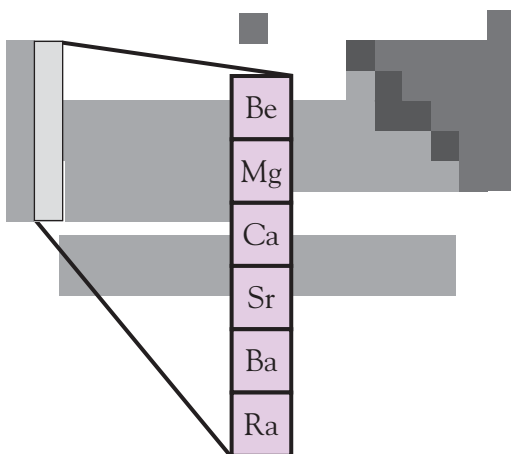


For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# THE GROUP 2 ELEMENTS:

## The Alkaline Earth Metals

## CHAPTER 12



Be
Mg
Ca
Sr
Ba
Ra

Although harder, denser, and less reactive than the alkali metals, the alkaline earth metals are more reactive and of lower density than a “typical” metal.

### Context: Calcium and magnesium—another biological balance

Just as organisms need a balance of sodium ion and potassium ion, so too there is a balance of the Group 2 metal ions, magnesium and calcium. Mirroring the alkali metal ions, magnesium ions are concentrated within cells, whereas calcium ions are concentrated in the extracellular fluids.

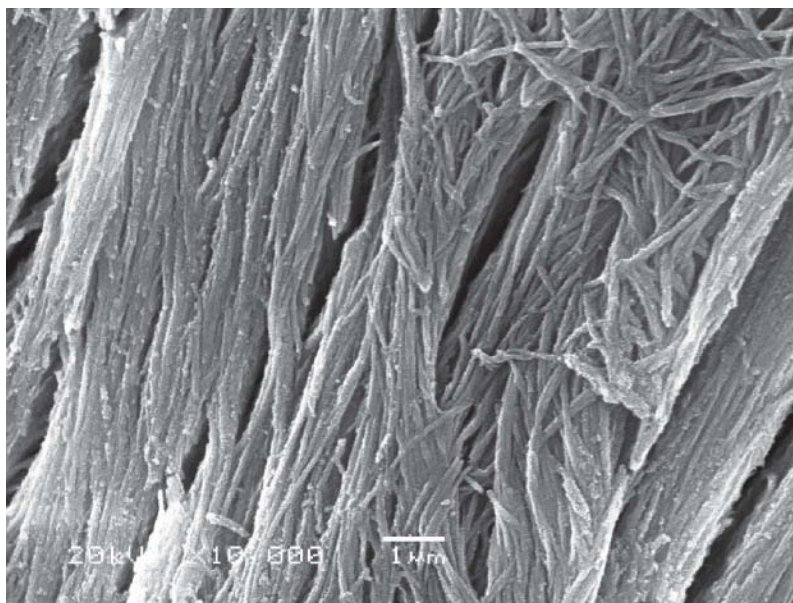
Calcium acts as a cell messenger and every muscle contraction, including the heart, involves calcium. Calcium deficiency can lead to osteoporosis and a range of other symptoms such as easy bruising, pins and needles sensation, and irregular heartbeat. High levels of calcium can cause kidney stones, bone pain, and nausea. Magnesium is found in every living cell, and is involved in the release of energy by adenosine triphosphate, ATP (see Chapter 15). Magnesium deficiency can cause dizziness, cramps, irregular heartbeat, and low calcium levels. Excessive magnesium intake can lead to nausea, low blood pressure, and heart attack.

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 12.1 Group Trends
- 12.2 Features of Alkaline Earth Metal Compounds
- 12.3 Trends in Alkaline Earth Metal Oxides
- 12.4 Beryllium
- 12.5 Magnesium
- 12.6 Calcium Carbonate
- 12.7 Cement
- 12.8 Calcium Chloride
- 12.9 Calcium Sulfate
- 12.10 Calcium Carbide
- 12.11 Biological Aspects
- 12.12 Element Reaction Flowcharts



Of the close to 1 kg of calcium in our bodies, 98% of it is in bone. This point illustrates a major difference between the Groups 1 and 2 ions. For Group 1, all common compounds are soluble. With Group 2, as we show in Section 12.2, there are major changes in solubility down the Group. In particular, descending the Group, the solubilities of Group 2 metal ions with high-charge anions decreases dramatically. The inorganic component of bone, calcium hydroxidophosphate, commonly written as  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , is a key example. It is the calcium compound, not the more soluble magnesium compound, which provides the highly insoluble inorganic component of bone.



A microphotograph of the calcium hydroxidophosphate crystals in the structure of bone.

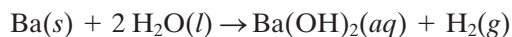
The crystals in bone illustrate three other important factors in inorganic chemistry. First, a higher lattice energy can sometimes be obtained by alternating different ions. In the case of natural bone, if each fourth anion is mono-negative hydroxide, a particularly stable lattice is formed. Second, bone is an example of biomineralization (see Section 12.12). That is, the cells crystallize the compound, not in chunky crystals as we synthesize in the laboratory, but in long interwoven needles to give bone strength. Third, although we write a simplistic formula for the inorganic compound, it is in fact an approximation. As discussed in Chapter 5, Section 5.8, compounds are not always precisely stoichiometric, for bone, it is found that hydrogen phosphate ions, carbonate ions, and even some magnesium ions are trapped in the structure.

## 12.1 Group Trends

In this section, we consider the properties of magnesium, calcium, strontium, and barium. Beryllium is discussed separately because it behaves chemically more like a metalloid. The properties of radium, the radioactive member of the group, are not known in as much detail.

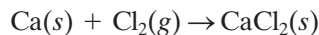
The alkaline earth metals are silvery and of fairly low density. As with the alkali metals, density generally increases with increasing atomic number (Table 12.1). The stronger metallic bonding of the alkaline earth metals is also reflected in both their higher melting points and their greater hardness. Although the metal density shows an increasing trend down the group, there are no clear patterns in melting points.

The alkaline earth metals are less chemically reactive than are the alkali metals, but they are still more reactive than the majority of the other metallic elements. For example, calcium, strontium, and barium all react with cold water, with barium reacting the most vigorously of all:

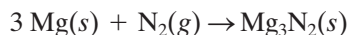


As with the alkali metals, reactivity increases as mass increases within the group. Thus, magnesium does not react with cold water, but it will react slowly with hot water to produce magnesium hydroxide and hydrogen gas.

The alkaline earth metals also react with many nonmetals. For example, heated calcium burns in chlorine gas to give calcium chloride:



The alkaline earth metals are unusual in a readiness to react with nitrogen gas on heating. For example, magnesium reacts with dinitrogen to form magnesium nitride:



VIDEO CLIP

**TABLE 12.1** Melting points and densities of the alkaline earth metals

Element	Melting point (°C)	Density (g·cm <sup>-3</sup> )
Mg	649	1.74
Ca	839	1.55
Sr	768	2.63
Ba	727	3.62

**WORKED EXAMPLE 12.1**

Would radium be expected to react with water? If so, write a balanced equation for the reaction.

**Answer**

As reactivity with water increases down the Group, radium would be expected to react violently with water to give radium hydroxide and hydrogen gas:

**12.2 Features of Alkaline Earth Metal Compounds**

We again exclude beryllium from the discussion because its properties are very different from those of the other members of Group 2. The alkaline earth metal ions always have an oxidation number of +2, and their compounds are mainly stable, colorless, ionic solids—unless a colored anion is present. The bonds in alkaline earth metal compounds are mostly ionic in character, but covalent behavior is particularly evident in compounds of magnesium. (Covalency dominates the chemistry of beryllium.) Unlike the alkali metals, in basic solution, the alkaline metals form insoluble hydroxides (Table 12.2).

**Ion Hydration**

In contrast to the larger, low-charge-density alkali metal ions, the salts of the smaller, higher-charge-density alkaline earth metal ions are almost always hydrated. For example, calcium chloride can be prepared as the hexahydrate, tetrahydrate, dihydrate, and monohydrate in addition to its anhydrous form. Table 12.3 shows the usual hydration number (number of molecules of water of crystallization) of some common alkaline earth metal compounds. As the charge density of the metal becomes smaller, so does the hydration number. Paradoxically, the hydroxides of strontium and barium are octahydrates, whereas those of magnesium and calcium are anhydrous.

**TABLE 12.2** A comparison of magnesium, calcium, and barium species under oxidizing conditions

	Very Acidic	Acidic	Basic	Very Basic
Magnesium	$\text{Mg}^{2+}(aq)$		$\text{Mg}(\text{OH})_2(s)$	
Calcium	$\text{Ca}^{2+}(aq)$			$\text{Ca}(\text{OH})_2(s)$
Barium	$\text{Ba}^{2+}(aq)$			$\text{Ba}(\text{OH})_2(s)$

**TABLE 12.3** Usual hydration number of common alkaline earth metal salts

Element	MCl <sub>2</sub>	M(NO <sub>3</sub> ) <sub>2</sub>	MSO <sub>4</sub>
Mg	6	6	7
Ca	6	4	2
Sr	6	4	0
Ba	2	0	0

### Patterns in Solubility of Alkaline Earth Metal Salts

Whereas all the common Group 1 salts are water soluble, many of those of Group 2 are insoluble. Generally it is the compounds with mono-negative anions, such as chloride and nitrate, that are soluble, and those with more than one negative charge, such as carbonate and phosphate, that are insoluble. A few salts of anions show striking trends in solubility: the sulfates change from soluble to insoluble down the Group, whereas the hydroxides change from insoluble to soluble (Table 12.4).

Barium atoms are strong absorber of X-rays. This is an important property in the context of visualizing the stomach and intestine for medical purposes. The elements in the soft tissues do not absorb X-rays. Because barium ion is such a good X-ray absorber, swallowing a solution containing barium should be an obvious way of imaging these organs. There is one disadvantage—barium ion is very poisonous. Fortunately, barium forms an extremely insoluble salt, barium sulfate. This compound is so insoluble ( $2.4 \times 10^{-3} \text{ g}\cdot\text{L}^{-1}$ ) that a slurry in water, the so called “barium meal,” can be safely swallowed, the organs X-rayed, and the compound later excreted.

### Thermodynamic Factors of the Solubility of Alkaline Earth Compounds

In Chapter 11, Section 11.4, we discussed the solubility of alkali metal halides in terms of thermodynamic functions. For the alkaline earth metals, the values of each function differ dramatically from those of the alkali metals, yet the net changes in entropy and enthalpy for the solution process are little different.

**TABLE 12.4** Solubilities of the alkaline earth metal hydroxides and sulfates

Metal	Hydroxide solubility (g·L <sup>-1</sup> )	Sulfate solubility (g·L <sup>-1</sup> )
Mg	0.0001	337
Ca	1.2	2.6
Sr	10	0.013
Ba	47	0.0002

**TABLE 12.5** Enthalpy factors in the solution process for magnesium chloride and sodium chloride

Compound	Lattice energy (kJ·mol <sup>-1</sup> )	Hydration enthalpy (kJ·mol <sup>-1</sup> )	Net enthalpy change (kJ·mol <sup>-1</sup> )
MgCl <sub>2</sub>	+2526	-2659	-133
NaCl	+788	-784	+4

First we will consider the enthalpy factors involved. The initial step of our enthalpy cycle is vaporization of the crystal lattice. For a salt of a di-positive cation, about three times the energy will be needed to vaporize the lattice as is needed for a mono-positive cation because there are much greater electrostatic attractions in the di-positive cation salts (2+ charge with 1- versus 1+ with 1-). Furthermore, per mole, three ions must be separated rather than two. However, the enthalpy of hydration of the di-positive ions will also be much greater than those of the mono-positive alkali metal ions.

As a result of the higher charge densities of the Group 2 ions, the water molecules are more strongly attracted to the “naked” cation, so there is a much greater release of energy when they form a solvation sphere around it. For example, the enthalpy of hydration of the magnesium ion is  $-1921 \text{ kJ}\cdot\text{mol}^{-1}$ , whereas that of the sodium ion is  $-435 \text{ kJ}\cdot\text{mol}^{-1}$  (the ratio of these two values is close to the ratio of their charge densities). Enthalpy data for magnesium chloride and sodium chloride are compared in Table 12.5. As these figures indicate, when (anhydrous) magnesium chloride is dissolved in water, the solution process is noticeably exothermic.

Now we will consider the entropy factors (Table 12.6). The lattice entropy of magnesium chloride is almost exactly one and a half times that of sodium chloride, reflecting the fact that three gaseous ions rather than two are being produced. However, because the magnesium ion has a much higher charge density, the entropy of hydration for the magnesium ion is significantly more negative than that for the sodium ion. There is a much more ordered environment around the magnesium ion, which is surrounded by the strongly held layers of water molecules. Thus, overall, the entropy factors do not favor the solution process for magnesium chloride. Recall that for sodium chloride, it was the entropy factor that favored solution.

**TABLE 12.6** Entropy factors in the solution process for magnesium chloride and sodium chloride, expressed as  $T\Delta S$  values

Compound	Lattice entropy (kJ·mol <sup>-1</sup> )	Hydration entropy (kJ·mol <sup>-1</sup> )	Net entropy change (kJ·mol <sup>-1</sup> )
MgCl <sub>2</sub>	+109	-143	-34
NaCl	+68	-55	+13

**TABLE 12.7** Calculated free energy changes for the solution process for magnesium chloride and sodium chloride

Compound	Enthalpy change (kJ·mol <sup>-1</sup> )	Entropy change (kJ·mol <sup>-1</sup> )	Free energy change (kJ·mol <sup>-1</sup> )
MgCl <sub>2</sub>	-133	-34	-99
NaCl	+4	+13	-11

Combining the enthalpy and entropy terms—keeping in mind that all of the data values have associated errors—we see that the solubility process results primarily from very small differences in very large energy terms (Table 12.7). Furthermore, for magnesium chloride, enthalpy factors favor solution and entropy factors oppose them, a situation that is the converse of that for sodium chloride.

It is the much higher lattice energy that partially accounts for the insolubility of the salts containing di-negative and tri-negative ions. As the charge increases, so does the electrostatic attraction that must be overcome in the lattice vaporization step. At the same time, there are fewer ions (two for the metal sulfates compared to three for the metal halides); hence, the total ion hydration enthalpy will be less than that for the salts with mono-negative ions. The combination of these two factors, then, is responsible for the low solubility.

**WORKED EXAMPLE 12.2**

Predict which would be the more soluble, MgF<sub>2</sub> or MgCl<sub>2</sub>?

**Answer**

As the F<sup>-</sup> ion is smaller than the Cl<sup>-</sup> ion, the lattice energy of magnesium fluoride will be greater than that of magnesium chloride. Therefore, MgF<sub>2</sub> will be expected to be less soluble than MgCl<sub>2</sub>. This is, in fact, found experimentally. ■

**WORKED EXAMPLE 12.3**

Predict which would be the more soluble, MgCrO<sub>4</sub> or BaCrO<sub>4</sub>?

**Answer**

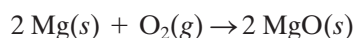
The chromate ion, CrO<sub>4</sub><sup>2-</sup>, is di-negative. Following from the trend in the solubilities of higher-charged anions, we would expect barium chromate to be less soluble than magnesium chromate. In fact, MgCrO<sub>4</sub> is significantly water soluble, while BaCrO<sub>4</sub> is highly insoluble. ■

## 12.3 Trends in Alkaline Earth Metal Oxides

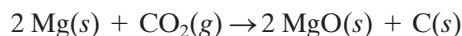
The Group 2 metals burn in air to yield the normal oxides, except for the member of the group with the lowest charge density—barium—which also forms some barium dioxide(2−).

### Magnesium Oxide

When ignited, magnesium metal burns with a bright white light. The intensity of the light is so great that damage to the retina can occur. The combustion of magnesium powder was used in early photography as a source of illumination:



The combustion reaction is so vigorous that it cannot be extinguished by using a conventional fire extinguisher material such as carbon dioxide. Burning magnesium even reacts with carbon dioxide to give magnesium oxide and carbon:

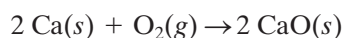


To extinguish reactive metal fires, such as those of magnesium, a class D fire extinguisher must be used (Classes A, B, and C are used to fight conventional fires.) Class D fire extinguishers contain either graphite or sodium chloride. Graphite produces a solid coating of metal carbide over the combusting surface and effectively smothers the reaction. Sodium chloride melts at the temperature of the burning magnesium and forms an inert liquid layer over the metal surface; it too prevents oxygen from reaching the metal.

Magnesium oxide has a very high melting point, 2825°C, so bricks of this compound are useful as industrial furnace linings. Such high-melting materials are known as *refractory compounds*. Crystalline magnesium oxide is an unusual compound because it is a good conductor of heat but a very poor conductor of electricity, even at high temperatures. It is this combination of properties that results in its crucial role in electric kitchen range elements. Magnesium oxide conducts the heat rapidly from a very hot coil of resistance wire to the metal exterior of the element without allowing any of the electric current to traverse the same route. Magnesium oxide is insoluble in water.

### Calcium Oxide

Calcium burns to give only the oxide:



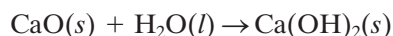
Commonly called *quicklime*, calcium oxide is produced in enormous quantities, particularly for use in steel production (see Chapter 20, Section 20.6) by heating calcium carbonate to over 1170°C:



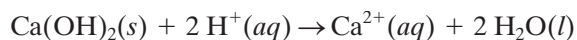
This high-melting oxide is unusual in a different way: when a flame is directed against blocks of calcium oxide, the blocks glow with a bright white light. This phenomenon is called *thermoluminescence*. Before the introduction

of electric light, theaters were lighted by these glowing chunks of calcium oxide; hence, the origin of the phrase “being in the limelight” for someone who attains a prominent position.

Calcium oxide reacts with water to form calcium hydroxide, a product that is referred to as *hydrated lime* or *slaked lime*:

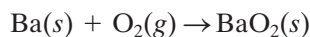
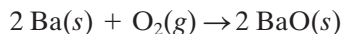


Hydrated lime is sometimes used in gardening to neutralize acid soils; however, it is not a wise way of accomplishing this because an excess of calcium hydroxide will make the soil too basic:



### Barium Oxide

In addition to forming the oxide, barium forms some dioxide(2−) in excess oxygen:



The formation of barium peroxide can be explained in terms of the charge density of barium ion ( $23 \text{ C}\cdot\text{mm}^{-3}$ ), which is as low as that of sodium ( $24 \text{ C}\cdot\text{mm}^{-3}$ ). Cations with such a low charge density are able to stabilize polarizable ions like the dioxide(2−) ion.

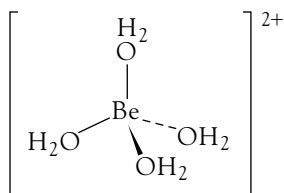
## 12.4 Beryllium

The element beryllium is steel gray and hard; it has a high melting point and a low density. It also has a high electric conductivity, so it is definitely a metal. Because of beryllium's resistance to corrosion, its low density, high strength, and nonmagnetic behavior, beryllium alloys are often used in precision instruments such as gyroscopes. A minor but crucial use is in the windows of X-ray tubes. Absorption of X-rays increases with the square of the atomic number, and beryllium has the lowest atomic number of all the air-stable metals. Hence, it is one of the most transparent materials for the X-ray spectrum.

The sources of beryllium are bertrandite,  $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$ , and the gemstone beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , which occurs in various colors because of trace amounts of impurities. When it is a light blue-green, beryl is called *aquamarine*; when it is deep green, it is called *emerald*. The green color is due to the presence of about 2 percent chromium(III) ion in the crystal structure. Of course, emeralds are not used for the production of metallic beryllium; the very imperfect crystals of colorless or brown beryl are used instead.

The chemistry of beryllium is significantly different from that of the other Group 2 elements because covalent bonding predominates in its compounds. The very small beryllium cation has such a high charge density ( $1100 \text{ C}\cdot\text{mm}^{-3}$ ) that it polarizes any approaching anion, and overlaps of electron density occur. Hence, the simple ionic compounds of beryllium tend to be found as tetrahydrates, such as

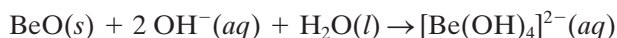
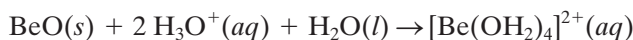




**FIGURE 12.1** Tetrahedral shape of the  $[\text{Be}(\text{OH}_2)_4]^{2+}$  ion.

$\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ , which actually consist of  $[\text{Be}(\text{OH}_2)_4]^{2+} \cdot 2\text{Cl}^-$  ions in the crystal lattice. This tetraaquaberyllium ion,  $[\text{Be}(\text{OH}_2)_4]^{2+}$ , in which the four oxygen atoms of the water molecules are covalently bonded to the beryllium ion, is also the predominant species in aqueous solution. Four coordination is the norm for beryllium, because of the small size of the beryllium ion (Figure 12.1).

Although beryllium is definitely metallic, it has one property that is more characteristic of nonmetals—an ability to form oxyanion species. “Normal” metal oxides generally react with acids to give cations but not with bases to form oxyanions. Thus, beryllium oxide is amphoteric (see Chapter 7, Section 7.5, and Chapter 9, Section 9.4), reacting not only with hydronium ion to form the tetraaquaberyllium ion,  $[\text{Be}(\text{OH}_2)_4]^{2+}$ , but also with hydroxide ion to form the tetrahydroxidoberyllate ion,  $[\text{Be}(\text{OH})_4]^{2-}$ :



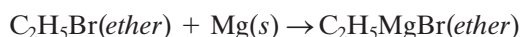
Beryllium and the other metals that exhibit amphoteric behavior (including aluminum and zinc) are sometimes called “weak” metals because they tend to be located close to the metalloids and to the metalloid/nonmetal boundary. In the case of beryllium, it is actually located next to boron, on the metalloid/nonmetal boundary. It is only because we fit the transition metal groups farther down into the short form of the periodic table that there appears to be a gap between beryllium and boron.

## 12.5 Magnesium

Magnesium is found in nature as one component in a number of mixed-metal salts such as carnallite,  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ , and dolomite,  $\text{CaMg}(\text{CO}_3)_2$ . These compounds are not simply mixtures of salts but are pure ionic crystals in which the alternating sizes of the cations provide a higher lattice energy. Thus, carnallite contains arrays of chloride anions with interspersed potassium and magnesium cations and water molecules in a ratio of 3:1:1:6. Another magnesium-containing mineral is magnesium sulfate heptahydrate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , commonly called *Epsom salts*.

### Reactions of Magnesium

The chemistry of magnesium differs from that of the lower Group 2 metals. Of particular importance, magnesium readily forms compounds containing covalent bonds. This behavior can be explained in terms of its comparatively high charge density ( $120 \text{ C} \cdot \text{mm}^{-3}$ ); calcium’s charge density is  $52 \text{ C} \cdot \text{mm}^{-3}$ ). For example, magnesium metal reacts with organic compounds called halocarbons (or alkyl halides) such as bromoethane,  $\text{C}_2\text{H}_5\text{Br}$ , in a solvent such as ethoxyethane,  $(\text{C}_2\text{H}_5)_2\text{O}$ , commonly called *ether*. The magnesium atom inserts itself between the carbon and halogen atoms, forming covalent bonds to its neighbors:

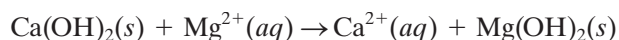


These organomagnesium compounds are referred to as *Grignard reagents*, and they are used extensively as intermediates in synthetic organic chemistry. We discuss Grignard reagents in more detail in Chapter 23, Section 23.4.

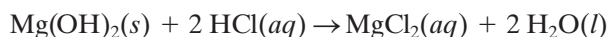
### The Industrial Extraction of Magnesium

Magnesium is the third most common ion in seawater (after sodium ion and chloride ion), and seawater is a major industrial source of this metal. In fact, 1 km<sup>3</sup> of seawater contains about 1 million tonnes of magnesium ion. With 10<sup>8</sup> km<sup>3</sup> of seawater on this planet, there is more than enough magnesium for our needs.

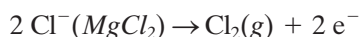
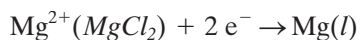
The Dow Chemical Company extraction process is based on the fact that magnesium hydroxide has a lower solubility than calcium hydroxide does. Thus, a suspension of finely powdered calcium hydroxide is added to the seawater, causing magnesium hydroxide to form:



The hydroxide is then filtered off and mixed with hydrochloric acid. The resulting neutralization reaction gives a solution of magnesium chloride:



The solution is evaporated to dryness, and the residue is placed in an electrolytic cell similar to the Downs cell used for the production of sodium. The magnesium collects on the surface of the cathode compartment and is siphoned off. The chlorine gas produced at the anode is reduced back to hydrogen chloride, which is then used to react with more magnesium hydroxide:



Providing an unreactive atmosphere over the molten magnesium is a real problem. For most reactive metal syntheses, such as sodium, the space above the molten metal can be filled with unreactive (and low-cost) nitrogen gas. However, as we discussed earlier, magnesium reacts with dinitrogen. Most plants currently use expensive sulfur hexafluoride, SF<sub>6</sub>, to blanket the molten magnesium to prevent contact with the reactive atmospheric gases. Unfortunately, sulfur hexafluoride is a potent greenhouse gas (see Chapter 16, Section 16.20), and losses to the atmosphere are quite significant. A lesser-used alternative blanketing compound is sulfur dioxide.

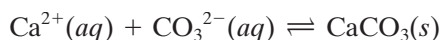
### Uses of Magnesium

Over half of the approximately  $4 \times 10^5$  tonnes of magnesium metal produced worldwide is used in aluminum-magnesium alloys. The usefulness of these alloys is due primarily to their low density. With a density less than twice that of water (1.74 g·cm<sup>-3</sup>), magnesium is the lowest-density construction metal. Such alloys are particularly important wherever the low density provides significant energy savings: in aircraft, railroad passenger cars, rapid transit vehicles, and bus bodies. In the 1970s, these alloys were used in the superstructure of warships because the

lower mass of the ship allowed higher speeds. However, during the Falkland Islands War of 1982, the British Royal Navy discovered a major disadvantage of this alloy—its flammability when subjected to missile attack. The U.S. Navy had already experienced accidents with the same alloy. An appreciation of the high reactivity of the alkaline earth metals might have prevented these mishaps.

## 12.6 Calcium Carbonate

Calcium is the fifth most abundant element on Earth. It is found largely as calcium carbonate in the massive deposits of chalk, limestone, and marble that occur worldwide. Chalk was formed in the seas, mainly during the Cretaceous period, about 135 million years ago, from the calcium carbonate skeletons of countless marine organisms. Limestone was formed in the same seas, but as a simple precipitate, because the solubility of calcium carbonate was exceeded in those waters:



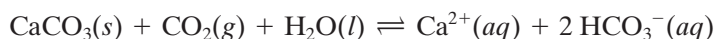
Some deposits of limestone became buried deep in the Earth's crust, where the combination of heat and pressure caused the limestone to melt. The molten calcium carbonate cooled again as it was pushed back up to the surface, eventually solidifying into the dense solid form that we call *marble*.

There are three naturally occurring crystalline forms of calcium carbonate: calcite, aragonite, and vaterite. A form of calcite, known as Iceland spar, is unusual in that it transmits two images of any object placed under it. The two images appear because the crystal has two different indices of refraction. Polarizing microscopes rely on Iceland spar (Nicol prisms) for their functioning. Calcite is thermodynamically favored at room temperature but by less than 5 kJ·mol<sup>-1</sup> over aragonite. Although calcite is by far the most common, aragonite is found in some places. Vaterite is extremely rare.

Both marble and limestone have been used as building materials and for sculptures. Unfortunately, the material is readily attacked by acid rain; thus World Heritage buildings such as the Parthenon in Greece and the Taj Mahal in India are in danger of corroding away:



Caves like Carlsbad Caverns and Mammoth Cave occur in beds of limestone. These structures are formed when rainwater seeps into cracks in the limestone. During the descent of rain through the atmosphere, carbon dioxide dissolves in it. The reaction of this dissolved acid oxide with the calcium carbonate produces a solution of calcium hydrogen carbonate:



The solution is later washed away, leaving a hole in the rock. This is a reversible reaction, and within caves, the evaporation of water from drips of calcium hydrogen carbonate solution results in the formation of calcium carbonate stalagmites and stalactites. This same reaction is causing major concern in the

## How Was Dolomite Formed?

One of the great mysteries of geochemistry is how the mineral dolomite was formed. Dolomite is found in vast deposits, including the whole of the Dolomites, an Italian mountain range. The chemical structure is  $\text{CaMg}(\text{CO}_3)_2$ ; that is, it consists of carbonate ions interspersed with alternating calcium and magnesium ions. Of particular interest, many of the world's hydrocarbon (oil) deposits are found in dolomite rock.

Yet this composition does not form readily. If you mix solutions of calcium ions, magnesium ions, and carbonate ions in the laboratory, you merely obtain a mixture of calcium carbonate crystals and magnesium carbonate crystals. For 200 years, geochemists have struggled with the

problem of how such enormous deposits were formed. To synthesize dolomite, temperatures of over  $150^\circ\text{C}$  are required—not typical conditions on the surface of the Earth! Furthermore, magnesium ion concentrations in seawater are far higher than those of calcium ion.

The most popular idea is that beds of limestone were formed first and then buried deep in the Earth. Water rich in magnesium ion is then postulated to have circulated through pores in the rock, selectively replacing some of the calcium ions with magnesium ions. It seems unlikely for this to have happened uniformly throughout thousands of cubic kilometers of rock, but at this time, it is the best explanation that we have.

context of increased levels of carbon dioxide in the atmosphere. As some of this dissolves in the oceans, so the above equilibrium will shift to the right, inhibiting the formation of corals and of shelled marine organisms.

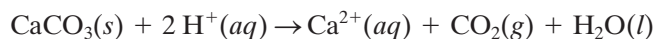
As was mentioned in Chapter 11, Section 11.12, only the alkali metals have a charge density low enough to stabilize the large polarizable hydrogen carbonate ion. Hence, when the water evaporates from the solution of calcium hydrogen carbonate, the compound immediately decomposes back to solid calcium carbonate:



It is deposited calcium carbonate that forms the stalagmites growing up from a cave floor and the stalactites descending from the roof of the cave.

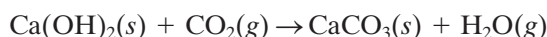
Calcium carbonate is a common dietary supplement prescribed to help maintain bone density. A major health concern today is the low calcium intake among teenagers. Low levels of calcium lead to larger pores in the bone structure, and these weaker structures mean easier bone fracturing and a higher chance of osteoporosis in later life. As we mentioned in the feature “Antacids” in Chapter 7, calcium carbonate is a popular antacid, although it also has a constipative effect. When one is traveling, it is advisable to drink low-mineral-content bottled water rather than local tap water because the tap water might well be significantly higher or lower in either calcium (constipative) or magnesium (laxative) ions than your system has become used to at home, thereby causing undesirable effects. (Of course, in certain parts of the world, there is also the danger of more serious health problems from tap water supplies, such as bacterial and viral infections.)

In the form of powdered limestone (commonly called *agricultural lime*), calcium carbonate is added to farmland to increase the pH by reacting with acids in the soil:



## 12.7 Cement

About 3500 years ago, it was first realized that a paste of calcium hydroxide and sand (mortar) could be used to bind bricks or stones together in the construction of buildings. The material slowly picked up carbon dioxide from the atmosphere, thereby converting the calcium hydroxide back to the hard calcium carbonate from which it had been made:



Lime mortar was perfected by the ancient Romans between 1600 and 2000 years ago. It was used to construct buildings and aqueducts, many of which are still standing. They also made the next important discovery: that mixing volcanic ash with the lime mortar gave a far superior product. This material was the precursor of our modern cements.

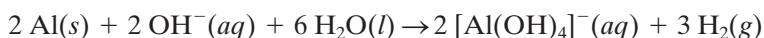
The production of cement is one of the largest modern chemical industries. Worldwide production is about 700 million tonnes, with the United States producing about 10 percent of that figure. Cement is made by grinding together limestone and shale (a mixture of aluminosilicates) and heating the mixture to about 2000°C. The chemical reaction releases large quantities of carbon dioxide and partially melts the components to form solid lumps called *clinker*. Clinker consists of a mixture of about 50 percent tricalcium silicate,  $\text{Ca}_3\text{SiO}_5$ , 30 percent dicalcium silicate,  $\text{Ca}_2\text{SiO}_4$ , and the remainder calcium aluminate,  $\text{Ca}_3\text{Al}_2\text{O}_6$ , and calcium ferroaluminate,  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ . The clinker is mixed with a small quantity of gypsum (calcium sulfate dihydrate) and ground to a fine powder. This mixture is known as *Portland cement*.

To make concrete, the powder is mixed with sand and aggregate (small rocks). Both the sand and aggregate consist of impure silicon dioxide possessing strong network covalent silicon-oxygen bonds. When water is added, the cement undergoes a variety of hydration reactions. A typical idealized reaction can be represented as:



The hydrated silicate, called *tobermorite gel*, forms strong crystals that adhere by means of strong silicon-oxygen bonds to the sand and aggregate, forming a sort of glue between the particles. Thus, the strength of the concrete derives from the network covalent bonds. Because the other product in this reaction is calcium hydroxide, the mixture should be treated as a corrosive material while it is hardening.

Although traditional cement will always be a mainstay of construction, autoclaved aerated concrete (AAC) is becoming increasingly popular. The cement mix contains aluminum metal, which reacts with the hydroxide ion formed in the above reaction as follows:



The millions of tiny gas bubbles cause the mixture to swell to five times its original volume. When the concrete has set, it is cut into blocks or slabs of

required size, then steam-cured in an oven (autoclaved). The hydrogen gas diffuses out of the structure and is replaced by air. This low-density material has high thermal insulation properties and can be made with waste fly ash from coal-burning power plants. At the end of the building's life, the panels can be disassembled, crushed, and remade into cement; hence, AAC is probably the most environmentally friendly construction material.

### WORKED EXAMPLE 12.4

Determine the oxidation number of iron in calcium ferroaluminate,  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ .

#### Answer

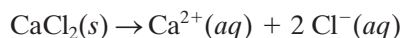
Calcium ion is always +2; aluminum ion, always +3; oxygen always -2. Thus:

$$4(+2) + 2(+3) + 2(\text{Ox. No. Fe}) + 10(-2) = 0$$

Ox. No. Fe = +3. ■

## 12.8 Calcium Chloride

Anhydrous calcium chloride is a white solid that absorbs moisture very readily (an example of deliquescence). As a result, it is sometimes used as a drying agent in the chemistry laboratory. The reaction to form the hexahydrate,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , is very exothermic, and this property is exploited commercially. One type of instant hot packs consists of two inner pouches, one water filled and the other containing anhydrous calcium chloride. Squeezing the pack breaks the inner partition between the pouches and allows the exothermic hydration reaction to occur. When the dividing partition is broken, calcium chloride solution forms. This process is highly exothermic:



With a 2+ charge cation, the lattice energy is high (about  $2200 \text{ kJ} \cdot \text{mol}^{-1}$ ), but at the same time, the enthalpy of hydration of the calcium ion is extremely high ( $-1560 \text{ kJ} \cdot \text{mol}^{-1}$ ), and that of the chloride ion is not insignificant ( $-384 \text{ kJ} \cdot \text{mol}^{-1}$ ). The sum of these energies yields an exothermic process. By contrast, there is a decrease in entropy ( $-256 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) as the small, highly charged cation is surrounded in solution by a very ordered sphere of water molecules, thereby diminishing the entropy of the water in the process. This reaction, then, is enthalpy driven.

Anhydrous calcium chloride, instead of sodium chloride, is also used for melting ice. Calcium chloride works in two ways. First, its reaction with water is highly exothermic (as we described previously); second, calcium chloride forms a freezing mixture that substantially reduces the melting point. Calcium

chloride is very water soluble: a mixture of 30 percent calcium chloride and 70 percent water by mass (the eutectic, or minimum, freezing mixture) will remain liquid down to  $-55^{\circ}\text{C}$ , a temperature much lower than the  $-18^{\circ}\text{C}$  produced by the best sodium chloride and water mixture. Another advantage of using the calcium salt is that the calcium ion causes less damage to plants than does the sodium ion.

The concentrated calcium chloride solution has a very “sticky” feel, and this property leads to another of its applications: it is sprayed on unpaved road surfaces to minimize dust problems. It is much less environmentally hazardous than oil, the other substance commonly used. The concentrated solution is also very dense, and for this reason, it is sometimes used to fill tires of earth-moving equipment to give them a higher mass and hence better traction.

## 12.9 Calcium Sulfate

Calcium sulfate is found as the dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , known as *gypsum*. Mineral deposits of pure, high-density gypsum, called *alabaster*, have been used for delicate sculptures. Gypsum is also used in some brands of blackboard chalk. When heated to about  $100^{\circ}\text{C}$ , the hemihydrate, known as *plaster of Paris*, is formed:



This white powdery solid slowly reacts with water to form long interlocking needles of calcium sulfate dihydrate. It is the strong, meshing crystals of gypsum that give plaster casts their strength. A more correct common name would be “gypsum casts.”

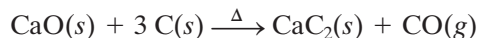
One of the major uses of gypsum is in the fire-resistant wallboard used for interior walls in houses and offices. Its nonflammability and low cost are two reasons for choosing this material. The fire protection results in part from the nonflammability of gypsum and its low thermal conductivity. In addition, the gypsum dehydration reaction is an endothermic process ( $+117\text{ kJ}\cdot\text{mol}^{-1}$ ), thus absorbing energy from the fire. Furthermore, each mole of liquid water produced absorbs the enthalpy of vaporization of water—another  $144\text{ kJ}\cdot\text{mol}^{-1}$ —as it becomes gaseous water. Finally, the gaseous water acts as an inert gas, decreasing the supply of dioxygen to the fire.

## 12.10 Calcium Carbide

This compound was first prepared by accident. Thomas “Carbide” Willson was endeavoring to prepare calcium metal by heating calcium oxide with carbon in an electric furnace. A product was formed, and it reacted with water to produce a gas as expected. However, the gas was not the expected hydrogen but ethyne (common name, *acetylene*). This synthesis had a major effect on late nineteenth century life. The solid calcium carbide could be easily stored and transported and addition of readily available water released a flammable gas. The manufacture of

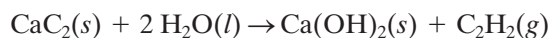


calcium carbide still uses the same method of heating carbon (coke) and calcium oxide at about 2000°C in an electric furnace:

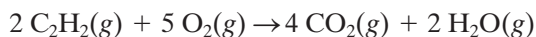


Even though  $\text{CaC}_2$  is commonly called calcium carbide, the compound does not contain the carbide ion,  $\text{C}^{4-}$ . Instead, it contains the dicarbide(2−) ion,  $\text{C}_2^{2-}$ , which is commonly called the *acetylide ion* or sometimes the *percarbide ion*. The compound adopts the sodium chloride crystal structure, with each anion site being occupied by a dicarbide(2−) unit (Figure 12.2).

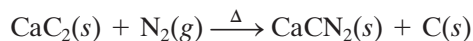
The major use of the carbide process today is to produce ethyne (acetylene) for oxyacetylene welding:



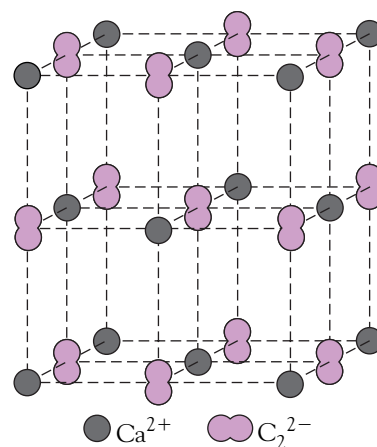
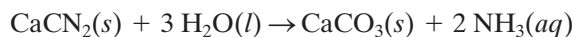
The very exothermic reaction with dioxygen gives carbon dioxide and water vapor:



Ethyne has been an ideal reactant for the synthesis of numerous organic compounds. In fact, the process was central to the founding of the company Union Carbide. In particular, calcium dicarbide(2−) reacts with atmospheric nitrogen, one of the few simple chemical methods of breaking the strong nitrogen-nitrogen triple bond. In the process, calcium dicarbide(2−) is heated in an electric furnace with nitrogen gas at about 1100°C:



The cyanamide ion,  $[\text{N}=\text{C}=\text{N}]^{2-}$ , is isoelectronic with carbon dioxide, and it also has the same linear structure. Calcium cyanamide is a starting material for the manufacture of several organic compounds, including melamine plastics. It is also used as a slow-release nitrogen-containing fertilizer:



**FIGURE 12.2** Crystal structure of calcium dicarbide(2−), which closely resembles the sodium chloride crystal structure.

## 12.11 Biological Aspects

### Biom mineralization

One of the new fields of research is biom mineralization: the formation of minerals by biological processes. This interdisciplinary field encompasses inorganic chemistry, biology, geology, biochemistry, and materials science.

The crucial difference between ordinary minerals and biom minerals is that biom minerals are grown specifically in the shape for which they are needed. In addition to their use as body frameworks, biom minerals have three other roles: as instruments, as parts of sensors, and for mechanical protection. Teeth are the most common inorganic instruments. In vertebrates, the enamel layer of teeth is predominantly hydroxyapatite, but this is not true for all organisms. Marine mollusks of the chiton family synthesize crystals of iron oxides to act in this role.

We have gravity- or inertia-sensitive sensors in our inner ear. These are spindle-shaped deposits of the aragonite form of calcium carbonate. Calcium



**TABLE 12.8** Some important biominerals and their functions

Chemical composition	Mineral Name	Occurrence and functions
$\text{CaCO}_3$	Calcite, aragonite	Exoskeletons (e.g., eggshells, corals, mollusk shells)
$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	Hydroxyapatite	Endoskeletons (vertebrate bones and teeth)
$\text{Ca}(\text{C}_2\text{O}_4)$	Whewellite (monohydrate), weddellite (dihydrate)	Calcium storage, passive defense of plants
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Gypsum	Gravity sensor
$\text{SrSO}_4$	Celestite	Exoskeleton (some marine unicellular organisms)
$\text{BaSO}_4$	Baryte	Gravity sensor
$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Silica	Exoskeletons, plant defenses
$\text{Fe}_3\text{O}_4$	Magnetite	Magnetic sensors, teeth of certain marine organisms
$\text{Fe}(\text{O})\text{OH}$	Goethite, lepidocrocite	Teeth of certain marine organisms

carbonate is relatively dense ( $2.9 \text{ g}\cdot\text{cm}^{-3}$ ); thus, the movement of this mineral mass with respect to the surrounding sensory cells gives us information on the direction and intensity of acceleration. One class of bacteria accumulates magnetic iron oxides, which they use to orient themselves with respect to the Earth's magnetic field.

Sea urchins provide an example of mechanical protection. They synthesize long, strong needles of calcium carbonate for defense. Such needle crystals are very different from the normal chunky calcite or aragonite crystals. Silicon dioxide crystals are used for defense by several plant species. One of these is the stinging nettle, where the brittle tips of the stinging hairs consist of silicon dioxide (silica). Table 12.8 shows some of the most important biominerals and their functions.

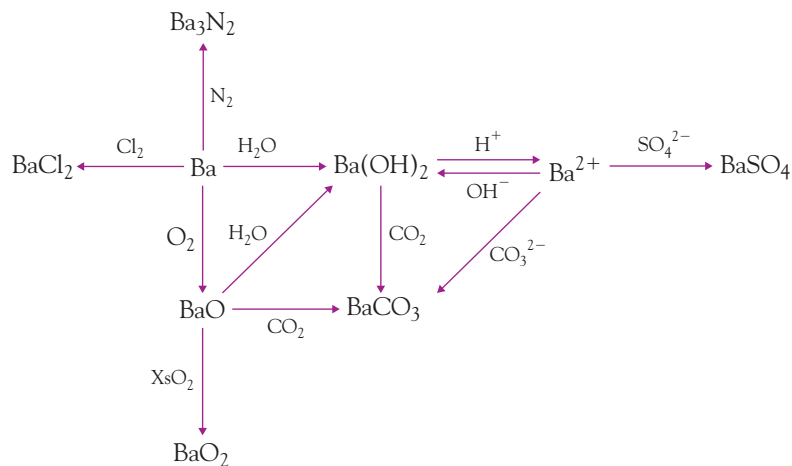
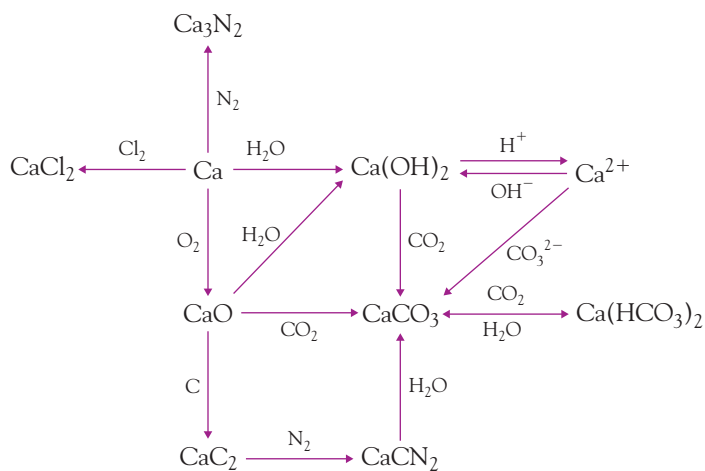
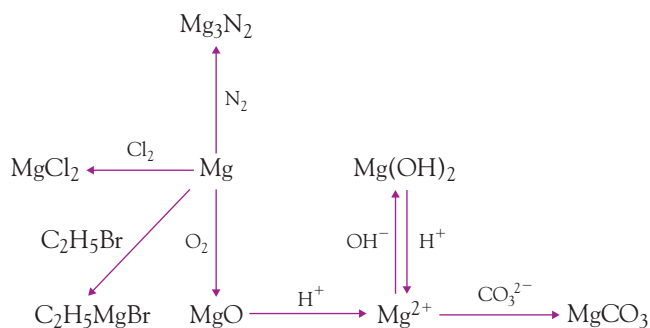
## Radium

The last of the alkaline earth metals to be extracted from its compounds was radium. Radium isotopes are formed as part of the radioactive decay sequence of uranium and thorium isotopes to lead isotopes. For example, radium-226, half-life 1600 years, is formed from the decay of uranium-238, while radium-228, half-life 6 years, is formed from the decay of thorium-232.

Marie Curie and André Debierne accomplished this task in Paris in 1910, delighting in the bright glow from this element, not realizing that it was the result of the element's intense and dangerous radiation. Aircraft instrument panels and watch dials were painted with radium compounds so they could be seen at night. The delicate task of painting the numbers on the displays was given to young women. Many of the "radium girls" as they became known, died horrible deaths from radiation-induced diseases. Also, during the 1930s, cabaret shows sometimes featured women dancers painted with radium salts so that they would literally glow in the dark. Some of the dancers, too, may have died of radiation-related diseases, never being aware of the cause. By contrast, radiation from radium compounds was used to destroy tumors, one of those so treated was Henrietta Lacks, from whom the immortal HeLa cells were obtained.

## 12.12 Element Reaction Flowcharts

The three most important elements of this group are magnesium, calcium, and barium, and their respective flowcharts are shown in the following:



## KEY IDEAS

- The Group 2 metals are harder, denser, and less reactive than the Group 1 metals.
- There are systematic patterns in the solubilities of the Group 2 metal salts.
- Beryllium is amphoteric and atypical of the group.
- Calcium carbide is one the several important salts of the Group 2 metal ions.

## EXERCISES

- 12.1** Write balanced chemical equations for the following processes: (a) heating calcium in dioxygen; (b) heating calcium carbonate; (c) evaporating a solution of calcium hydrogen carbonate; (d) heating calcium oxide with carbon.
- 12.2** Write balanced chemical equations for the following processes: (a) adding strontium to water; (b) passing sulfur dioxide over barium oxide; (c) heating calcium sulfate dihydrate; (d) adding strontium dicarbide( $2-$ ) to water.
- 12.3** For the alkaline earth elements (except beryllium), which will (a) have the most insoluble sulfate; (b) be the softest metal?
- 12.4** For the alkaline earth metals (except beryllium), which will (a) have the most insoluble hydroxide; (b) have the greatest density?
- 12.5** Explain why entropy factors favor the solution of sodium chloride but not that of magnesium chloride.
- 12.6** Explain why the salts of alkaline earth metals with mono-negative ions tend to be soluble, while those with di-negative ions tend to be insoluble.
- 12.7** What are the two most important common features of the Group 2 elements?
- 12.8** Explain why the solid salts of magnesium tend to be highly hydrated.
- 12.9** Suggest why the hydrated beryllium ion has the formula  $[\text{Be}(\text{OH}_2)_4]^{2+}$ , while that of magnesium is  $[\text{Mg}(\text{OH}_2)_6]^{2+}$ .
- 12.10** How does the chemistry of magnesium differ from that of the lower members of the Group 2 metals? Suggest an explanation.
- 12.11** Explain briefly how caves are formed in limestone deposits.
- 12.12** What are the main raw materials for the manufacture of cement?
- 12.13** Summarize the industrial process for the extraction of magnesium from seawater.
- 12.14** How is calcium cyanamide obtained from calcium oxide?
- 12.15** Several of the alkaline earth metal compounds have common names. Give the systematic name for (a) lime; (b) milk of magnesia; (c) Epsom salts.
- 12.16** Several of the alkaline earth metal compounds have common names. Give the systematic name for (a) dolomite; (b) marble; (c) gypsum.
- 12.17** Why is lead commonly used as a shielding material for X-rays?
- 12.18** The dissolving of anhydrous calcium chloride in water is a very exothermic process. However, dissolving calcium chloride hexahydrate causes a very much smaller heat change. Explain this observation.
- 12.19** Discuss briefly the similarities between beryllium and aluminum.
- 12.20** In this chapter, we have ignored the radioactive member of the group, radium. On the basis of group trends, suggest the key features of the properties of radium and its compounds.
- 12.21** Describe briefly the importance of magnesium ion to life on Earth.
- 12.22** What is the calcium-containing structural material in vertebrates?
- 12.23** Describe and write corresponding chemical equations showing how you would prepare from magnesium metal each of the following: (a) magnesium chloride monohydrate; (b) anhydrous magnesium chloride.
- 12.24** Write balanced chemical equations corresponding to each transformation in the element reaction flowcharts for magnesium, calcium, and barium (page 307).

## BEYOND THE BASICS

**12.25** From the appropriate data in Appendix 2, calculate the enthalpy and entropy change when plaster of Paris is formed from gypsum. Calculate the temperature at which the process of dehydration becomes significant; that is, when  $\Delta G^\ominus = 0$ .

**12.26** Calculate the radius of a dicarbide,  $\text{C}_2^{2-}$ , ion given that calcium dicarbide( $2-$ ), which adopts a sodium chloride lattice, has a lattice energy of  $-2911 \text{ kJ}\cdot\text{mol}^{-1}$ .

**12.27** The common hydrate of magnesium sulfate is the heptahydrate,  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ . In the crystal structure, how many water molecules are likely to be associated with the cation? With the anion? Give your reasoning.

**12.28** Adding powdered limestone (calcium carbonate) to a lake affected by acid rain can decrease the availability of phosphate ion, an important nutrient, but not that of nitrate ion, another nutrient. Write a balanced equation and calculate the standard free energy change for the process to confirm its spontaneity.

**12.29** Which of the following gaseous species should be the most stable:  $\text{BeH}$ ,  $\text{BeH}^+$ , or  $\text{BeH}^-$ ? Show your reasoning.

**12.30** Which would you expect to have a higher melting point, magnesium oxide or magnesium fluoride? Explain your reasoning.

**12.31** We focus on reactions involving oxygen and water because they are the predominant reactive species on this

planet. What would be the parallel reaction to that of calcium oxide with water on a planet whose environment was dominated by gaseous dinitrogen and liquid ammonia?

**12.32** Lanthanum, one of the lanthanoid elements, is often regarded by biochemists as a useful analog for calcium, the major difference being the charge of tripositive  $\text{La}^{3+}$  contrasted to dipositive  $\text{Ca}^{2+}$ . Assuming this analogy, predict: (a) the reaction between lanthanum metal and water; (b) which of the following lanthanum salts are soluble or insoluble in water: sulfate, nitrate, chloride, phosphate, fluoride.

**12.33** Beryllium metal can be obtained by the reaction of beryllium fluoride with magnesium metal at  $1300^\circ\text{C}$ . Show that the reaction is thermodynamically spontaneous even at  $25^\circ\text{C}$ . Is the reaction likely to be more or less favorable at  $1300^\circ\text{C}$ ? Give your reasoning without a calculation. Why, then, is beryllium commercially synthesized at such a high temperature?

**12.34** Suggest why the  $\text{BeI}_4^{2-}$  ion is not known, even though the  $\text{BeCl}_4^{2-}$  ion exists.

**12.35** Molten beryllium chloride is a poor electrical conductor. However, dissolving sodium chloride in beryllium chloride results in a conducting solution with an optimum conductivity at an  $\text{NaCl}:\text{BeCl}_2$  ratio of 2:1. Suggest an explanation.

## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



# THE GROUP 13 ELEMENTS

## CHAPTER 13

B
Al
Ga
In
Tl

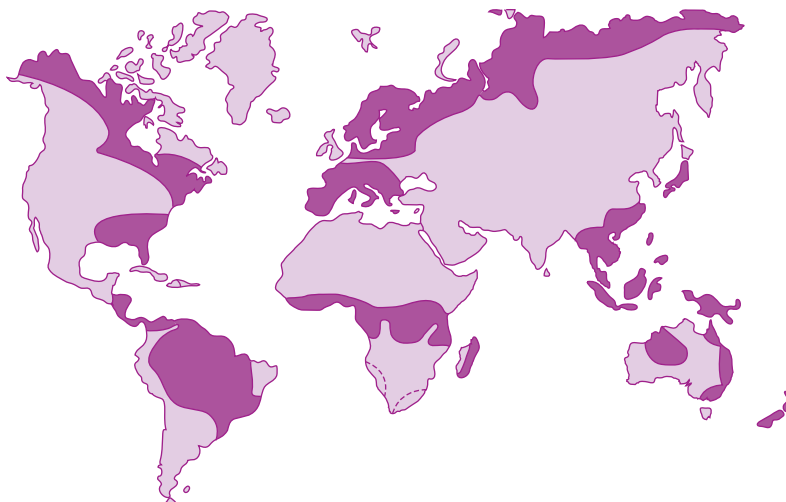
						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 13.1** Group Trends
- 13.2** Boron
- 13.3** Borides
- 13.4** Boranes
- 13.5** Boron Halides
- 13.6** Aluminum
- 13.7** Aluminum Halides
- 13.8** Aluminum Potassium Sulfate
- 13.9** Aluminides
- 13.10** Biological Aspects
- 13.11** Element Reaction Flowcharts

Boron and aluminum are the only members of Group 13 that are of major importance. Boron has some unusual chemistry—particularly its hydrides. Aluminum is one of the most widely used metals, and the properties of its compounds will be the main focus of this chapter.

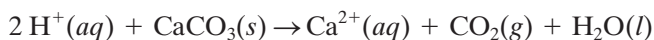
### Context: Aluminum—The Toxic Ion

Aluminum is a highly abundant ion in the rocks and minerals of this planet. Unfortunately, it is highly toxic (see Section 13.11). The toxicity is of particular importance in the context of the world's food supplies. There are several factors which control the fertility of soils. Two ions are in excess of a plant's needs: aluminum and manganese. There are also four ions for which deficiencies are common: phosphorus, calcium, magnesium, and molybdenum. But the most crucial limitation on farming is an excess of aluminum ion in the soil. As we discuss in Section 13.6, the solubility of aluminum ion is highly pH dependent. At a pH range of about 6 to 8, insoluble aluminum compounds are formed, outside that range, and of crucial importance at lower pH, soluble aluminum cations predominate. Thus, anywhere on Earth where the soil is acid, high aluminum ion is actually the culprit of preventing economic farming. The following figure shows the land where acid soils are prevalent.



World acid soils. Areas of predominance are shown in dark mauve.

So what can be done? Neutralization of the soils would be the preferable solution. The lowest-cost treatment would use calcium carbonate:



However, to treat the acidic farmable land surface would be phenomenally expensive. An alternative route is to genetically develop crop species which are aluminum-ion tolerant. Such research needs to be a high priority at a time when climate variation is increasing.

### 13.1 Group Trends

Boron exhibits mostly nonmetallic behavior and is classified as a metalloid, whereas the other members of Group 13 are metals. But even the metals have no simple pattern in melting points, although their boiling points do show a decreasing trend as the mass of the elements increases (Table 13.1). The reason for this lack of order is that each element in the group is organized a different

**TABLE 13.1** Melting and boiling points of the Group 13 elements

Element	Melting point (°C)	Boiling point (°C)
B	2180	3650
Al	660	2467
Ga	30	2403
In	157	2080
Tl	303	1457

**TABLE 13.2** Charge densities of Period 3 metal ions

Group	Ion	Charge density ( $\text{C}\cdot\text{mm}^{-3}$ )
1	$\text{Na}^+$	24
2	$\text{Mg}^{2+}$	120
13	$\text{Al}^{3+}$	364

way in the solid phase. Boron forms clusters of 12 atoms, aluminum adopts a face-centered cubic structure, gallium forms a unique structure containing pairs of atoms, while indium and thallium each form other, different structures. It is only when the elements are melted and the crystal arrangements destroyed that we see, from the decreasing boiling points as the group is descended, that the interatomic bond becomes weaker.

As we would expect, boron, classified as a metalloid, favors covalent bond formation. However, covalency is common among the metallic members of the group as well. The reason for the covalent behavior can be attributed to the high charge and small radius of each metal ion. The resulting high-charge density of Group 13 ions is sufficient to polarize almost any approaching anion enough to produce a covalent bond (Table 13.2). The only way to stabilize the ionic state of Group 13 elements is to hydrate the metal ion. For aluminum, the enormous hydration enthalpy of the tri-positive ion,  $-4665 \text{ kJ}\cdot\text{mol}^{-1}$ , is almost enough on its own to balance the sum of the three ionization energies,  $+5137 \text{ kJ}\cdot\text{mol}^{-1}$ . Thus, the hydrated aluminum compounds that we regard as ionic do not contain the aluminum ion,  $\text{Al}^{3+}$ , as such, but the hexaaquaaluminum ion,  $[\text{Al}(\text{OH}_2)_6]^{3+}$ .

It is in Group 13 that we first encounter elements possessing more than one oxidation state. Aluminum has the +3 oxidation state, whether the bonding is ionic or covalent. However, gallium, indium, and thallium have a second oxidation state of +1. For gallium and indium, the +3 state predominates, whereas the +1 state is most common for thallium (see Chapter 9, Section 9.6). At this point, it is appropriate to note that formulas can sometimes be deceiving. Gallium forms a chloride,  $\text{GaCl}_2$ , a compound implying that a +2 oxidation state exists. However, the actual structure of this compound is now established as  $[\text{Ga}]^+[\text{GaCl}_4]^-$ ; thus, the compound actually contains gallium in both +1 and +3 oxidation states.

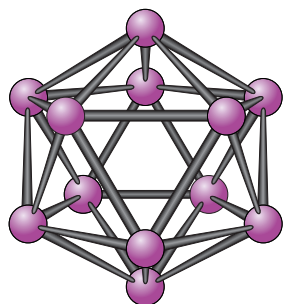
## 13.2 Boron

Boron is the metalloid of Group 13. The element can be obtained from its oxide by heating with a reactive metal such as magnesium:

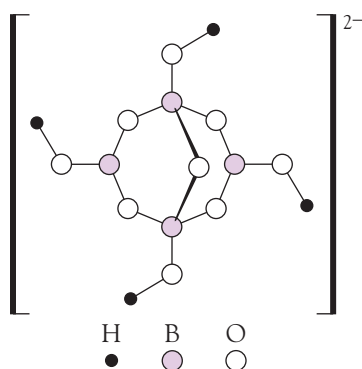


The magnesium oxide can be removed by reaction with acid. It is difficult to obtain the element in a very pure form. There are claims of many different

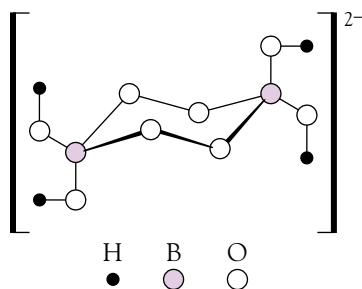




**FIGURE 13.1** Icosahedral arrangement of boron,  $B_{12}$ .



**FIGURE 13.2** Actual structure of the borate ion in borax.



**FIGURE 13.3** Structure of the peroxoborate ion.

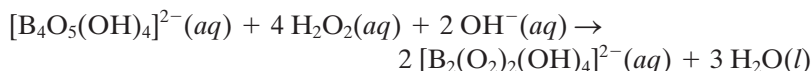
allotrope; however, it seems that all element forms, probably better considered as polymorphs, contain clusters of 12 boron atoms. Each cluster has a geometric arrangement known as an icosahedron (Figure 13.1). Pure boron has a pure crystalline form which is black with a metallic luster, similar to that of silicon. In fact, the chemistry of boron resembles that of silicon, a link known as the diagonal relationship (Chapter 9, Section 9.5).

Boron is a rare element in the Earth's crust, but fortunately there are several large deposits of its salts. These deposits, which are found in locations that once had intense volcanic activity, consist of the salts borax and kernite, which are conventionally written as  $Na_2B_4O_7 \cdot 10H_2O$  and  $Na_2B_4O_7 \cdot 4H_2O$ , respectively. Total annual worldwide production of boron compounds amounts to over 3 million tonnes. The world's largest deposit is found at Boron, California; it covers about  $10 \text{ km}^2$ , with beds of kernite up to 50 m thick. The actual structure of borate ions is much more complex than the simple formulas would indicate. For example, borax actually contains the  $[B_4O_5(OH)_4]^{2-}$  ion, shown in Figure 13.2.

About 35 percent of boron production is used in the manufacture of borosilicate glass. Conventional soda glass suffers from thermal shock; that is, when a piece of glass is heated strongly, the outside becomes hot and tries to expand, while the inside is still cold because glass is such a poor conductor of heat. As a result of stress between the outside and the inside, the glass cracks. When the sodium ions in the glass structure are replaced by boron atoms, the degree of glass expansion (more precisely called *thermal expansivity*) is less than half that of conventional glass. As a result, containers made of borosilicate glass (sold under trademarks such as Pyrex) are capable of being heated without great danger of cracking. Glass compositions are discussed in Chapter 14, Section 14.14.

In the early part of the twentieth century, the major use for boron compounds was as a cleaning agent called *borax*. This use has declined below that for glassmaking, consuming only 20 percent of production. In detergent formulations, it is no longer borax but sodium peroxoborate,  $NaBO_3$ , that is used. Once again, the simple formula does not show the true structure of the ion, which is  $[B_2(O_2)_2(OH)_4]^{2-}$  (Figure 13.3).

The peroxoborate ion is prepared by the reaction of hydrogen peroxide with borax in base:

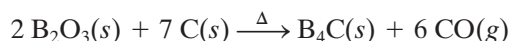


This ion acts as an oxidizing agent as a result of the two peroxo groups ( $-O-O-$ ) linking the boron atoms. About  $5 \times 10^5$  tonnes of sodium peroxoborate are produced every year for European detergent manufacturing companies. It is a particularly effective oxidizing (bleaching) agent at the water temperatures used in European washing machines ( $90^\circ\text{C}$ ), but it is ineffective at the water temperatures usually used in North American washing machines ( $70^\circ\text{C}$ ). In North America, hypochlorites (see Chapter 17, Section 17.9) are used instead.

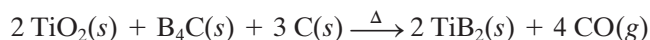
Boron is a vital component of nuclear power plants because it is a strong absorber of neutrons. Boron-containing control rods are lowered into reactors to maintain the nuclear reaction at a steady rate. Borates are used as wood preservatives, as a fire retardant in fabrics, and as a flux in soldering. In this last application, the borates melt on the hot pipe surface and react with metal oxide coatings, such as copper(II) oxide on copper pipes. The metal borates (such as copper(II) borate) can be easily removed to give a clean metal surface for the soldering.

### 13.3 Borides

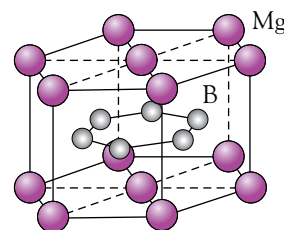
Boron forms a large number of binary compounds. These compounds are all very hard, high melting, and chemically resistant, and they have become of increasing importance as materials that can be used for such purposes as rocket nose cones. However, the stoichiometry of these compounds is far from simple. The most important of the compounds is boron carbide, which has the empirical formula  $B_4C$ . Even though by name it is a carbide, the structure is boron based. The structure is better represented as  $B_{12}C_3$  because it consists of  $B_{12}$  icosahedra, as in the element itself, with carbon atoms linking all the neighboring icosahedra. One preparative method is the reduction of diboron trioxide with carbon:



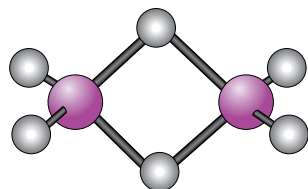
Boron carbide is one of the hardest substances known. Its fibers have enormous tensile strength and are used in bulletproof clothing. High-density boron carbide armor tiles are placed under the seats of Apache attack helicopters, protecting the occupants from ground fire. A more common use is in some lightweight high-performance bicycle frames, where boron carbide is embedded in an aluminum matrix. Boron carbide is also used as a starting material for preparing other tough materials such as titanium boride:



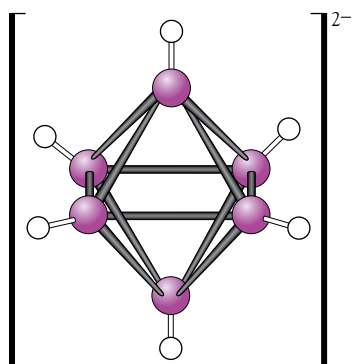
Titanium boride belongs to a different class of borides. These borides consist of hexagonal layers of boron ions isoelectronic and isostructural with the graphite allotrope of carbon. The metal ions are located in hexagonal arrays between the  $B_6^{6-}$  layers. Each boron atom has a  $1-$  charge, and the stoichiometry of this class of borides corresponds to metals in their  $+2$  oxidation state. Another of the hexagonal layer borides is magnesium boride,  $MgB_2$ , or, more correctly,  $Mg_3B_6$  (Figure 13.4). This compound is very inexpensive and readily available, yet it was only in 2001 that it was accidentally discovered to be superconducting at low temperatures. Magnesium boride retains its superconductivity up to 39 K, the highest value for a simple (and inexpensive) compound. Research is ongoing to see if there are any close relatives of magnesium boride that exhibit superconductivity to much higher temperatures.



**FIGURE 13.4** Ion-lattice diagram of magnesium boride,  $Mg_3B_6$ .



**FIGURE 13.5** Structure of diborane,  $B_2H_6$ .



**FIGURE 13.6** Structure of  $[B_6H_6]^{2-}$ .

## 13.4 Boranes

Boron is second only to carbon in the number of hydrides that it forms. Over 50 neutral boranes,  $B_nH_m$ , and an even larger number of borane anions,  $B_nH_m^{x-}$ , are known. There are three reasons why the chemistry of boranes is important.

1. The shapes of borane molecules are different from those of other hydrides.
2. The bonding in boranes has required the expansion of molecular orbital theory.
3. The reaction chemistry of the boranes has interesting parallels to, and differences from, hydrocarbon chemistry.

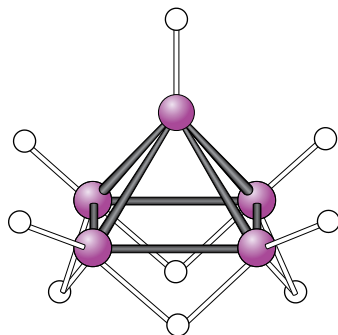
### Structures of Boranes

The simplest borane is  $B_2H_6$  (Figure 13.5). As can be seen from Figure 13.5, one of the most unique aspects of borane chemistry is that hydrogen atoms often act as bridges between neighboring boron atoms. Also, the boron atoms often form triangular units. Any polyhedron containing triangular faces (such as an octahedron) is generically known as a deltahedron.

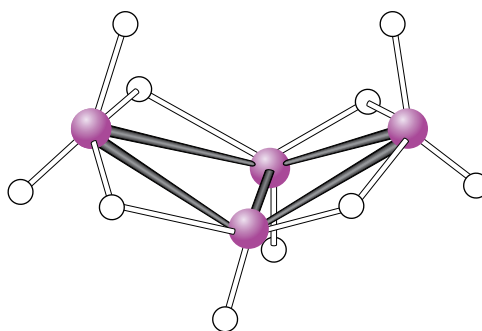
There are three common classes of boranes and borane anions:

1. The *closo*-cluster, where the boron atoms form a closed deltahedral cage. The generic formula is  $[B_nH_m]^{2-}$ , for example,  $[B_6H_6]^{2-}$  (Figure 13.6).
2. The *nido*-cluster, an open cage cluster derived from a closed deltahedron with one boron atom missing. The common generic formulas are  $B_nH_{(n+4)}$  or  $[B_nH_{(n+3)}]^-$ , for example,  $B_2H_6$ ,  $B_5H_9$  (Figure 13.7), and  $[B_5H_8]^-$ .
3. The *arachno*-cluster, an open cage cluster derived from a closed deltahedron with two boron atoms missing. The common generic formulas are  $B_nH_{(n+6)}$  or  $[B_nH_{(n+5)}]^-$ , for example,  $B_4H_{10}$  (Figure 13.8) and  $[B_4H_9]^-$ .

All of the compounds have positive  $\Delta_f G^\ominus$  values; that is, they are thermodynamically unstable with respect to decomposition into their constituent elements. To name a borane, the numbers of boron atoms are indicated by the normal prefixes, while the numbers of hydrogen atoms are denoted by Arabic



**FIGURE 13.7** Structure of  $B_5H_9$ .



**FIGURE 13.8** Structure of  $B_4H_{10}$ .

numbers in parentheses. Hence,  $B_4H_{10}$  is called tetraborane(10) and  $B_5H_9$  is pentaborane(9).

### Bonding in Boranes

The discovery that the simplest borane had the molecular formula  $B_2H_6$  (not  $BH_3$ ) proved to be a major headache for inorganic chemists. How could the bonding be explained? Traditionally, a hydrogen atom was believed to form only one covalent bond. In Chapter 10, Section 10.4, we saw that the trihydrogen ion,  $H_3^+$ , contained a triangle of three hydrogen atoms sharing one electron pair. The bonding in most boranes involves similar three-atom one-electron-pair bonds.

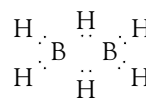
As can be seen from the structure in Figure 13.5, in  $B_2H_6$ , two hydrogen atoms link, or bridge, the pair of boron atoms. The utilization of hydrogen atoms as bridges means that one electron pair can satisfy the bonding requirements of two boron atoms. Each terminal hydrogen atom forms a normal two-electron bond with a boron atom. Each boron atom then has one electron left, and this is paired with the electron of one of the bridging hydrogen atoms (Figure 13.9).

The shape of the molecule can be described as approximately tetrahedral around each boron atom, with the bridging hydrogen atoms in what are sometimes called “banana bonds.” The hydridic bonds behave like weak covalent bonds (Figure 13.10).

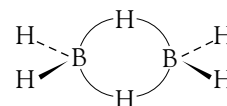
The bonding in a diborane molecule can be described in terms of hybridization concepts. According to these concepts, the four bonds, separated by almost equal angles, would correspond to  $sp^3$  hybridization. Three of the four hybrid orbitals will contain single electrons from the boron atom. Two of these half-filled orbitals would then be involved in bonding with the terminal hydrogen atoms. This arrangement would leave one empty and one half-filled hybrid orbital.

To explain how we make up the eight electrons in the  $sp^3$  orbital set, we consider that the single half-filled hybrid  $sp^3$  orbitals of the two boron atoms overlap with each other and with the  $1s$  orbital of a bridging hydrogen atom at the same time. This arrangement will result in a single orbital that encompasses all three atoms (a *three-center bond*). This orbital is capable of containing two electrons (Figure 13.11). An identical arrangement forms the other  $B-H-B$  bridge. The bonding electron distribution of diborane is shown in Figure 13.12.

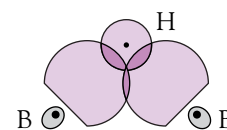
Alternatively, we can consider the molecular orbital explanation. The detailed molecular orbital diagram for this eight-atom molecule is complex. Although molecular orbitals relate to the molecule as a whole, it is sometimes possible to identify molecular orbitals that are involved primarily in one particular bond. In this case, we find that the mixing of the orbital wave functions of the atoms in each bridge bond results in the formation of three molecular orbitals. When we compare the energies of the atomic orbitals with those of the molecular orbitals, we find that one molecular orbital is lower in energy ( $\sigma$  bonding), one is higher in energy ( $\sigma$  antibonding), and the third has an energy level equivalent to the mean energy of the three component atomic orbitals ( $\sigma$  nonbonding). This is very similar to the molecular orbital diagram derived for the bonding in the trihydrogen ion (Chapter 10, Section 10.4).



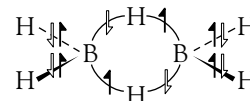
**FIGURE 13.9** Electron-pair arrangement in diborane,  $B_2H_6$ .



**FIGURE 13.10** Geometry of the diborane molecule.

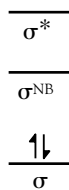


**FIGURE 13.11** Overlap of the  $sp^3$  hybrid orbitals of the two boron atoms with  $1s$  orbital of the bridging hydrogen atom.



**FIGURE 13.12** The electron pairing that is consistent with  $sp^3$  hybridization for each boron atom and with the two-electron, three-atom  $B-H-B$  bridging bonds. The electrons contributed by the hydrogen atoms are the open half-headed arrows.

Molecular  
orbitals

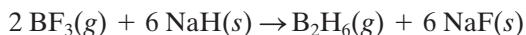


**FIGURE 13.13** The molecular orbitals that are involved in the hydridic bridge.

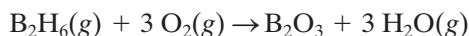
The bridging hydrogen atom contributes one electron, and each boron atom contributes one-half electron. This arrangement fills the bonding orbital between the three atoms (Figure 13.13). Because there is one bonding orbital shared between two pairs of atoms, the bond order for each B—H component must be  $\frac{1}{2}$ . The same arguments apply to the other bridge. From bond energy measurements, we do indeed find each B—H bridging bond to be about half the strength of a terminal B—H bond, although it is still in the energy range of a true covalent bond, unlike the much weaker protonic bridges in hydrogen-bonded molecules. Of equal importance, the set of molecular orbitals shows that the structure makes maximum use of the few boron electrons. The presence of more electrons would not strengthen the bond because these electrons would enter nonbonding molecular orbitals.

### Synthesis and Reactions of Boranes

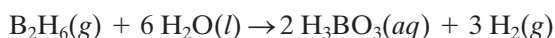
About 200 tonnes of diborane are produced each year. The industrial synthesis is accomplished by the reaction of boron trifluoride with sodium hydride to produce toxic, colorless diborane:



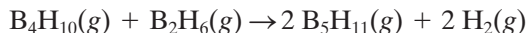
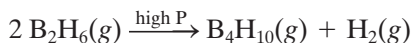
The boranes possess partially negatively charged hydrogen atoms because of the low electronegativity of boron. This reversed polarity of the bond results in a high chemical reactivity for these compounds. For example, diborane, like most of the neutral boranes, catches fire in air and explodes when mixed with pure dioxygen. The extremely exothermic reaction produces diboron trioxide and steam:



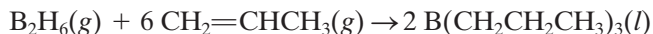
Reaction with water to give boric acid (sometimes written as  $\text{B}(\text{OH})_3$ ) and hydrogen is also very exothermic:



Most of the other boranes are synthesized from diborane. For example, tetraborane(10) is formed from the condensation of two diborane molecules, then pentaborane(11) is formed by reaction with another molecule of diborane:



Diborane is an important reagent in organic chemistry. The gas reacts with unsaturated hydrocarbons (those containing double or triple carbon-carbon bonds) to form alkylboranes. For example, diborane reacts with propene:



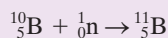
The product of this *hydroboration* reaction can be reacted with a carboxylic acid to give a saturated hydrocarbon, with hydrogen peroxide to give an alcohol, or with chromic acid to give a ketone or a carboxylic acid. Hydroboration is a favored route of organic synthesis for two reasons: the initial hydride addition

## Boron Neutron Capture Therapy

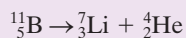
One of the many avenues under investigation for fighting cancer is boron neutron capture therapy (BNCT). The fundamental principle of this therapy is to have a radioactive source selectively within malignant cells. The radiation would then destroy only those cells, leaving healthy cells untouched. This approach is of particular interest in the context of inoperable brain tumors or as a means of killing any tiny clusters of tumor cells that remain following surgical removal of the main tumor. BNCT is a simple and promising concept but difficult to turn into reality.

In the 1950s, boron was proposed as the key element in BNCT. A stable boron compound would be infiltrated into a tumor and irradiated with neutrons, converting it to a radioactive isotope, and then the radiation would destroy the malignant cell. Why boron? is an obvious question. The answer relates to nuclear chemistry. The ability of an atomic nucleus to capture a particle depends not on the size of the nucleus but on the nuclear structure. Thus, each nucleus is assigned an effective cross-sectional area; that is, the larger the effective cross-sectional area, the easier it is for a neutron to impact the nucleus. The area is expressed in units of barns, where 1 barn =  $10^{-24}$  cm<sup>2</sup>. Boron-10 (with odd numbers of protons and neutrons) has an exceptionally large effective cross-sectional area, whereas the cross-sectional areas of hydrogen, carbon, and nitrogen, the major components of cells, are quite small (Table 13.3). For that reason, boron is an ideal target.

When a neutron impacts a boron-10 nucleus, boron-11 is initially formed:



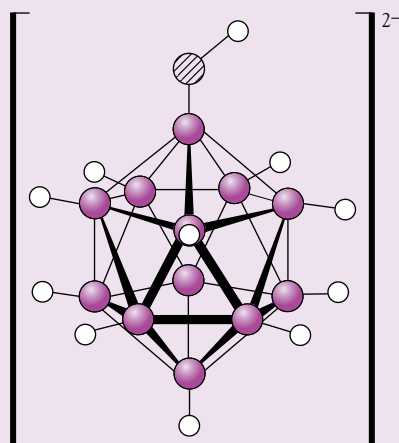
This species is radioactive, with a very short lifetime, fissioning to helium-4 and lithium-7 with the release of energy:



This fission energy is enough to propel the two particles about one cell width in opposite directions, damaging whatever molecules they encounter. About 1 billion boron atoms would be enough to completely destroy the cell.

And this is the challenge: to deliver high concentrations of a boron compound specifically to malignant cells. Early medical research used borate ion, but this proved to be ineffective. Progress in boron hydride chemistry was the breakthrough. The new boron hydrides have a high boron content, are kinetically stable, and can be linked to organic units.

One of the simplest “second-generation” ions was  $(\text{B}_{12}\text{H}_{11}\text{SH})^{2-}$  (Figure 13.14), commonly called *B<sub>12</sub>H*. This was the first family of boron species that showed a significantly greater boron concentration in the tumor compared to that in the blood. The third generation of compounds, currently under development, has four cage-type boranes linked to one large organic molecule and shows even more promise. Nevertheless, many more years of research are needed before BNCT becomes a simple, safe means of fighting small nests of malignant cells that cannot be destroyed by any other means.



**FIGURE 13.14** Structure of the  $(\text{B}_{12}\text{H}_{11}\text{SH})^{2-}$  ion.

**TABLE 13.3** Some effective neutron cross-sectional areas

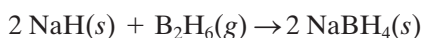
Isotope	Hydrogen-1	Boron-10	Carbon-12	Nitrogen-14	Oxygen-16
Neutron cross section (barn)	0.3	$3.8 \times 10^3$	$3.4 \times 10^{-3}$	1.8	$1.8 \times 10^{-4}$



is accomplished under very mild conditions, and a wide variety of final products is possible (depending on the other reagent used).

### The Tetrahydridoborate Ion

The only other species of boron used on a large scale is the tetrahydridoborate ion,  $\text{BH}_4^-$ . By contrast to the highly reactive neutral boranes, this anion can even be recrystallized from cold water as the sodium salt. The crystal structure of sodium tetrahydridoborate is interesting because it adopts the sodium chloride structure, with the whole  $\text{BH}_4^-$  ion occupying the same sites as the chloride ion does. Sodium tetrahydridoborate is of major importance as a mild reducing agent, particularly in organic chemistry, where it is used to reduce aldehydes to primary alcohols and ketones to secondary alcohols without reducing other functional groups such as carboxylic groups. The reaction of diborane with sodium hydride is used to produce sodium tetrahydridoborate:

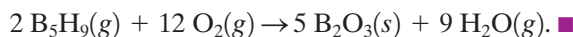


#### WORKED EXAMPLE 13.1

Write the balanced chemical equation for the reaction between  $\text{B}_5\text{H}_9$  and the dioxygen of the air.

#### Answer

In all the combustion reactions of boranes, diboron trioxide,  $\text{B}_2\text{O}_3(s)$ , is one product, and water vapor the other product. So now it is just necessary to balance:



## 13.5 Boron Halides

The two halides of interest are boron trifluoride and boron trichloride. Boron trifluoride is relevant in the context of bonding; in fact, it is the prototypical Lewis acid. Boron trichloride illustrates the high chemical reactivity of most nonmetal chlorides compared to ionic chlorides.

### Boron Trifluoride

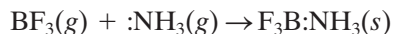
Boron has only three valence electrons, so any boron compound that has simple covalent bonding will be electron deficient with respect to the octet rule. Thus, we saw that the simplest boron hydride dimerizes to give  $\text{B}_2\text{H}_6$ , in which there are two hydridic bridge bonds. Boron trifluoride, however, does not dimerize: it remains as the simple trigonal planar compound  $\text{BF}_3$ . A study of the molecule shows that the boron-fluorine bond energy is extremely high ( $613 \text{ kJ}\cdot\text{mol}^{-1}$ ). This bond energy is far higher than that for any conventional single bond; for example, the carbon-fluorine bond energy is  $485 \text{ kJ}\cdot\text{mol}^{-1}$ .

To explain the surprising stability of the electron-deficient molecule and the strong covalent bond,  $\pi$  bonding as well as  $\sigma$  bonding is postulated to exist

in the compound. The boron atom has an empty  $2p_z$  orbital at right angles to the three  $\sigma$  bonds with the fluorine atoms. Each fluorine atom has a full  $2p$  orbital parallel to the boron  $2p_z$  orbital. A delocalized  $\pi$  system involving the empty  $p$  orbital on the boron and one full  $p$  orbital on each of the fluorine atoms can be formed (Figure 13.15).

Experimental evidence supports this explanation: when boron trifluoride reacts with a fluoride ion to form the tetrahedral tetrafluoroborate ion,  $\text{BF}_4^-$ , the B—F bond length increases from 130 pm in boron trifluoride to 145 pm in the tetrafluoroborate ion. This lengthening would be expected because the  $2s$  and three  $2p$  orbitals of the boron in the tetrafluoroborate ion are used to form four  $\sigma$  bonds. Hence, there are no orbitals available for  $\pi$  bonding in the tetrafluoroborate ion, and so the B—F bond in this ion would be a “pure” single bond.

By using the vacant  $2p_z$  orbital, boron trifluoride can behave as a powerful Lewis acid. The classic illustration of this behavior is the reaction between boron trifluoride and ammonia, where the nitrogen lone pair acts as the electron pair donor (see Chapter 7, Section 7.6):



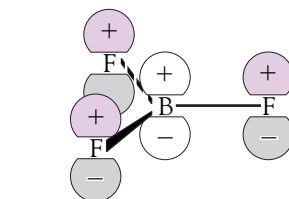
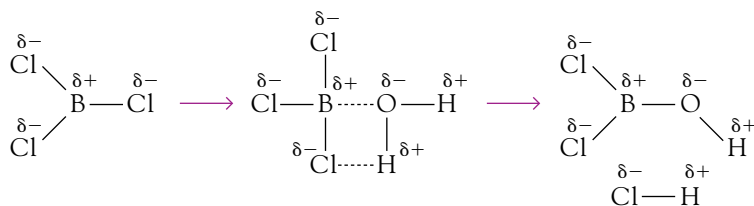
About 4000 tonnes of boron trifluoride is used industrially in the United States every year as both a Lewis acid and a catalyst in organic reactions.

### Boron Trichloride

As we cross the periodic table, the chloride of boron is the first chloride we encounter that exists as small covalently bonded molecules. As such, it is quite typical. Ionic chlorides are solids that dissolve in water to form hydrated cations and anions. However, the typical small-molecule covalent chloride is a gas or liquid at room temperature and reacts violently with water. For example, bubbling boron trichloride (a gas above  $12^\circ\text{C}$ ) into water produces boric acid and hydrochloric acid:



We can predict the products of these reactions in terms of the relative electronegativities of the two atoms. In this case, the electronegativity of chlorine is much greater than that of boron. Hence, as a water molecule approaches the boron trichloride molecule, we can picture the partially positive hydrogen being attracted to the partially negative chlorine atom, while the partially negative oxygen atom is attracted to the partially positive boron atom (Figure 13.16). A bond shift occurs, and one chlorine atom is replaced by a hydroxyl group. When this process happens two more times, the result is boric acid.

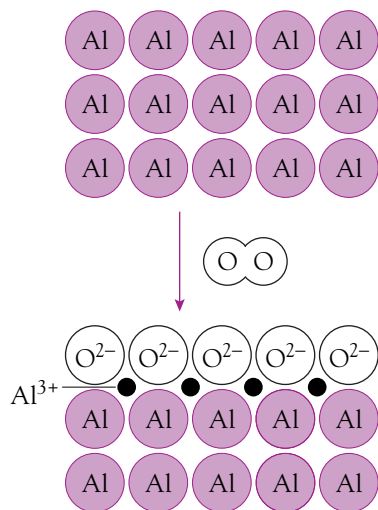


**FIGURE 13.15** Proposed  $\pi$ -bonding in boron trifluoride, involving the full  $p$  orbitals (shaded) on the fluorine atoms and the empty  $p_z$  orbital on the boron atom.

**FIGURE 13.16** First step of the postulated mechanism for hydrolysis of boron trichloride.



## 13.6 Aluminum



**FIGURE 13.17** Formation of a single oxide layer on the surface of aluminum metal. The small aluminum 3+ ions are indicated by the solid circles.

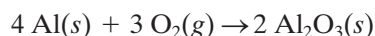
Because aluminum is a metal with a high negative standard reduction potential, it might be expected to be very reactive. This is indeed the case. Why, then, can aluminum be used as an everyday metal rather than consigned to the chemistry laboratory like sodium? The answer is found in its reaction with oxygen gas. Any exposed surface of aluminum metal rapidly reacts with dioxygen to form aluminum oxide,  $\text{Al}_2\text{O}_3$ . An impermeable oxide layer, between  $10^{-4}$  and  $10^{-6}$  mm thick, then protects the layers of aluminum atoms underneath. This can happen because the oxide ion has an ionic radius (124 pm) similar to the metallic radius of the aluminum atom (143 pm). As a result, the surface packing is almost unchanged because the small aluminum ions (68 pm) fit into interstices in the oxide surface structure. The process is shown in Figure 13.17.

To increase their corrosion resistance, aluminum products are *anodized*. In other words, the aluminum product is used as the anode in an electrochemical cell, and additional aluminum oxide is deposited as an electrolytic product over the naturally formed layers. This anodized aluminum possesses an oxide layer about 0.01 mm thick, and this very thick oxide coating has the useful property of absorbing dyes and pigments so that a colored surface can be produced.

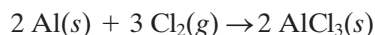
The particular attraction of aluminum as a construction metal is its low density ( $2.7 \text{ g}\cdot\text{cm}^{-3}$ ), second only to that of magnesium ( $1.7 \text{ g}\cdot\text{cm}^{-3}$ )—disregarding the very reactive alkali metals. For instance, compare the density of aluminum with that of either iron ( $7.9 \text{ g}\cdot\text{cm}^{-3}$ ) or gold ( $19.3 \text{ g}\cdot\text{cm}^{-3}$ ). Aluminum is a good conductor of heat, a property accounting for its role in cookware. It is not as good as copper, however. To spread heat more evenly from the electrical element (or gas flame), higher-priced pans have a copper-coated bottom. Aluminum also is exceptional as a conductor of electricity, hence its major role in electric power lines and home wiring. The major problem with using aluminum wiring occurs at the connections. If aluminum is joined to an electrochemically dissimilar metal, such as copper, an electrochemical cell will be established under damp conditions. This development causes oxidation (corrosion) of the aluminum. For this reason, use of aluminum in home wiring is now discouraged.

### Chemical Properties of Aluminum

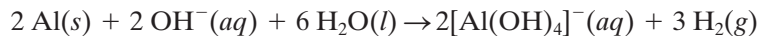
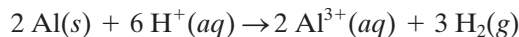
As we discussed in Chapter 9, Section 9.4, much of aluminum chemistry resembles that of scandium more than it does the lower chemically unreactive members of Group 13. For example, aluminum powder will burn in a flame to give a dust cloud of aluminum oxide:



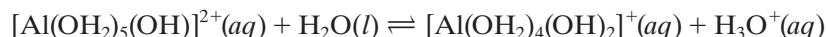
and aluminum will burn very exothermically with halogens, such as dichlorine:



There is also the diagonal similarity with beryllium (Chapter 9, Section 9.5). For example, aluminum, like beryllium, is an amphoteric metal, reacting with both acid and base:



In aqueous solution, the aluminum ion is present as the hexaaquaaluminum ion,  $[\text{Al}(\text{OH}_2)_6]^{3+}$ , but it undergoes a hydrolysis reaction to give a solution of the pentaquahydroxidoaluminum ion,  $[\text{Al}(\text{OH}_2)_5(\text{OH})]^{2+}$ , and the hydronium ion, and then to the tetraaquadihydroxidoaluminum ion:

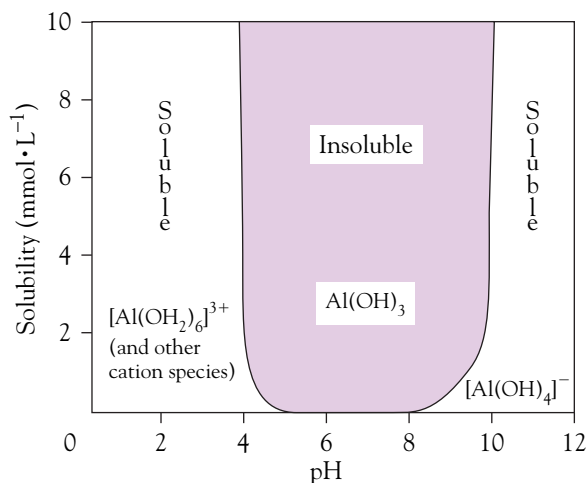
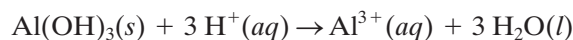


Thus, solutions of aluminum salts are acidic, with almost the same acid ionization constant as ethanoic (acetic) acid. The mixture in antiperspirants commonly called *aluminum chlorhydrate* is, in fact, a mixture of the chloride salts of these two hydroxo ions. It is the aluminum ion in these compounds that acts to constrict pores on the surface of the skin.

Addition of hydroxide ion to aluminum ion first gives a gelatinous precipitate of aluminum hydroxide, but this product redissolves in excess hydroxide ion to give the aluminate ion (more precisely called the *tetrahydroxidoaluminate ion*):



As a result, aluminum 3+ is soluble at low and high pHs but insoluble under neutral conditions (Figure 13.18). Aluminum hydroxide is used in a number of antacid formulations. Like other antacids, the compound is an insoluble base that will neutralize excess stomach acid:



**FIGURE 13.18** Aluminum ion solubility as a function of pH.

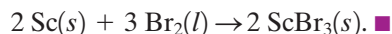


**WORKED EXAMPLE 13.2**

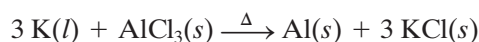
Predict the balanced equation for the reaction of scandium metal with liquid bromine.

**Answer**

As scandium and aluminum have many chemical similarities through the ( $n$ ) and ( $n + 10$ ) linkage, it would be predicted that scandium would react with a halogen in the same way as aluminum:

**The Industrial Extraction of Aluminum**

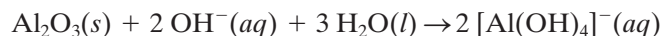
The German chemist Friedrich Wöhler (better known for his synthesis of urea) was among the first to prepare pure aluminum metal. So expensive was aluminum in the mid-nineteenth century that Emperor Napoleon III used aluminum tableware for special state occasions. Wöhler did so by the chemical process of heating potassium metal with aluminum chloride in a redox reaction:



The discovery of an electrolytic reduction method by the French chemist Henri Sainte-Claire Deville and the decreasing cost of electricity caused the price of metallic aluminum to drop dramatically in the late nineteenth century. However, the production of the metal on a large scale required a method that would use an inexpensive, readily available ore. This route was found independently in 1886 by two young chemists: one in France, Paul Héroult, and one in the United States, Charles Hall. Hence, the process is known as the Hall-Héroult process. Charles Hall was assisted by his sister, Julia, who kept detailed notes of the experiments, although it is now known that she played a quite minor role in the discovery.

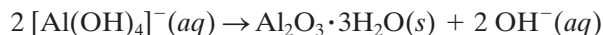
Aluminum is the most abundant metal in the Earth's crust, mostly in the form of clays. To this day, there is no economical route for the extraction of aluminum from clay. However, in hot, humid environments, the more soluble ions are leached from the clay structure to leave the ore bauxite (impure hydrated aluminum oxide). Thus, the countries producing bauxite are mainly those near the equator, Australia being the largest source, followed by Guinea, Brazil, Jamaica, and Suriname.

The first step in the extraction process is the purification of bauxite. This step is accomplished by digesting (heating and dissolving) the crushed ore with hot sodium hydroxide solution to give the soluble aluminate ion:

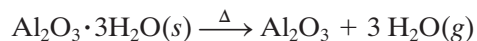


The insoluble materials, particularly iron(III) oxide, are filtered off as “red mud.” In Chapter 20, Section 20.6, we point out that iron(III) ion and aluminum ion have many similarities, but they differ in that aluminum is amphoteric,

reacting with hydroxide ion, whereas iron(III) oxide does not react with hydroxide ion. On cooling, the equilibrium in the solution shifts to the left, and white aluminum oxide trihydrate precipitates, leaving soluble impurities in solution:

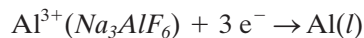


The hydrate is heated strongly in a rotary kiln (similar to that used in cement production) to give anhydrous aluminum oxide:

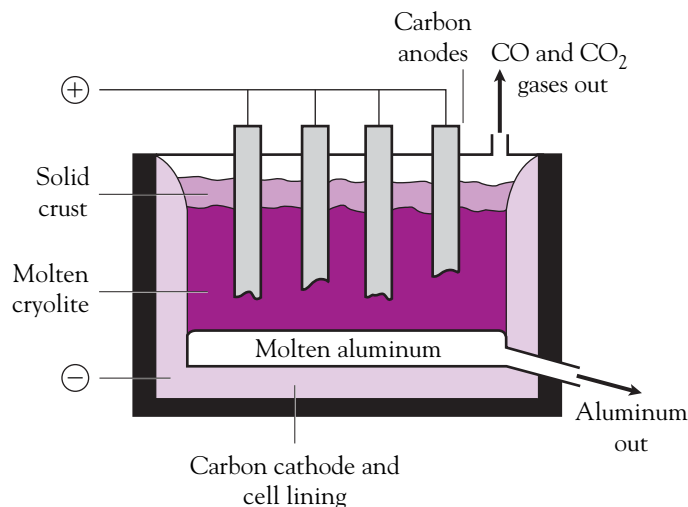


With its high ion charges, aluminum oxide has a very large lattice energy and hence a high melting point (2040°C). However, to electrolyze the aluminum oxide, it was necessary to find an aluminum compound with a much lower melting point. Hall and Héroult simultaneously announced the discovery of this lower-melting-point aluminum compound, the mineral cryolite, whose chemical name is sodium hexafluoroaluminate,  $\text{Na}_3\text{AlF}_6$ .

The detailed chemistry that occurs in the electrolytic cell is still poorly understood, but the cryolite acts as the electrolyte (Figure 13.19). The aluminum oxide is dissolved in molten cryolite at about 950°C. Molten aluminum is produced at the cathode, and the oxygen that is produced at the anode oxidizes the carbon to carbon monoxide (and some carbon dioxide):



About 25 percent of the output of aluminum metal is used in the construction industry, and lesser proportions are used to manufacture aircraft, buses, and railroad passenger cars (18 percent), containers and packaging (17 percent), and electric power lines (14 percent). Aluminum is becoming increasingly favored for automobile construction. With its lower density, fuel



**FIGURE 13.19** Electrolytic cell for aluminum production.

consumption for the same-size vehicle is reduced significantly. For example, each tonne of steel replaced by a tonne of aluminum decreases the carbon dioxide emissions by 20 tonnes over the life of the vehicle. In 1960, the average North American vehicle contained about 2.5 kg of aluminum, while in 2009, the figure was about 200 kg.

### Environmental Issues of Aluminum Production

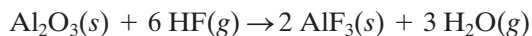
Aluminum production yields four by-products that create major pollution problems:

1. Red mud, which is produced from the bauxite purification and is highly basic
2. Hydrogen fluoride gas, which is produced when cryolite reacts with traces of moisture in the aluminum oxide
3. Oxides of carbon, which are produced at the anode
4. Fluorocarbons, which are produced by reaction of fluorine with the carbon anode

In October 2010, approximately one million cubic meters of red mud from the Ajka aluminum extracting plant in Hungary was released into the surrounding countryside when a reservoir wall collapsed. Fifteen square miles of land were contaminated and all life in the nearby Marcal River was rapidly destroyed.

To reduce the red mud disposal problem, the slurry is poured into settling tanks, from which the liquid component, mainly sodium hydroxide solution, is removed and recycled or neutralized. The solid, mostly iron(III) oxide, can then be used as landfill or shipped to iron smelters for extraction of the iron.

The problem of what to do with the emissions of hydrogen fluoride gas has been solved to a large extent by absorbing the hydrogen fluoride in a filter bed of aluminum oxide. The product of this process is aluminum fluoride:



This fluoride can be added periodically to the melt, thereby recycling the hydrogen fluoride.

A partial solution to the problem of disposing of the large volumes of the oxides of carbon that are produced is to burn the poisonous carbon monoxide, a process giving carbon dioxide and providing some of the heat required to operate the aluminum plant. However, the electrolytic method inevitably produces these two gases, and until an alternative, economical process is devised, aluminum production will continue to contribute carbon dioxide to the atmosphere.

For each tonne of aluminum, about 1 kg of tetrafluoromethane,  $\text{CF}_4$ , and about 0.1 kg of hexafluoroethane,  $\text{C}_2\text{F}_6$ , are produced. These compounds are significant greenhouse gases. The fluorocarbon problem has not yet been solved, and it is the focus of a major research effort by aluminum companies. One advance has been the addition of lithium carbonate to the molten mixture in the electrolytic cell. The presence of lithium carbonate lowers the melting point of the mixture, resulting in a higher current and hence a more efficient cell. At the same time, the presence of the compound reduces fluorine emissions by 25 to 50 percent, thus reducing the production of fluorocarbons.

Fluorosilicic acid is another by-product of the electrolysis process. Until recently, there was little use for this very weak acid. Now, however, it has become a favored source of fluoride ion in the fluoridation of domestic water supplies (see Chapter 17, Section 17.4). At the 1 ppm concentrations in the water supply, the hexafluorosilicate ion will be predominantly hydrolyzed to silicic acid, hydronium ion, and fluoride ion:



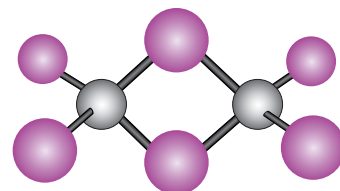
The process is very energy intensive, requiring currents of about  $3.5 \times 10^4$  A at 6 V. In fact, about 25 percent of the cost of aluminum metal is derived from its energy consumption. The production of 1 kg of aluminum consumes about 2 kg of aluminum oxide, 0.6 kg of anodic carbon, 0.1 kg of cryolite, and 16 kWh of electricity. The large energy requirement of the production process favors those countries with inexpensive energy sources. Thus, Canada and Norway, neither of which is a bauxite producer or large aluminum consumer, make the top five of aluminum metal producers. Both countries have low-cost hydroelectric power and deep-water ports favoring easy import of ore and export of aluminum metal. The bulk of the value added to the material comes through the processing steps. Even though the developed world relies heavily on developing countries for the raw material, the latter receive comparatively little in the way of income from the mining phase.

Aluminum recycling is crucial to the increased use of aluminum. The recycling process uses only a small fraction of the energy needed to extract aluminum from its ore. Recycling also avoids the environmental problems of the smelting process. Thus, of all the metals, aluminum reclamation is probably the most important for the environment.

## 13.7 Aluminum Halides

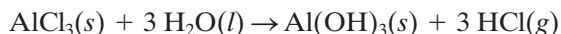
The aluminum halides constitute an interesting series of compounds: aluminum fluoride melts at 1290°C, aluminum chloride sublimates at 180°C, and aluminum bromide and iodide melt at 98°C and 190°C, respectively. Thus, the fluoride has the characteristic high melting point of an ionic compound, whereas the melting points of the bromide and iodide are typical of small-molecule covalent compounds. The aluminum ion has a charge density of  $364 \text{ C} \cdot \text{mm}^{-3}$ , so we expect all anions, except the small fluoride ion, to be polarized to the point of covalent bond formation with aluminum. In fact, aluminum fluoride does have a typically ionic crystal structure with arrays of alternating cations and anions. The bromide and iodide both exist as covalently bonded dimers,  $\text{Al}_2\text{Br}_6$  and  $\text{Al}_2\text{I}_6$ , analogous to diborane, with two bridging halogen atoms (Figure 13.20).

The chloride forms an ionic-type lattice structure in the solid, which collapses in the liquid phase to give molecular  $\text{Al}_2\text{Cl}_6$  dimers. Thus, the ionic and covalent forms must be almost equal in energy. These dimers are also formed when solid aluminum chloride is dissolved in low-polarity solvents.

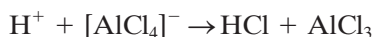
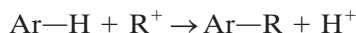
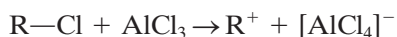


**FIGURE 13.20** Structure of aluminum iodide,  $\text{Al}_2\text{I}_6$ .

Even though anhydrous aluminum chloride appears to adopt an ionic structure in the solid phase, its reactions are more typical of a covalent chloride. This covalent behavior is particularly apparent in the solution processes of the anhydrous aluminum chloride. As mentioned in the previous section, the hexahydrate actually contains the hexaaquaaluminum ion,  $[\text{Al}(\text{OH}_2)_6]^{3+}$ . It dissolves quietly in water, although the solution is acidic as a result of hydrolysis. Anhydrous aluminum chloride, however, reacts very exothermically with water in the typical manner of a covalent chloride, producing a hydrochloric acid mist:



Anhydrous aluminum chloride is an important reagent in organic chemistry. In particular, it is used as a catalyst for the substitution of aromatic rings in the *Friedel-Crafts reaction*. The overall reaction can be written as the reaction between an aromatic compound,  $\text{Ar}-\text{H}$ , and an organochloro compound,  $\text{R}-\text{Cl}$ . The aluminum chloride reacts as a strong Lewis acid with the organochloro compound to give the tetrachloridoaluminate ion,  $\text{AlCl}_4^-$ , and the carbo cation. The carbo cation then reacts with the aromatic compound to give the substituted aromatic compound,  $\text{Ar}-\text{R}$ , and a hydrogen ion. The latter decomposes the tetrachloridoaluminate ion, regenerating aluminum chloride:



### 13.8 Aluminum Potassium Sulfate

In Chapter 5, Section 5.5, we discussed the family of compounds called the *alums*,  $\text{M}^+\text{M}^{3+}(\text{SO}_4^{2-})_2 \cdot 12\text{H}_2\text{O}$ . The compound that gave its name to the series is alum, in which the mono-positive ion is potassium and the tri-positive ion is aluminum. The only common water-soluble mineral of aluminum, it has played an important role in the dyeing industry. To adsorb a dye permanently onto cloth, the cloth is first soaked in a solution of alum. The alum reacts with the cloth surface to form a layer of aluminum hydroxide, to which dye molecules readily bond.

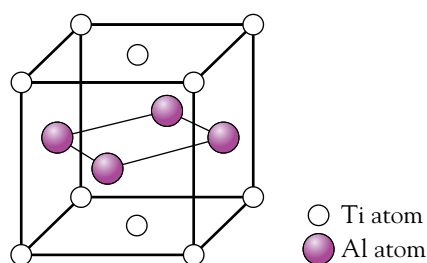
Because of its usefulness, alum has been a valuable import item from Asia since the time of the Romans, nearly 2000 years ago. Alum crystallizes from an equimolar mixture of potassium sulfate and aluminum sulfate to give the formulation of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . Alum crystals have very high lattice stability because the sulfate anions are packed between alternating potassium and hexaaquaaluminum ions. The compound is sometimes used to stop minor bleeding (such as accidental cuts during shaving) because it

causes coagulation of proteins on the surface of cells without killing the cells themselves.

## 13.9 Aluminides

In the search for new high-performance materials, one new “family” of strong but low-density materials has come to prominence: the aluminides. These intermetallic compounds usually have precise stoichiometries and are therefore often referred to as compounds, not alloys (see Chapter 4, Section 4.5). Because the aluminides form a series, for convenience, aluminum is always named second, even if it is not the more electronegative of the atoms.

There are four metal aluminides of current interest: magnesium aluminide (also called magnalium), having two common stoichiometries,  $\text{Mg}_2\text{Al}_3$  and  $\text{Mg}_{17}\text{Al}_{12}$ ; nickel aluminide,  $\text{Ni}_3\text{Al}$ ; tantalum(III) aluminide,  $\text{TaAl}_3$ ; and titanium aluminide,  $\text{TiAl}$  (Figure 13.21). The most important application of these materials is for aircraft engines. With weight saving so important in aircraft, finding strong low-density materials for aircraft gas turbine blades has become a priority among engine manufacturers. Titanium aluminide is not only low density ( $4 \text{ g}\cdot\text{cm}^{-3}$ ) and mechanically strong, but also corrosion resistant, and as a result, it is used for the turbine blades of the new Boeing 787 and 747-8 aircraft.



**FIGURE 13.21** The ion-lattice diagram of titanium aluminide,  $\text{TiAl}$ .

### WORKED EXAMPLE 13.3

Show that the ion-lattice diagram in Figure 13.21 has a stoichiometry corresponding to the formula of titanium aluminide.

#### Answer

Recalling from Chapter 5, Section 5.3, that corner sites contain  $\frac{1}{8}$  of an atom or ion, and those on a cell face contain  $\frac{1}{2}$  of an atom or ion, we can deduce:

The top titanium layer contains:  $1(\frac{1}{2}) + 4(\frac{1}{8}) = 1 \text{ atom Ti}$

The middle aluminum layer contains:  $4(\frac{1}{2}) = 2 \text{ atom Al}$

The bottom titanium layer contains:  $1(\frac{1}{2}) + 4(\frac{1}{8}) = 1 \text{ atom Ti}$

Therefore, the unit cell contains two atoms each of titanium and aluminum. ■



## 13.10 Biological Aspects

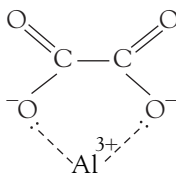
### The Essentiality of Boron

Boron is an essential micronutrient in plants. The element is believed to play a major role in the synthesis of one of the bases for RNA formation and in cellular activities, such as carbohydrate synthesis. After zinc, boron is the most common soil deficiency worldwide. The class of plants known as dicots have much higher boron requirements than monocots. Crops most susceptible to boron deficiency and that often require boron supplements are alfalfa, carrot, coffee, cotton, peanut, sugar beet, sunflower, rutabaga (swede), and turnip. There is growing evidence that boron is an essential element for mammals, possibly in bone formation.

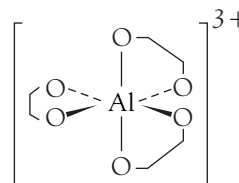
### The Toxicity of Aluminum

As mentioned in the Context at the beginning of this chapter, aluminum is a highly toxic metal. Fortunately, under near-neutral conditions aluminum ion forms insoluble compounds, minimizing its bioavailability (see Section 13.6). Fish are particularly at risk from aluminum toxicity. Research has shown that the damage to fish stocks in acidified lakes is not due to the lower pH but to the higher concentrations of aluminum ion in the water that result from the lower pH. In fact, an aluminum ion concentration of  $5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$  is sufficient to kill fish.

Also in the Context, we described how acid soils solubilize aluminum which is toxic to cells. However, some plants are naturally resistant to aluminum toxicity. These plants excrete oxalate ion, citrate ion, and malate ion. Recalling Chapter 7, Section 7.6, using Pearson Hard-Soft Acid-Base Theory, “hard” aluminum ions will be attracted to “hard” oxygen-containing ions. As we will discuss in Chapter 19, the two negative oxygens of these ions can attach to a metal ion, such as aluminum (Figure 13.22). In fact, three of the ions will completely surround the aluminum ions, preventing them from entering the cells (Figure 13.23). Genetic engineers are now working on the introduction of organic acid-generating genes into important food crop species, which will hopefully lead to better crop yields.



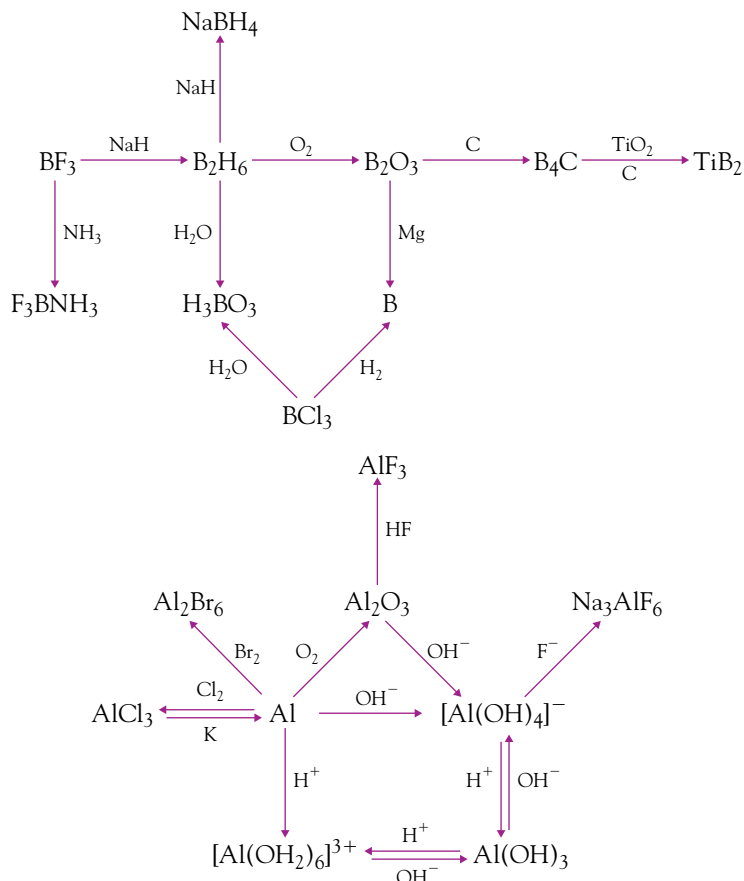
**FIGURE 13.22** The bonding of an aluminum ion to an oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ .



**FIGURE 13.23** A schematic diagram of three oxalate ions bonded to an aluminum ion.

## 13.11 Element Reaction Flowcharts

Boron and aluminum are the only two Group 13 elements that we have discussed in depth.



### KEY IDEAS

- The +3 oxidation state predominates in this group but mostly in covalent compounds.
- Boron has a unique chemistry, particularly among the boranes.
- Aluminum is a reactive amphoteric metal.
- The extraction of aluminum is accomplished by an electrical reduction method.

### EXERCISES

**13.1** Write balanced chemical equations for the following chemical reactions:

- (a) liquid potassium metal with solid aluminum chloride

- (b) solid diboron trioxide with ammonia gas at high temperature  
 (c) aluminum metal with hydroxide ion  
 (d) tetraborane,  $\text{B}_4\text{H}_{10}$ , and dioxygen

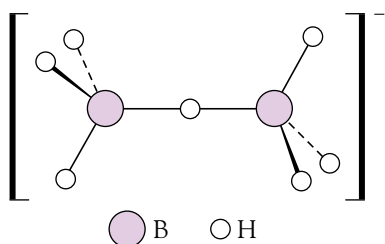
**13.2** Write balanced chemical equations for the following chemical reactions:

- liquid boron tribromide with water
- aluminum metal with hydrogen ion
- thallium(I) hydroxide solution with carbon dioxide gas

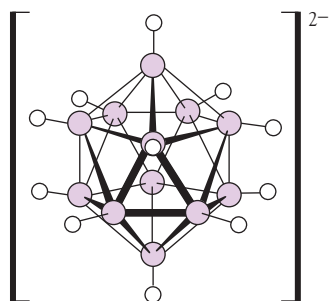
**13.3** Construct an electron-dot structure for the peroxoborate ion. Thus, deduce the oxidation number of the bridging oxygen atoms.

**13.4** Boron carbide has the empirical formula of  $B_4C$ . What is a more correct representation of this compound? Give your reasoning.

**13.5** The figure below shows the structure of the borane anion,  $B_2H_7^-$ . To which family does this borane belong?



**13.6** The figure below shows the structure of the borane anion,  $B_{12}H_{12}^{2-}$ . To which family does this borane belong?



**13.7** From bond energy data, calculate the enthalpy of formation of boron trifluoride. What two factors result in its particularly high value?

**13.8** From bond energy data, calculate the enthalpy of formation of boron trichloride (gaseous). Why is the value so different from that of boron trifluoride?

**13.9** With a very high charge density, aluminum would not be expected to exist widely as a free  $3+$  ion, yet it does exist in the form of a hydrated  $3+$  ion. Explain why.

**13.10** Explain briefly why sheets of aluminum do not oxidize completely to aluminum oxide even though aluminum is a highly reactive metal.

**13.11** Explain briefly why solutions of aluminum chloride are strongly acidic.

**13.12** Magnesium metal only reacts with acids, whereas aluminum reacts with both acids and bases. What does this behavior tell you about aluminum?

**13.13** Explain the potential environmental hazards from aluminum smelting.

**13.14** Why are aluminum smelters sometimes located in countries other than those that produce the ore or consume much of the metal?

**13.15** Contrast the bonding in the different aluminum halides.

**13.16** Why is alum a commonly used salt of aluminum?

**13.17** On the basis of aluminum chemistry, suggest the bonding in scandium chloride in the solid phase and in the species which makes some of the gas phase.

**13.18** Explain why thallium(I) compounds are usually ionic species while thallium(III) compounds are more covalent in their behavior.

**13.19** Gallium(III) fluoride,  $GaF_3$ , sublimates at  $950^\circ C$ , while gallium(III) chloride,  $GaCl_3$ , melts at  $78^\circ C$ . Suggest an explanation for the significant difference.

**13.20** Compare and contrast the chemistry of boron and silicon.

**13.21** Why is aluminum a particular environmental problem in the context of acid rain?

**13.22** Write balanced chemical equations corresponding to each transformation in the element reaction flowcharts for boron and aluminum (page 331).

## BEYOND THE BASICS

**13.23** The metallic, covalent, and ionic (six-coordinate) radii for aluminum are 143 pm, 130 pm, and 54 pm. Explain why these values are different.

**13.24** Aluminum fluoride,  $AlF_3$ , is insoluble in pure liquid hydrogen fluoride but dissolves readily in liquid hydrogen fluoride-containing sodium fluoride. When boron trifluoride

is bubbled into the solution, aluminum fluoride precipitates. Write two equations to represent these observations and suggest what is happening in each case using an appropriate acid-base concept.

**13.25** When aluminum chloride is dissolved in benzene,  $C_6H_6$ , a dimer,  $Al_2Cl_6$  is obtained. However, when the compound is dissolved in diethylether,  $(C_2H_5)_2O$ , a chemical reaction occurs to give a species containing one aluminum atom. Suggest the identity of the compound.

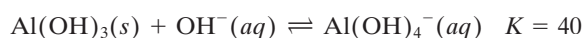
**13.26** When beryllium chloride is vaporized, a dimer of formula  $Be_2Cl_4$  is formed. Suggest a structure for the dimer. Explain your reasoning.

**13.27** A solution of beryllium ion,  $[Be(OH_2)_4]^{2+}(aq)$ , is strongly acidic. Write a balanced chemical equation for the first step in the process. Explain why you would expect this ion to be acidic.

**13.28** Zeolite-A,  $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$ , is a good ion exchanger, removing such ions as calcium and magnesium from water supplies. What mass of zeolite should a home water softener unit contain if it is to completely remove calcium and magnesium ions at a total concentration of  $2.0 \times 10^{-3} \text{ mol} \cdot L^{-1}$  from a flow-through of  $1.0 \times 10^6 \text{ L}$  of water before it needs recharging?

**13.29** The aluminosilicate mineral phlogopite has the formula  $KMg_3[AlSi_3O_{10}](OH)_2$ . Determine the value of  $x$ .

**13.30** Construct a Pourbaix diagram for aluminum, showing the species  $Al(s)$ ,  $Al^{3+}(aq)$ ,  $Al(OH)_3(s)$ , and  $Al(OH)_4^-(aq)$ , given  $K_{sp}(Al(OH)_3(s)) = 1 \times 10^{33}$  and:



In the range of possible pH and  $E^0$  values for natural waters, what are the only species likely? Why is this diagram relevant to the acid rain problem?

**13.31** The enthalpy of formation of gallium(I) chloride is  $+38 \text{ kJ} \cdot \text{mol}^{-1}$ , while that of gallium(III) chloride is  $-525 \text{ kJ} \cdot \text{mol}^{-1}$ . Show why gallium(I) chloride should be thermodynamically unstable.

**13.32** When damp, aluminum sulfide,  $Al_2S_3$ , produces the “rotten egg” smell of hydrogen sulfide. Write a balanced equation for the reaction and suggest an explanation for it.

**13.33** Aluminum chloride dissolves in the basic solvent  $CH_3CN$  to give a 1:1 (cation:anion) conducting solution. The cation has the formula  $[Al(NCCCH_3)_6]^{3+}$ . Suggest the formula of the anion and write a balanced chemical equation for the reaction.

**13.34** Boron forms a compound of formula  $B_2H_2(CH_3)_4$ . Draw a probable structure for this compound.

**13.35** When gallium(III) salts are dissolved in water, the  $[Ga(OH_2)_6]^{3+}(aq)$  ion is initially formed, but a white precipitate of  $GaO(OH)$  slowly forms. Write a balanced chemical equation for the process and suggest how the gallium(III) ion can be kept in solution.

**13.36** Thallium forms a selenide of formula  $TlSe$ . What does the oxidation state of thallium appear to be? What is a more likely structure of the compound?

**13.37** Gallium forms an analogous vapor-phase compound to diborane:  $Ga_2H_6$ , digallane. However, aluminum forms a solid polymeric hydride,  $[AlH_3]_x$ . Why is the difference in behavior not surprising?

**13.38** Gallium dichloride,  $GaCl_2$ , is a diamagnetic compound that is a 1:1 electrolyte in solution containing a simple cation and a tetrachloro anion. Suggest a possible structure for the compound.

**13.39** At very low temperatures, the compound  $B_3F_5$  can be synthesized. Spectroscopic evidence shows that the molecule contains two types of fluorine environments in a ratio of 4:1 and two types of boron environments in a ratio of 2:1. Suggest a structure for this molecule.

**13.40** Boric acid,  $H_3BO_3$ , also written as  $B(OH)_3$ , acts as a weak acid in water. However, it does not do so by loss of a hydrogen ion. Instead, it acts as a Lewis acid toward the hydroxide ion. Write a balanced equation for the reaction of boric acid with water.

**13.41** Calculate an approximate value for the bond energy for the bridging B—H bond in diborane using the data tables in the appendices. In comparison with the normal B—H bond energy, what does this suggest about the bond order? Is this result compatible with the bond order (per bond) deduced from the molecular orbital diagram (Figure 13.12)?

**13.42** Instead of the commonly used reaction of hydrocarbons with air as a high-performance aircraft fuel, it was once proposed to use diborane with air. If  $\Delta_{\text{combustion}} H^0(B_2H_6(g)) = -2165 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_{\text{combustion}} H^0(C_2H_6(g)) = -1560 \text{ kJ} \cdot \text{mol}^{-1}$ , calculate the comparative energy per gram of diborane compared to per gram of ethane. Use the data tables in the appendices to calculate the entropy change in each reaction. Suggest why the entropy of combustion values are so different. What would be some practical disadvantages of using diborane?

**13.43** Calculate the standard enthalpy of formation of diboron trioxide, given that  $\Delta_{\text{combustion}}H^\circ(\text{B}_2\text{H}_6)(g) = -2165 \text{ kJ}\cdot\text{mol}^{-1}$ . Use the data tables in the appendices for the other values required.

**13.44** Boron forms two isoelectronic anions:  $\text{BO}_2^-$  and  $\text{BCl}_2^{5-}$ . Construct an electron-dot structure for each ion. There is a third member of this series:  $\text{BN}_2^{n-}$ . Predict the charge on this ion.

**13.45** Zirconium forms a boride of formula  $\text{ZrB}_{12}$ , which adopts a sodium chloride lattice structure. Is it more likely that the compound is ionic— $[\text{Zr}^{4+}][\text{B}_{12}^{4-}]$ —or simply based on zirconium atoms and a neutral  $\text{B}_{12}$  cluster? Metallic radius, Zr = 159 pm; ionic radius,  $\text{Zr}^{4+} = 72 \text{ pm}$ ; covalent radius, B = 88 pm. Explain your reasoning.

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## ADDITIONAL RESOURCES

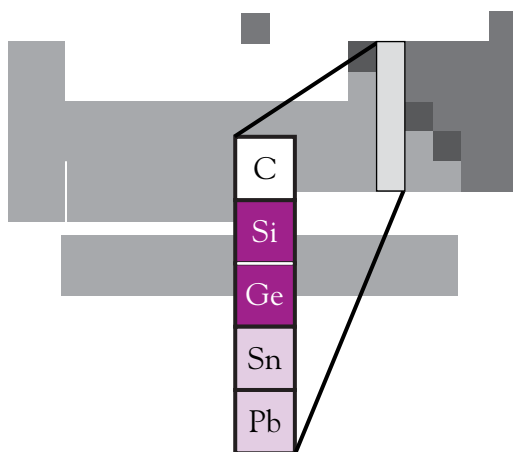
For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# THE GROUP 14 ELEMENTS

## CHAPTER 14



C
Si
Ge
Sn
Pb

This group contains a nonmetal (carbon), two metalloids (silicon and germanium), and two weakly electropositive metals (tin and lead). Carbon has the most important chemistry of the group. It is the variety of oxoanions, many of which are found in minerals, that makes silicon chemistry interesting. The weakly metallic properties of tin and lead contrast sharply with the properties of the alkali supermetals.

### Context: Cermets—The Toughest Materials

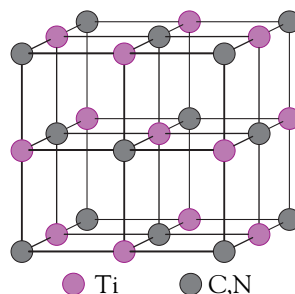
In the Context of Chapter 4, we introduced the concept of composite materials, in particular, metal matrix composites (MMCs). Cermets (ceramic-metallic materials) are the opposite of MMCs, with the compound as the matrix and embedded metal particles. Whereas MMCs are strong, low-density materials, cermets are usually materials designed for their hardness combined with lowish density. These properties, together with the high conductivity of the incorporated metal, make cermets ideal for such purposes as high-speed lightweight cutting tools.

The first cermets used oxides as the matrix, such as magnesium oxide and aluminum oxide. For strong, hard materials, carbides (Section 14.5) or nitrides are now used. A common matrix is a compound of titanium with carbon or nitrogen, or a combination of carbon and nitrogen. The compounds all have a 1:1 cation-anion formulation; that is, titanium carbide, TiC; titanium nitride, TiN; or titanium carbonitride, Ti(C,N).

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 14.1** Group Trends
- 14.2** Contrasts in the Chemistry of Carbon and Silicon
- 14.3** Carbon
- 14.4** Isotopes of Carbon
- 14.5** Carbides
- 14.6** Carbon Monoxide
- 14.7** Carbon Dioxide
- 14.8** Carbonates and Hydrogen Carbonates
- 14.9** Carbon Sulfides
- 14.10** Carbon Halides
- 14.11** Methane
- 14.12** Cyanides
- 14.13** Silicon
- 14.14** Silicon Dioxide
- 14.15** Silicates
- 14.16** Aluminosilicates
- 14.17** Silicones
- 14.18** Tin and Lead
- 14.19** Biological Aspects
- 14.20** Element Reaction Flowcharts

Each of these compounds adopts the sodium chloride lattice structure seen in the following figure.



The ion-lattice diagram of titanium carbonitride.

## 14.1 Group Trends

The first three elements of Group 14 have very high melting points, a characteristic of network covalent bonding for nonmetals and metalloids, whereas the two metals in the group have low melting points and, common to all metals, long liquid ranges (Table 14.1). All the Group 14 elements form compounds in which they *catenate* (form chains of atoms with themselves). The ability to catenate decreases down the group.

Now that we have reached the middle of the main groups, the nonmetallic properties are starting to predominate. In particular, multiple oxidation states become common. All members of Group 14 form compounds in which they have an oxidation number of +4. This oxidation state involves covalent bonding, even for the two metals of the group. In addition, an oxidation state of  $-4$  exists for the three nonmetals/metalloids when they are bonded to more electropositive elements. Tin and lead also have an oxidation state of +2, which is the only oxidation state in which they form ionic compounds (see Section 14.18). For silicon, there is no common compound in which silicon exists in a +2 oxidation state; in contrast, the +2 oxidation state of lead is the most stable and in the +4 state lead is strongly oxidizing. One of the few common examples of carbon in the +2 oxidation state is the reducing compound carbon monoxide.

**TABLE 14.1** Melting and boiling points of the Group 14 elements

Element	Melting point (°C)	Boiling point (°C)
C	Sublimes at 4100	
Si	1420	3280
Ge	945	2850
Sn	232	2623
Pb	327	1751

## 14.2 Contrasts in the Chemistry of Carbon and Silicon

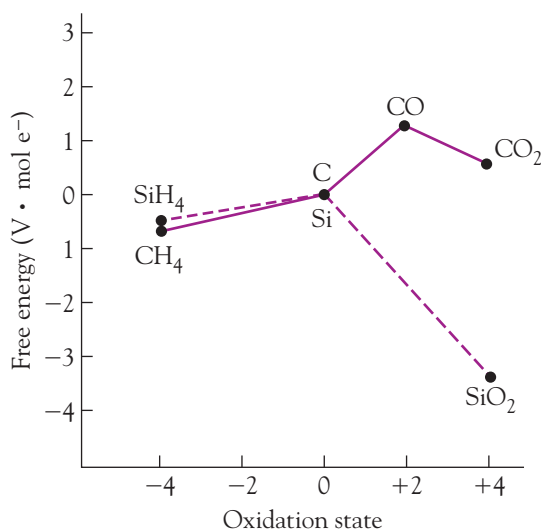
For Groups 14 to 17, there is a significant difference in the chemistry between the Period 2 member and those in subsequent periods. The Frost diagram shown in Figure 14.1 indicates the contrast in thermodynamic stabilities between carbon and silicon species. Particularly noticeable is the exceptional stability of silicon dioxide.

### The Dioxides of Carbon and Silicon

Carbon dioxide and silicon dioxide share the same type of formula, yet their properties are very different. Carbon dioxide is a colorless gas at room temperature, whereas solid silicon dioxide melts at 1600°C and boils at 2230°C. The difference in boiling points is due to bonding factors. Carbon dioxide consists of small, triatomic, nonpolar molecular units whose attraction to one another is due to dispersion forces (Figure 14.2).

By contrast, silicon dioxide contains a network of silicon-oxygen covalent bonds in a giant molecular lattice. Each silicon atom is bonded to four oxygen atoms, and each oxygen atom is bonded to two silicon atoms, an arrangement consistent with the  $\text{SiO}_2$  stoichiometry of the compound (Figure 14.3).

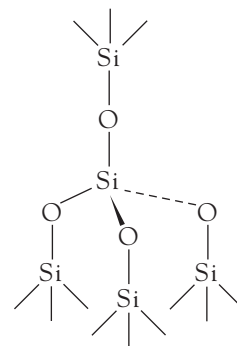
How can we explain this difference? First, the carbon-oxygen single bond is much weaker than the carbon-oxygen double bond (Table 14.2). Hence, it is energetically more favorable to form two  $\text{C}=\text{O}$  double bonds than the four  $\text{C}-\text{O}$  single bonds needed for carbon dioxide to be analogous to silicon dioxide. In the case of silicon, silicon-oxygen single bonds are very strong. Since multiple bonds in compounds of elements from Period 3 and higher periods have energies that are not much greater than those of the corresponding single bonds, for silicon, four single bonds (with partial multiple bond character) are much more preferable than two conventional double bonds.



**FIGURE 14.1** Frost diagram in acid solution for carbon and silicon.



**FIGURE 14.2** The structure of carbon dioxide.



**FIGURE 14.3** The structure of silicon dioxide.



**TABLE 14.2** Bond energies of carbon and silicon bonds with oxygen

Carbon bonds	Bond energy (kJ·mol <sup>-1</sup> )	Silicon bonds	Bond energy (kJ·mol <sup>-1</sup> )
C—O	358	Si—O	452
C=O	799	Si=O	642

### The Catenation of Carbon

Carbon has two properties that enable it to form such an extensive range of compounds: *catenation* (the ability to form chains of atoms) and multiple bonding (that is, the ability to form double and triple bonds). Extensive use of multiple bonding is found in compounds of carbon, nitrogen, and oxygen. Carbon shows the greatest propensity for catenation of all elements. For catenation, three conditions are necessary:

1. A bonding capacity (valence) greater than or equal to 2
2. An ability of the element to bond with itself; the self-bond must be about as strong as its bonds with other elements
3. A kinetic inertness of the catenated compound toward other molecules and ions

We can see why catenation is frequently found in carbon compounds but only rarely in silicon compounds by comparing bond energy data for these two elements (Table 14.3). Notice that the energies of the carbon-carbon and carbon-oxygen bonds are very similar. However, the silicon-oxygen bond is much stronger than that between two silicon atoms. Thus, in the presence of oxygen, silicon will form —Si—O—Si—O— chains rather than —Si—Si— linkages. We will see later that the silicon-oxygen chains dominate the chemistry of silicon. There is much less of an energy “incentive” to break carbon-carbon bonds in favor of the formation of carbon-oxygen bonds.

**TABLE 14.3** Bond energies of various carbon and silicon bonds

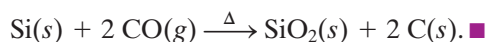
Carbon bonds	Bond energy (kJ·mol <sup>-1</sup> )	Silicon bonds	Bond energy (kJ·mol <sup>-1</sup> )
C—C	346	Si—Si	222
C—O	358	Si—O	452

### WORKED EXAMPLE 14.1

Would you expect heated silicon to burn in carbon monoxide? If so write a balanced chemical equation for the reaction.

#### Answer

From the Frost diagram in Figure 14.1, the thermodynamic stability of silicon dioxide would suggest silicon should readily reduce carbon monoxide to carbon and itself be oxidized to silicon dioxide.



## 14.3 Carbon

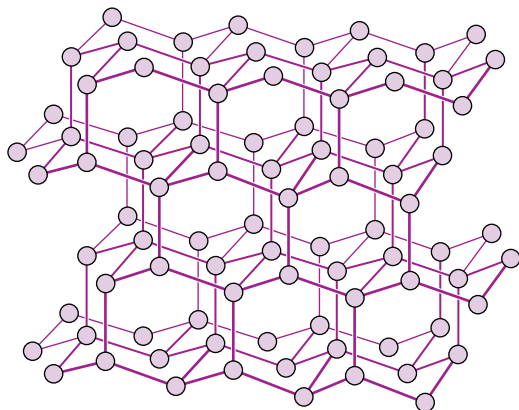
Diamond and graphite have been known throughout much of recorded history, but we now know of a whole new family of allotropes.

### Diamond

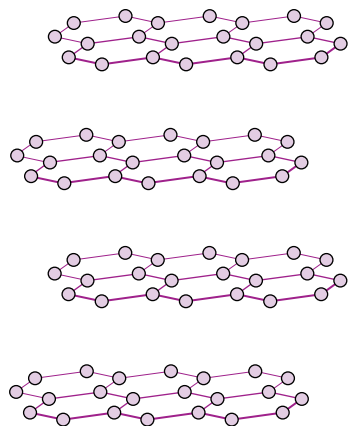
In the diamond form of carbon, there is a network of single, tetrahedrally arranged covalent bonds (Figure 14.4). Diamond is an electrical insulator but an excellent thermal conductor, being about five times better than copper. We can understand the thermal conductivity in terms of the diamond structure. Because the giant molecule is held together by a continuous network of covalent bonds, little movement of individual carbon atoms can occur. Hence, any added heat energy will be transferred as molecular motion directly across the whole diamond. Diamond is a solid to over 4000°C because an enormous amount of energy is needed to break these strong covalent bonds.

In “normal” diamond, the arrangement of the tetrahedra is the same as that in the cubic ZnS-sphalerite ionic structure (see Chapter 5, Section 5.3). There is also an extremely rare form, lonsdaleite (named after the famous crystallographer Kathleen Lonsdale), in which the tetrahedra are arranged in the hexagonal ZnS-wurtzite structure (also shown in Chapter 5, Section 5.3).

The density of diamond ( $3.5 \text{ g}\cdot\text{cm}^{-3}$ ) is much greater than that of graphite ( $2.2 \text{ g}\cdot\text{cm}^{-3}$ ), so a simple application of the Le Châtelier principle indicates that diamond formation from graphite is favored under conditions of high pressure. Furthermore, to overcome the considerable activation energy barrier accompanying the rearrangement of covalent bonds, high temperatures also are required. Diamonds are now readily synthesized but the crystals produced are small and not of gem quality, although they are ideal for drill bits and as grinding material. It is also possible to make diamond films over surfaces using chemical vapor deposition, in which hydrocarbon-containing vapors and gases are passed at very low pressures over a surface. High energy, such as intense microwaves, are used to decompose the compounds, depositing carbon atoms in layers on the material surface.



**FIGURE 14.4** The structure of diamond.



**FIGURE 14.5** The structure of graphite.

## Graphite

The structure of graphite is quite different from that of diamond. Graphite consists of layers of carbon atoms (Figure 14.5). Within the layers, covalent bonds hold the carbon atoms in six-membered rings. The carbon-carbon bond length in graphite is 141 pm. These bonds are much shorter than those in diamond (154 pm) but very similar to the 140-pm bonds in benzene,  $C_6H_6$ . This similarity in bond lengths suggests a possible explanation for the short interatomic distance in graphite—there is multiple bonding between the carbon atoms within layers. Like benzene, graphite is assumed to have a delocalized  $\pi$  electron system throughout the plane of the carbon rings resulting from overlap of the  $2p_z$  orbitals at right angles to the plane of the rings. This arrangement would result in a net  $1\frac{1}{3}$  bond between each pair of carbon atoms. The measured bond length is consistent with this assumption.

The distance between the carbon layers is very large (335 pm) and is more than twice the value of the van der Waals radius of a carbon atom. Hence, the attraction between layers is very weak. In the common hexagonal form of graphite (see Figure 14.4), alternating layers are aligned to give an *abab* arrangement. When you look at the sequential layers, one-half of the carbon atoms are located in line with carbon atoms in the planes above and below, and the other half are located above and below the centers of the rings.

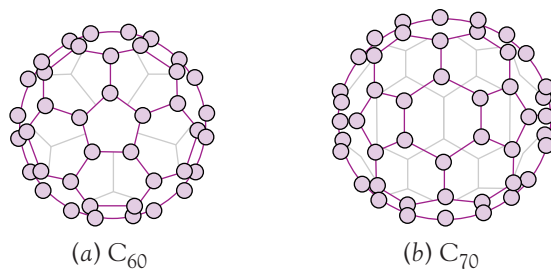
The layered structure of graphite accounts for one of its most interesting properties: a high electric conductivity. More specifically, the conductivity in the plane of the sheets is about 5000 times greater than that at right angles to the sheets. Graphite is also an excellent lubricant by virtue of the ability of sheets of carbon atoms to slide over one another. However, this is not quite the whole story. Graphite also adsorbs gas molecules between its layers. Thus, many chemists argue that the graphite sheets are gliding on molecular “ball bearings”; namely, the adsorbed gas molecules.

Even though graphite is thermodynamically more stable than diamond, it is kinetically more reactive as a result of the separation of the carbon sheets. A wide range of substances from alkali metals through the halogens to metal halide compounds are known to react with graphite. In the resulting products, the graphite structure is essentially preserved, with the intruding atoms or ions fitting between the layers in a fairly stoichiometric ratio. We encountered these graphite intercalation compounds earlier in Chapter 11, Section 11.4.

Graphite is used in lubricants, as electrodes, and as graphite-clay mixtures in lead pencils. The common mixture in pencil leads is designated “HB.” The higher-clay (harder) mixtures are designated by increasing “H” numbers, for example, “2H,” and the higher-graphite (softer) mixtures are designated by increasing “B” numbers. There is no lead in a lead pencil. The term originated from the similarity between the streak left on a surface from a soft lead object and that from graphite.

## Fullerenes

Fullerenes constitute a family of structures in which the carbon atoms are arranged in a spherical or ellipsoidal structure. To make such a structure, the



**FIGURE 14.6** The structures of C<sub>60</sub> and C<sub>70</sub>.

carbon atoms form five- and six-membered rings, similar to the pattern of lines on a soccer ball (the early name for C<sub>60</sub> was *soccerane*). The C<sub>60</sub> allotrope (Figure 14.6a), buckminsterfullerene, is the easiest to prepare. The C<sub>70</sub> allotrope (Figure 14.6b) is the next most commonly available fullerene.

This allotrope family was named after R. Buckminster Fuller, a genius of the twentieth century. His name is particularly associated with the geodesic dome, an architectural design of tremendous strength that has the same structural arrangement as the C<sub>60</sub> molecule. Contrary to general belief, however, he did not invent the dome. This was done by Walter Bauersfeld in Germany, but Buckminster Fuller did make major improvements to the design and popularized it.

Diamond and graphite are insoluble in all solvents because they have network covalent structures. The fullerenes have covalent bonds within the units, but only dispersion forces hold the units together in the solid phase. As a result, they are very soluble in nonpolar solvents such as hexane and toluene. Although black in the solid phase, fullerenes display a wide range of colors in solution: C<sub>60</sub> gives an intense magenta-purple color, C<sub>70</sub> is wine red, and C<sub>76</sub> is bright yellow-green. All the fullerenes sublime when heated, a property providing further evidence of the weak intermolecular forces.

The C<sub>60</sub> molecules pack together in the same way metal atoms do, forming a face-centered cubic arrangement. The fullerenes have low densities (about 1.5 g·cm<sup>-3</sup>), and they are nonconductors of electricity. The fullerenes are easily reduced to anions by reaction with Group 1 and Group 2 metals. For example, rubidium fits within the interstices in the C<sub>60</sub> lattice to give Rb<sub>3</sub>C<sub>60</sub>. This compound is a superconductor at temperatures below 28 K because its structure is actually [Rb<sup>+</sup>]<sub>3</sub>[C<sub>60</sub><sup>3-</sup>]. The extra electrons associated with the fullerenes are free to move throughout the crystal, just like those in a metal. Since the cavities in the fullerenes are quite large, it is possible to fit a metal ion within the structure. An example of this is La@C<sub>82</sub>, where the @ symbol is used to indicate that the 3+ metal ion is within the fullerene. Chemical reaction with the surface of the fullerenes is also possible; thus, reaction with fluorine results in the formation of colorless C<sub>60</sub>F<sub>60</sub>.

Of the fullerene series, C<sub>60</sub> is the easiest to produce, followed by C<sub>70</sub>. Even-numbered fullerenes from C<sub>70</sub> to well over C<sub>100</sub> are known. The smallest stable fullerene synthesized is C<sub>36</sub>, a reactive black solid that gives a golden yellow solution. C<sub>36</sub> is expected to be the smallest stable fullerene feasible on the basis of the strained bonds needed to close such a small sphere. The smallest

fullerene prepared,  $C_{20}$ , a spheroid based solely on pentagonal units, exists only fleetingly.

### Carbon Nanotubes

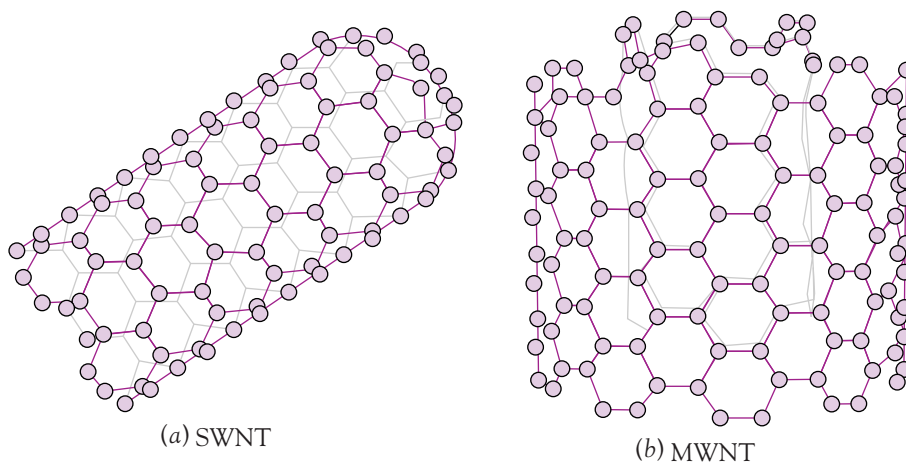
Nanotubes are essentially tiny strips of graphite sheet, rolled into tubes, and capped with half a fullerene at each end. They can be made by heating graphite in an inert atmosphere under patented conditions to about  $1200^{\circ}\text{C}$ . Because the carbon atoms in nanotubes are held together by covalent bonds, the tubes are immensely strong—they have about 100 times the strength of an equivalent strand of steel. Thus, nanotubes could be used as superstrong materials. Provided the carbon hexagons are aligned precisely with the long axis of the nanotube, the material is an excellent electrical conductor. This behavior opens the possibility for bundles of nanotubes to be the electrical equivalent of optical fibers. However, if there is a “twist” in the hexagons, giving a spiral arrangement, the material behaves as a semiconductor. Open-ended nanotubes also have potential for the reversible storage of hydrogen gas, suggesting they may play a role in the future hydrogen-based economy.

There are two classes of nanotubes: the single-walled nanotubes (SWNTs) and the multiwalled nanotubes (MWNTs) (Figure 14.7). The SWNTs consist of simple carbon nanotubes, whereas the MWNTs consist of concentric layers of nanotubes like a coaxial cable. It is the SWNTs that have the greater promise, but at present they are very expensive to synthesize.

### Graphene

Graphite, fullerenes, and nanotubes are all based on hexagonal rings of carbon atoms. A single flat sheet of these hexagonal rings is called *graphene*. It was believed impossible to peel a single layer of carbon rings from graphite; then in 2004, a team of researchers at the University of Manchester, England, did so by the simple procedure of using adhesive tape. The material cannot be called graphite because, by definition, graphite is a three-dimensional structure with dispersion-force attraction between layers.

**FIGURE 14.7** The structures of (a) single-walled nanotubes (SWNT) and (b) multiwalled nanotubes (MWNT).



Being just one atom thick, graphene (sometimes called *atomic chicken wire*) is totally transparent. It behaves as a metalloid with unusual electrical and magnetic properties and, with the atoms being held together by a  $\sigma$  and a conjugated  $\pi$  system, it is very strong. The edges of sheets can be oxidized to form graphene oxide and then water molecules can be used to “stitch” graphene plates together to form large two-dimensional sheets of graphene. Although the uses of graphene have not been fully explored, a graphene sheet has been used as the ultimate gas sensor, detecting a single molecule of nitrogen dioxide.

### Impure Carbon

The major uses of carbon are as an energy source and as a reducing agent. For reducing purposes, an impure form of carbon (coke) is used. This material is produced by heating coal in the absence of air. In this process, the complex coal structure breaks down, boiling off hydrocarbons and leaving behind a porous, low-density, silvery, almost metallic-looking solid. Essentially, coke is composed of microcrystals of graphite that have small proportions of some other elements, particularly hydrogen, bonded in their structure. Much of the distillate produced by the coking process can be used as raw materials in the chemical industry, but the oily and watery wastes are a cocktail of carcinogens. Coke is utilized in the production of iron from iron ore and in other pyrometallurgical processes. Coke production is considerable, and about  $5 \times 10^8$  tonnes are used worldwide every year.

Carbon black is a very finely powdered form of carbon. This impure micrographite is produced by incomplete combustion of organic materials. It is used in extremely large quantities—about  $1 \times 10^7$  tonnes per day. Mixed with rubber, carbon black strengthens tires and reduces wear. About 3 kg of carbon black is used for the average automobile tire, and it is the carbon content that gives a tire its black color.

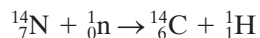
Another form of carbon known as activated carbon has a very high surface area—typically  $10^3 \text{ m}^2 \cdot \text{g}^{-1}$ . This material is used for the industrial decolorizing of sugar and in gas filters, as well as for removing impurities from organic reactions in the laboratory. The physical chemistry of the absorption process is complex, but in part it works by the attraction of polar molecules to the carbon surface.

Blocks of carbon are industrially important as electrodes in electrochemical and thermochemical processes. For example, about 7.5 million tonnes of carbon are used each year just in aluminum smelters. And, of course, the summer season always increases the consumption of carbon in home barbecues.

## 14.4 Isotopes of Carbon

Natural carbon contains three isotopes: carbon-12 (98.89 percent), the most prevalent isotope; a small proportion of carbon-13 (1.11 percent); and a trace of carbon-14. Carbon-14 is a radioactive isotope with a half-life of  $5.7 \times 10^3$  years. With such a short half-life, we would expect little sign of this isotope on Earth. Yet it is prevalent in all living tissue because the isotope is constantly

being produced by reactions between cosmic ray neutrons and nitrogen atoms in the upper atmosphere:



The carbon atoms react with oxygen gas to form radioactive molecules of carbon dioxide. These are absorbed by plants in photosynthesis. Creatures that eat plants and creatures that eat the creatures that eat plants will all contain the same proportion of radioactive carbon. After the death of the organism, there is no further intake of carbon, and the carbon-14 already present in the body decays. Thus, the age of an object can be determined by measuring the amount of carbon-14 present in a sample. This method provides an absolute scale of dating objects that are between 1000 and 20 000 years old.

Carbon is another element for which isotope effects are particularly important—in fact, the proportion of carbon-13 can vary from 0.99 percent to 1.10 percent, depending on the carbon source. When carbon dioxide is absorbed by plants and converted to sugars, different photosynthetic pathways result in different fractionation of the carbon isotopes. For example, from the carbon isotope ratio, we can tell whether a sugar sample is derived from sugarcane or sugar beets. These isotope ratio tests have become invaluable in checking consumer foodstuffs for quality, such as the possible adulteration of honey or wine with low-cost sugar solution. In the chemistry laboratory, there are many applications of isotope effects, including the correlation of infrared absorption spectra with molecular vibrations.

### WORKED EXAMPLE 14.2

Carbon-14 decays to give nitrogen-14 and an electron. Write a nuclear equation for the reaction.

#### Answer

Expulsion of an electron from a nucleus keeps the mass number (nucleon number) the same, but increases the atomic number (number of protons) by one.



## 14.5 Carbides

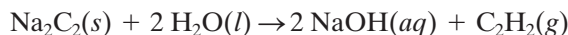
Binary compounds of carbon with less electronegative elements (except hydrogen) are called *carbides*. Carbides are hard solids with high melting points. Despite this commonality of properties, there are, in fact, three types of bonding in carbides: ionic, covalent, and metallic.

### Ionic Carbides

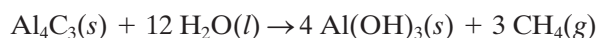
Ionic carbides are formed by the most electropositive elements: the alkali and alkaline earth metals and aluminum. Most of these ionic compounds contain



the dicarbide( $2-$ ) ion, which we discussed in the context of calcium dicarbide (see Chapter 12, Section 12.11). The ionic carbides are the only carbides to show much chemical reactivity. In particular, they react with water to produce ethyne,  $C_2H_2$ , commonly called acetylene:



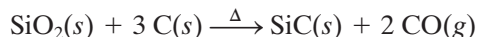
From their formulas, the red beryllium carbide,  $Be_2C$ , and the yellow aluminum carbide,  $Al_4C_3$ , appear to contain the  $C^{4-}$  ion. The high-charge-density cations  $Be^{2+}$  and  $Al^{3+}$  are the only ions that can form stable lattices with such a highly charged anion. However, the cations are so small and highly charged and the anion so large that we assume there must be a large degree of covalency in the bonding. Nevertheless, these two carbides do produce methane,  $CH_4$ , when they react with water, as would be expected if the  $C^{4-}$  ion were present:



### Covalent Carbides

Because most nonmetals are more electronegative than carbon, there are few covalent carbides. Silicon carbide,  $SiC$ , and boron carbide,  $B_4C$  (discussed in Chapter 13, Section 13.3), are the common examples; both are very hard and have high melting points. Silicon carbide is used as a grinding and polishing agent in metallurgical applications, and it is the only nonoxide ceramic product of large-scale industrial importance. Worldwide production of this compound is about  $7 \times 10^5$  tonnes.

Silicon carbide, which is bright green when pure, is produced when carbon and silicon dioxide are heated together in an electric furnace at about  $2300^\circ C$  for approximately 18 hours. The production of this compound is extremely energy intensive, and between 6 and 12 kWh of electricity is needed to produce 1 kg of silicon carbide:



There is tremendous interest in silicon carbide as a material for high-temperature turbine blades, which operate at temperatures that cause metals to lose their strength. Silicon carbide is also being used for the backing of high-precision mirrors because it has a very low coefficient of expansion. This property minimizes distortion problems because silicon carbide mirrors undergo only a negligible change in shape as temperatures fluctuate.

A key to the wider use of silicon carbide is the ability to form it into shapes (for such uses as long-lasting engine blocks or replacement human joints). With its very high melting point, that has been impossible until now. A considerable amount of current research is focusing on the synthesis of liquid organosilicon compounds. These can be poured into molds and the compound heated to a high enough temperature that decomposition occurs, leaving silicon carbide in the required shape. Silicon carbide is certainly a promising material for this century.



## Metallic Carbides

Metallic carbides are compounds in which the carbon atoms fit within the crystal structure of the metal itself, and they are usually formed by the transition metals. To form a metallic carbide, the metal must assume a close-packed structure, and the atoms usually have a metallic radius greater than 130 pm. The carbon atoms can then fit into the octahedral holes (interstices) in the structure; hence, metallic carbides are also called *interstitial carbides*. If all the octahedral holes are filled, the stoichiometry of these compounds is 1:1.

Because metallic carbides retain the metallic crystal structure, they look metallic and conduct electricity. They are important because they have very high melting points, show considerable resistance to chemical attack, and are extremely hard. The most important of these compounds is tungsten carbide (WC), of which about 20 000 tonnes are produced annually worldwide. Most of the material is used in cutting tools.

Some metals with a radius below 130 pm form metallic carbides, but their metal lattices are distorted. As a result, such compounds are more reactive than true interstitial carbides. The most important of these almost-interstitial carbides is  $\text{Fe}_3\text{C}$ , commonly called *cementite*. It is microcrystals of cementite that cause carbon steel to be harder than pure iron.

## MAX Phases

Following the synthesis of the ternary carbide,  $\text{Ti}_3\text{SiC}_2$ , chemists realized there was a whole family of related compounds. These layered, hexagonal-structure compounds have the generic formula  $\text{M}_{(n+1)}\text{AX}_{(n)}$ , where  $n = 1, 2$ , or  $3$ . As shown in Figure 14.8, M is an early transition metal, A is a main-group element, and X is either carbon and/or nitrogen. Thus, like the titanium compounds described in the chapter opening Context, carbides and nitrides overlap considerably in their roles in new and novel materials. Some examples of MAX phases are  $\text{Hf}_2\text{PbC}$  and  $\text{Nb}_2\text{AsC}$  (211 phases);  $\text{V}_3\text{AlC}_2$  (312 phases); and  $\text{Ti}_4\text{AlN}_3$  (413 phases).

These carbides and nitrides possess unusual properties which combine the best attributes of metals and ceramics. For example, they have high melting points, low rates of corrosion, yet they are good thermal and electrical conductors. When the surface of a MAX phase is polished, it is indistinguishable from a metal. These ternary compounds enlarge yet further the available repertoire of novel materials.

**FIGURE 14.8** Elements that combine to form MAX phases.

																H																	He
Li	Be	M	Early transition metal										A	Group A element										B	C	N	O	F	Ne				
																														Na	Mg	X	C and/or N
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																

**WORKED EXAMPLE 14.3**

Write a balanced chemical equation for the probable reaction of beryllium carbide with water.

**Answer**

Beryllium carbide is one of the only two ionic carbides to contain the  $\text{C}^{4-}$  ion. These react with water to form methane. The other product would be beryllium hydroxide, and as magnesium hydroxide is insoluble (see Chapter 12), beryllium hydroxide is also likely to be insoluble. So the equation is:

**Moissanite: The Diamond Substitute**

Until 1998, the only lower-cost substitute for diamond was cubic zirconia,  $\text{ZrO}_2$  (see Chapter 5, Section 5.8). Now the development of a commercial synthesis of a hexagonal form of silicon carbide has led to the introduction of a new gemstone, moissanite. Moissanite had been discovered in the 1890s in the Diablo Canyon, Arizona, meteorite impact crater and was named after the chemist Henri Moissan. But until recently, it could not be synthesized in large crystals. The synthesis of moissanite resulted from research into new semiconductor materials for LED and computer use. Although most of the output of pure silicon carbide is still for the high-tech industry, an increasing proportion is for the gemstone market.

Moissanite is an analog of lonsdaleite (discussed in Section 14.3) in which alternate carbon atoms are replaced by silicon atoms. With its close similarity to diamond in composition and structure, it is not surprising that its properties, too, resemble those of diamond (Table 14.4).

Moissanite is almost as hard as diamond, is about the same density, and, with a higher refractive index than diamond, actually “sparkles” more than a diamond. Thus, when comparing a diamond and a moissanite, most people believe the moissanite to be the real diamond. The standard technique to identify a diamond is to measure its thermal conductivity. Although a nonmetal, diamond has an extremely high thermal conductivity, similar to that of many metals. The conductivity results from the strong covalent bonds throughout the lattice structure; hence, any molecular vibrations (heat) will be transmitted rapidly through the structure. Because moissanite has a similar structure, it, too, has high thermal conductivity, and so the traditional method of diamond identification will not eliminate a moissanite. However, examination of a moissanite crystal under a microscope reveals characteristic double refraction for moissanite together with differences in surface polish and inclusions from diamonds.

**TABLE 14.4** A comparison of the properties of diamond, moissanite, and cubic zirconia

	Hardness (Moh's scale)	Refractive index	Density ( $\text{g}\cdot\text{cm}^{-3}$ )
C, diamond	10	2.24	3.5
SiC, moissanite	9.25–9.5	2.65–2.69	3.2
$\text{ZrO}_2$ , cubic zirconia	8.5	2.15	5.8

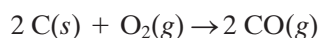
## 14.6 Carbon Monoxide

The carbon-oxygen bond in carbon monoxide is very short, about the length that would be expected for a triple bond. Figure 14.9 shows a simplified energy-level diagram for carbon monoxide for the molecular orbitals derived from 2p atomic orbitals. This model gives a bond order of 3 from the filling of one  $\sigma$ -bonding orbital and two  $\pi$ -bonding orbitals.

### Properties of Carbon Monoxide

Carbon monoxide is a colorless, odorless gas. It is very poisonous because it has a 300-fold greater affinity for blood hemoglobin than does oxygen; thus, quite low concentrations of carbon monoxide in air are sufficient to prevent oxygen absorption in the lungs. Without a continuous supply of oxygen, the brain loses consciousness, and death follows unless the supply of oxygenated hemoglobin is restored.

Carbon monoxide is produced when any carbon-containing compound, including carbon itself, is burned with an amount of oxygen insufficient for complete combustion:

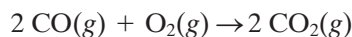


The pure gas is prepared in the laboratory by warming methanoic (formic) acid with concentrated sulfuric acid. In this decomposition, the sulfuric acid acts as a dehydrating agent:

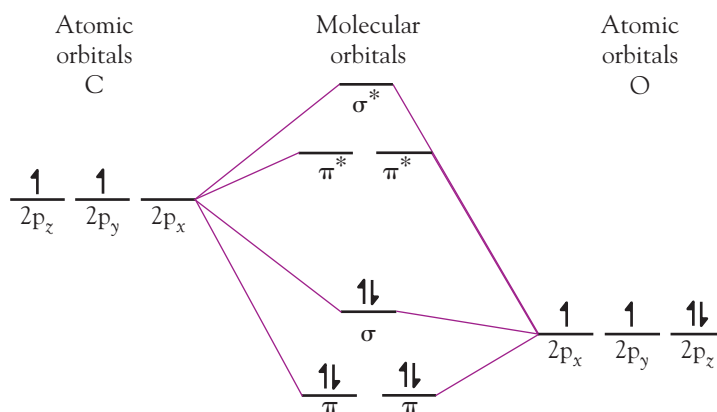


### Reactions of Carbon Monoxide

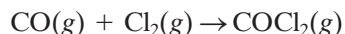
Carbon monoxide is quite reactive; for example, it burns with a blue flame to carbon dioxide:



**FIGURE 14.9** Partial simplified molecular-orbital-energy-level diagram for carbon monoxide.

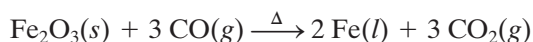


It reacts with chlorine gas in the presence of light or hot charcoal, which serve as catalysts, to give carbonyl chloride,  $\text{COCl}_2$ , a compound better known as the poison gas *phosgene*:

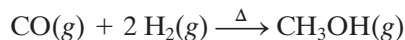


Although carbonyl chloride is usually recalled as one of the first gases used in warfare, it is actually an industrial chemical produced on the scale of millions of tonnes per year. Carbonyl chloride is especially useful as a starting material for the synthesis of many important compounds such as the polycarbonates that are used widely as tough, low-density transparent materials.

As the Frost diagram in Figure 14.1 shows, carbon monoxide is a strong reducing agent. It is used industrially in this role; for example, in the smelting of iron(III) oxide to iron metal (see Chapter 20, Section 20.6):



Carbon monoxide is also an important starting material in industrial organic chemistry. Under high temperatures and pressures, carbon monoxide will combine with hydrogen gas (a mixture known as *synthesis gas*) to give methanol,  $\text{CH}_3\text{OH}$ :



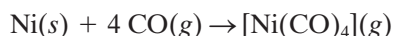
Mixing carbon monoxide with ethene,  $\text{C}_2\text{H}_4$ , and hydrogen gas produces propanal,  $\text{CH}_3\text{CH}_2\text{CHO}$ , a reaction known as the *OXO process*:



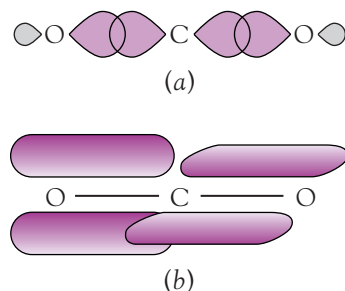
The active catalytic species in this process is a cobalt compound containing covalent bonds to both hydrogen and carbon monoxide,  $[\text{HCo}(\text{CO})_4]$ , and it is similar compounds of metals with carbon monoxide that we consider next.

## Metal Carbonyls

Carbon monoxide forms numerous compounds with transition metals. In these highly toxic, volatile compounds, the metal is considered to have an oxidation number of zero. Among the simple carbonyls are tetracarbonylnickel(0),  $[\text{Ni}(\text{CO})_4]$ ; pentacarbonyliron(0),  $[\text{Fe}(\text{CO})_5]$ ; and hexacarbonylchromium(0),  $[\text{Cr}(\text{CO})_6]$ . Many of the metal carbonyls can be prepared simply by heating the metal with carbon monoxide under pressure. For example, when heated, nickel reacts with carbon monoxide to give the colorless gas tetracarbonylnickel(0):



These compounds are often used as reagents for the preparation of other low-oxidation-number compounds of transition metals. The chemistry of carbonyl compounds is discussed more fully in Chapter 22, Section 22.6.



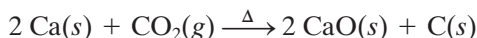
**FIGURE 14.10** (a) The  $\sigma$  bonds between the atoms of a carbon dioxide molecule. (b) The two  $\pi$  bonds between the same atoms.

## 14.7 Carbon Dioxide

Bond lengths and bond strengths indicate that there are double bonds between the carbon and oxygen atoms in the carbon dioxide molecule. We would predict this bonding pattern both from an electron-dot representation and from simple hybridization theory. On the basis of hybridization theory, we assume that  $\sigma$  bonds are formed from  $sp$  hybrid orbitals. The remaining  $p$  orbitals, which are at right angles to the bond direction, then overlap to form two  $\pi$  molecular orbitals (Figure 14.10).

### Properties of Carbon Dioxide

Carbon dioxide is a dense, colorless, odorless gas that does not burn or, normally, support combustion. The combination of high density and inertness has led to its use for extinguishing fires. Because it is about one- and-a-half times denser than air under the same conditions of temperature and pressure, it flows, almost like a liquid, until air currents mix it with the gases of the atmosphere. Thus, it is effective at fighting floor-level fires but almost useless for fighting fires in ceilings. However, carbon dioxide will react with burning metals, such as calcium:

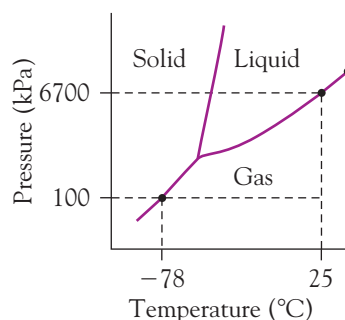


Carbon dioxide is unusual because it has no liquid phase at normal atmospheric pressures. Instead, the solid sublimates directly to the gas phase. To obtain the liquid phase at room temperature, a pressure of 6.7 MPa (67 times standard atmospheric pressure) must be applied, as shown in the phase diagram in Figure 14.11. Carbon dioxide is usually conveyed in tank cars and cylinders in the liquid form. When the pressure is released, some of the liquid carbon dioxide vaporizes, but the heat absorbed in the expansion process (overcoming the dispersion forces between molecules) is enough to cool the remaining liquid below its sublimation point,  $-78^\circ\text{C}$  at atmospheric pressure. By inverting the cylinder and opening the valve, solid carbon dioxide, “dry ice,” can be collected in a gauze bag or in a  $\text{CO}_2$  “patty maker” at room temperature.

Carbon dioxide is an important industrial chemical. Each year, over 40 million tonnes are used in the United States alone. Half of this quantity is needed as a refrigerant, and another 25 percent is used to carbonate soft drinks. It is also used as a propellant in some aerosol cans and as a pressurized gas to inflate life rafts and life vests.

There are a number of sources of industrial carbon dioxide, including as a by-product in the manufacture of ammonia, molten metals, cement, and from sugar fermentation processes. And, of course, we exhaust carbon dioxide into the atmosphere during the complete combustion of any carbon-containing substance: wood, natural gas, gasoline, coal, and oil.

In the laboratory, carbon dioxide is most conveniently prepared by adding dilute hydrochloric acid to marble chips (chunks of impure calcium carbonate),



**FIGURE 14.11** Phase diagram for carbon dioxide.

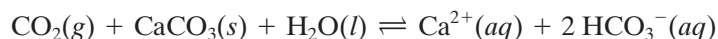
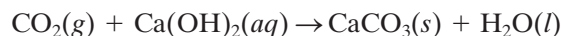


although any dilute acid with a carbonate or hydrogen carbonate can be used (for example, Alka-Seltzer tablets or baking powder):

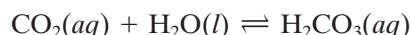


### Reactions of Carbon Dioxide

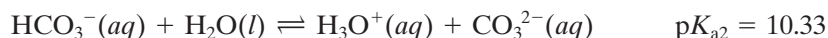
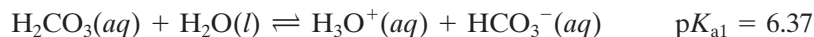
To identify carbon dioxide, the *limewater test* is used. In this test, a gas is bubbled into a saturated solution of calcium hydroxide. If the gas is carbon dioxide, a white precipitate of calcium carbonate forms. Addition of more carbon dioxide results in the disappearance of the precipitate to give soluble calcium ions and hydrogen carbonate ions:



In aqueous solution, almost all the carbon dioxide is present as  $\text{CO}_2(aq)$ ; only 0.37 percent is present as carbonic acid,  $\text{H}_2\text{CO}_3(aq)$ :

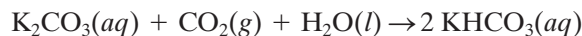
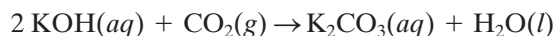


Carbonic acid is an extremely weak diprotic acid, as can be seen from the  $\text{p}K_a$  values corresponding to each of the ionization steps:



It is fortunate for us that the equilibrium lies to the left, not to the right, and that carbonic acid is a weak acid, because it means that carbonation of beverages will not cause them to become unpleasantly acidic. The high solubility of carbon dioxide in water has been explained in terms of carbon dioxide molecules being trapped inside clusters of hydrogen-bonded water molecules—rather like the clathrates (see Chapter 10, Section 10.7) in the solid phase.

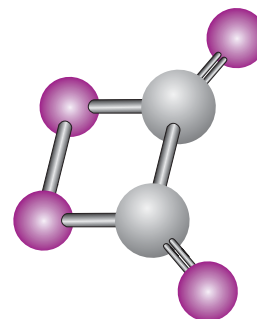
Because it is an acid oxide, carbon dioxide reacts with bases to give carbonates. The presence of excess carbon dioxide results in the formation of the hydrogen carbonates of the alkali and alkaline earth elements:



### Dicarbon Tetroxide (1,2-dioxetanedione)

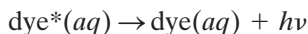
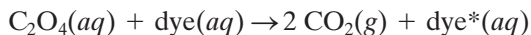
The most common method of producing phosphorescent light (“glow sticks”) involves the formation of the intermediate dicarbon tetroxide (Figure 14.12), the dimer of carbon dioxide, known also by its organic chemistry name of 1,2-dioxetanedione.

For the production of light, hydrogen peroxide is reacted with an organic compound, often bis(2,4,6-trichlorophenyl)oxalate, to give trichlorophenol and dicarbon tetroxide. The dicarbon tetroxide then reacts with the organic dye, with electrons in the dye molecules being raised to an excited state (dye\*),



**FIGURE 14.12** The structure of the dicarbon tetroxide,  $\text{C}_2\text{O}_4$ , molecule.

while the dicarbon tetroxide decomposes to carbon dioxide. The electrons in the excited state then return over time to the ground state, releasing the energy from the dye in the form of light (phosphorescence):



### Carbonia

As we discussed in Section 14.2, silicon dioxide forms a single-bonded network covalent crystal lattice. Carbon dioxide, however, forms individual molecules with carbon-oxygen double bonds. Chemists theorized that if a network covalent version of carbon dioxide could be synthesized, it might have the strength of silica but a much lower density. In 2006, this new allotrope was first formed. The key to its synthesis is not just high pressure but also a high enough temperature to provide the energy for bond breaking and re-forming. A pressure of 80 GPa and a temperature of 1800 K proved to work, and the carbon-based equivalent of silica, named *carbonia* by analogy, was produced. Since then, both crystalline and glassy (amorphous) carbonia have been synthesized. Although carbonia remains stable down to room temperature, pressure must be maintained above 1 GPa. Nevertheless, the synthesis of carbonia enables chemists to find a new parallel between the chemistry of carbon and that of the other members of Group 14.

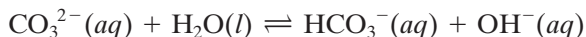
## 14.8 Carbonates and Hydrogen Carbonates

### Carbonates

The carbonate ion is planar and the three carbon-oxygen bonds in the carbonate ion are all the same length and are significantly shorter than a single bond. We can represent the partial multiple-bond character using a combination of solid and dashed lines, as we did in Chapter 3, Section 3.2, for the nitrate ion (Figure 14.13).

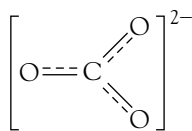
The bonding can be considered in terms of a  $\sigma$  framework that is centered on the carbon atom and uses  $\text{sp}^2$  hybrid orbitals. The electron pair in the remaining p orbital of the carbon atom can then form a  $\pi$  bond that is delocalized (shared) over the whole ion (Figure 14.14). With the  $\pi$  bond shared three ways, each carbon-oxygen bond would have a bond order of  $1\frac{1}{3}$ .

The carbonate ion is very basic in aqueous solution as a result of a hydrolysis reaction that gives hydrogen carbonate and hydroxide ion:

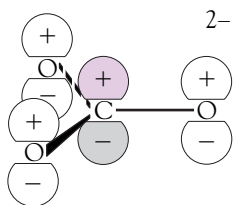


Thus, concentrated solutions of even that “harmless” household substance sodium carbonate, commonly called *washing soda*, should be treated with respect (although not with fear).

Most carbonates are insoluble, the exceptions being ammonium carbonate and the alkali metal carbonates. The alkali metal carbonates (except that of lithium) do not decompose when heated. Lithium carbonate and carbonates of



**FIGURE 14.13** Representation of the partial bonds of the carbonate ion.

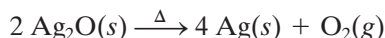


**FIGURE 14.14** Orbitals involved in the  $\pi$  bond in the carbonate ion.

other moderately electropositive metals, such as calcium, give the metal oxide and carbon dioxide when heated:

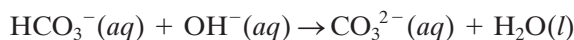
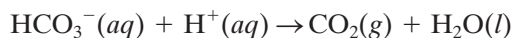


For the carbonates of weakly electropositive metals, such as silver, the metal oxide is itself decomposed by heat. Thus, the final products are the metal, carbon dioxide, and oxygen:



## Hydrogen Carbonates

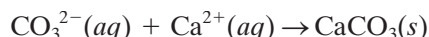
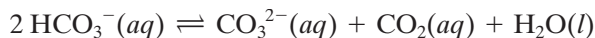
The hydrogen carbonate ion reacts with acids to give carbon dioxide and water and with bases to give the carbonate ion:



As we discussed in Chapter 11, Section 11.12, only the alkali metals (except lithium) form solid compounds with the hydrogen carbonate ion,  $\text{HCO}_3^-$ , and even these decompose to the carbonate when heated:



When lithium or any Group 2 metal ion solution is added to a solution of hydrogen carbonate ion, a precipitate of the carbonate is formed. For example, addition of calcium ion to hydrogen carbonate ion gives a precipitate of calcium carbonate:



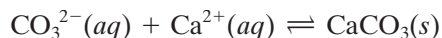
### WORKED EXAMPLE 14.4

If addition of a solution of calcium ion to a solution of hydrogen carbonate ion causes a precipitate of calcium carbonate, how is it that caves form in limestone strata?

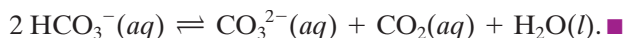
#### Answer

Le Châtelier's Principle provides the answer.

Solid calcium carbonate is in equilibrium with solution calcium ions and carbonate ions according to the solubility product relationship:



If the concentration of carbon dioxide is high enough in the rainwater, the hydrogen carbonate-carbonate equilibrium will shift left, ultimately reducing the carbonate ion concentration below that required for the solubility product and the calcium carbonate will dissolve.



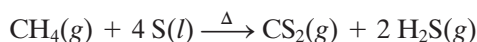


## 14.9 Carbon Sulfides

Carbon forms both a sulfide,  $\text{CS}_2$ , of industrial importance and an oxysulfide,  $\text{COS}$ , of environmental significance.

### Carbon Disulfide

Carbon disulfide is the sulfur analog of carbon dioxide, and it has the same linear geometry. The compound is a colorless, highly flammable, low-boiling liquid with a pleasant smell when pure, but the commercial grade of the compound usually contains very foul-smelling impurities. It is highly toxic, causing damage to the brain and nervous system and, eventually, death. Carbon disulfide is prepared industrially by passing methane gas over molten sulfur at about  $700^\circ\text{C}$ , then cooling the products, from which carbon disulfide condenses:



Over one million tonnes of this reagent are consumed each year, mainly in the production of cellophane and viscose rayon polymers. It is also the starting material for the manufacture of carbon tetrachloride. We tend to forget that industrial chemistry is rarely the conversion of one naturally occurring substance directly to some required product. More often, the product is itself only a reagent in the production of many other compounds.

### Carbonyl Sulfide

We are becoming increasingly aware of the complexity of the Earth's atmosphere and of the role of some inorganic compounds that we have ignored in the past as laboratory curiosities without any real-world use. One of these compounds is carbonyl sulfide, written as  $\text{COS}$ , although its double-bonded structure,  $\text{S}=\text{C}=\text{O}$ , resembles that of carbon dioxide. Carbonyl sulfide is the most abundant sulfur-containing gas in the global background atmosphere as a result of its low chemical reactivity; the total amount is estimated as about  $5 \times 10^6$  tonnes. It is the only sulfur-containing gas to penetrate the stratosphere (except when very powerful volcanic eruptions directly inject sulfur dioxide into the upper atmosphere). The gas is one of the several sulfur-containing compounds produced by soil and marine organisms; another important one is dimethyl sulfide,  $(\text{CH}_3)_2\text{S}$ .

## 14.10 Carbon Halides

### Carbon Tetrahalides

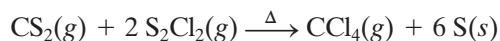
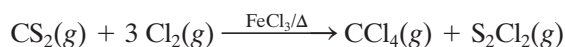
The major divisions of chemistry—inorganic, organic, physical, and analytical—are inventions of chemists attempting to organize this vast and continually growing science. Yet chemistry does not fit into neat little compartments, and the carbon tetrahalides are compounds that belong to the realms of both organic and inorganic chemistry. As a result, they have two sets of names:

carbon tetrahalides, according to inorganic nomenclature, and tetrahalomethanes, according to organic nomenclature.

All of the tetrahalides contain the carbon atom tetrahedrally coordinated to the four halogen atoms. The phases of the tetrahalides at room temperature reflect the increasing strength of the intermolecular dispersion forces. Thus, carbon tetrafluoride is a colorless gas; carbon tetrachloride is a dense, almost oily liquid; carbon tetrabromide, a pale yellow solid; and carbon tetraiodide, a bright red solid.

Carbon tetrachloride is an excellent nonpolar solvent. However, in recent years, the discovery of its cancer-causing ability has made it a solvent of last resort. Carbon tetrachloride is also a greenhouse gas and, in the upper atmosphere, a potent ozone destroyer. It is therefore important to minimize emissions of this compound from industrial plants.

The major industrial route for the synthesis of carbon tetrachloride involves the reaction of carbon disulfide with chlorine. In this reaction, iron(III) chloride is the catalyst. In the first step, the products are carbon tetrachloride and disulfur dichloride. Then at a higher temperature, addition of more carbon disulfide produces additional carbon tetrachloride and sulfur. The sulfur can be reused in the production of a new batch of carbon disulfide:



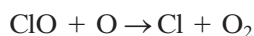
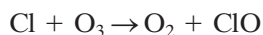
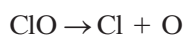
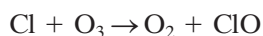
## Chlorofluorocarbons

In 1928, Thomas Midgley, Jr., a General Motors chemist, first synthesized dichlorodifluoromethane,  $\text{CCl}_2\text{F}_2$ . This discovery was made as part of a search to find a good, safe refrigerant material. A refrigerant is a compound that, at room temperature, is a gas at low pressures but a liquid at high pressures. Reducing the pressure on the liquid causes it to boil and absorb heat from the surroundings (such as the inside of a refrigerator). The gas is then conveyed outside the cooled container, where it is compressed. Under these conditions, it reliquefies, releasing the enthalpy of vaporization to the surroundings as it does so.

At the time they were discovered, the chlorofluorocarbon family (CFCs), also known as *freons*, appeared to be a chemist's dream. They were almost completely unreactive, and they were nontoxic. As a result, they were soon used in air-conditioning systems, as blowing agents for plastic foams, as aerosol propellants, as fire-extinguishing materials, as degreasing agents of electronic circuits, and as anesthetics—to name but a few uses. Annual production amounted to nearly 700 000 tonnes in the peak years. Their lack of reactivity is partly due to the lack of a hydrolysis pathway, but in addition, the high strength of the carbon-fluorine bond confers extra protection against oxidation.

Of the simple CFCs,  $\text{CFCl}_3$  (CFC-11) and  $\text{CF}_2\text{Cl}_2$  (CFC-12) were the most widely used. It was not until the 1970s that the great stability of these compounds—their “best” property—was recognized as a threat to the environment. The Montreal Protocol, agreed to by all countries in 1987, resulted

in the banning of these compounds. However, the CFCs are so stable that they will remain in the atmosphere for hundreds of years. Some of these molecules were diffusing into the upper atmosphere (stratosphere), where ultraviolet light cleaved a chlorine atom from each of them. The chlorine atom then reacted with ozone molecules in a series of steps that can be represented in a simplified and not wholly accurate form as:



The chlorine atom is then free to repeat the cycle time and time again, destroying enormous numbers of ozone molecules. Incidentally, these chemical species are not those that you can find in a chemistry laboratory, but at the low pressures existing in the upper atmosphere, even free chlorine and oxygen atoms can exist for measurable periods.

The lesson, of course, is clear. Just because a compound is chemically inert in the laboratory does not mean that it is harmless. No product of the chemical industry can be released into the environment without first considering its impact. At the same time, hindsight is a wonderful thing. It is only in recent years that we have become aware of the importance of the ozone layer and of the many chemical reactions that occur in it (discussed in Chapter 16, Section 16.4). The more crucial moral is that research into the chemical cycles in nature must continue to be funded. If we do not know how the world works at the chemical level, then it will be impossible to predict the effect of any human perturbation.

### 14.11 Methane

The simplest compound of carbon and hydrogen is methane,  $\text{CH}_4$ , a colorless, odorless gas. There are enormous quantities of this gas, commonly called natural gas, in underground deposits and in deposits under the seabed (see Chapter 10, Section 10.7). Methane is one of the major sources of thermal energy in use today because it undergoes an exothermic combustion reaction:



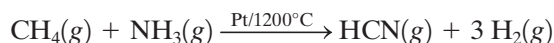
Because methane is undetectable by our basic senses (sight and smell), a strong-smelling, organic-sulfur-containing compound is added to the gas before it is supplied to customers. We can therefore detect any methane leakage by the odor of the additive.

Many scientists are particularly concerned by the rising concentration of methane. Although it is only present at the parts per billion (ppb) level, compared to parts per million (ppm) for carbon dioxide, methane is currently the gas whose concentration in the atmosphere is rising most rapidly. The methane

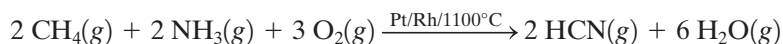
molecule absorbs infrared wavelengths different from those currently being absorbed by carbon dioxide and water vapor. There have always been traces of methane in the atmosphere as a result of vegetation decay in marshes. However, the proportion in the atmosphere has risen drastically over the last century. The rise is due in part to the rapid growth in the number of cattle and sheep (members of the grazing animals, the ruminants). All ruminants produce large quantities of methane in their digestive tracts, and this gas is expelled into the atmosphere. In addition, methane is generated in the wet soils of paddy fields in which rice is grown. Leakages from aging natural gas pipelines is of growing concern, as, of course, is the release of methane from hydrate deposits.

## 14.12 Cyanides

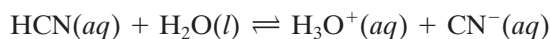
Most people are aware of the toxicity of hydrogen cyanide, HCN, and the cyanide ion,  $\text{CN}^-$ , yet few realize their industrial importance. In fact, over one million tonnes of hydrogen cyanide are manufactured each year. There are two modern methods of synthesis of hydrogen cyanide. The *Degussa process* involves the reaction of methane with ammonia at high temperature with a platinum catalyst:



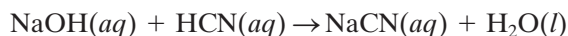
while the *Andrussow process* is similar but requires the presence of dioxygen:



Hydrogen cyanide is a liquid at room temperature as a result of strong hydrogen bonding between each hydrogen atom and the nitrogen atom of a neighboring molecule. It is extremely toxic, very low concentrations having a faint almond-like odor. The liquid is miscible with water to form an extremely weak acid:



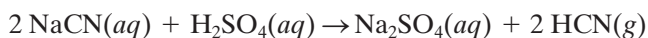
About 70 percent of hydrogen cyanide is used to produce many important polymers, including nylon, melamine, and the family of acrylic plastics. Of the remainder, close to 15 percent is converted to sodium cyanide by simple neutralization:



the salt being obtained by crystallization from the solution. The cyanide ion is used in the extraction of gold and silver from their ores (see Chapter 21, Section 21.11).

The cyanide ion is isoelectronic with carbon monoxide, and both these species react readily with hemoglobin, blocking uptake of dioxygen. The cyanide ion interferes with enzyme processes as well. Hydrogen cyanide itself is poisonous. In the late 1920s, many U.S. states introduced poisoning with hydrogen cyanide as a method of execution. The gas chamber was a sealed room containing

a chair. Beneath the chair hung glass containers filled with sodium or potassium cyanide. At the warden's signal, the containers were released by remote control into a bath of sulfuric acid. The hydrogen cyanide produced was of high enough concentration to cause unconsciousness within seconds and death within five minutes.

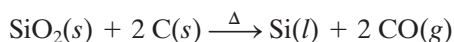


### 14.13 Silicon

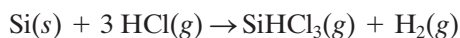
About 27 percent by mass of the Earth's crust is silicon. However, silicon itself is never found in nature as the free element but only in compounds containing oxygen-silicon bonds. The element is a gray, metallic-looking, crystalline solid. Although it looks metallic, it is not classified as a metal because it has a low electrical conductivity.

About half a million tonnes per year of silicon are used in the preparation of metal alloys. Although alloy manufacture is the major use, silicon plays a crucial role in our lives as the semiconductor that enables computers to function. The purity level of the silicon used in the electronics industry has to be exceedingly high. For example, the presence of only 1 ppb of phosphorus is enough to drop the specific resistance of silicon from 150 to 0.1  $\text{k}\Omega\cdot\text{cm}$ . As a result of the expensive purification process, ultrapure electronic-grade silicon sells for over 1000 times the price of metallurgical grade (98 percent pure) silicon.

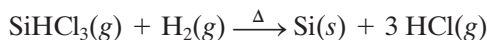
The element is prepared by heating silicon dioxide (quartz) with coke at over  $2000^\circ\text{C}$  in an electrical furnace. Liquid silicon (melting point  $1400^\circ\text{C}$ ) is drained from the furnace:



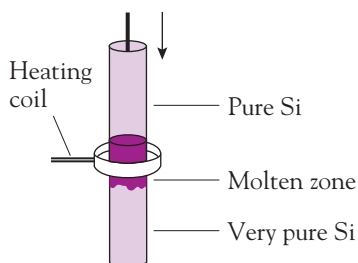
To obtain ultrapure silicon, the crude silicon is heated at  $300^\circ\text{C}$  in a current of hydrogen chloride gas. The trichlorosilane product,  $\text{SiHCl}_3$ , can be distilled and redistilled until the impurity levels are below the parts per billion level:



The reverse reaction is spontaneous at  $1000^\circ\text{C}$ , depositing ultrapure silicon. The hydrogen chloride can be reused in the first part of the process:



The ultrapure single crystals needed for solar cells are produced by zone refining (Figure 14.15). This process depends on the fact that the impurities are more soluble in the liquid phase than in its solid phase. A rod of silicon is moved through a high-temperature electric coil that partially melts the silicon. As part of the rod moves beyond the coil, the silicon resolidifies; during the solidification process, the impurities diffuse into the portion of the rod that is still molten. After the entire rod has passed through the coil, the impurity-rich



**FIGURE 14.15** Zone refining method for the purification of silicon.

top portion can be removed. The procedure can be repeated until the desired level of purity (less than 0.1 ppb impurity) is obtained.

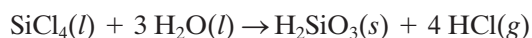
Computing devices can function because the silicon chips have been selectively “doped”; that is, controlled levels of other elements are introduced. If traces of a Group 15 element, such as phosphorus, are mixed into the silicon, then the extra valence electron of the added element is free to roam throughout the material. Conversely, doping with a Group 3 element will result in electron “holes.” These holes act as sinks for electrons. A combination of electron-rich and electron-deficient silicon layers makes up the basic electronic circuit. This is a somewhat simplified description of how such devices function, and any interested reader should consult a text on the physics and technology of semiconductors for a more detailed discussion.

### Silicon Hydrides

Silicon forms a variety of hydrides analogous to the saturated hydrocarbons, such as  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$ ,  $\text{Si}_3\text{H}_8$ , and  $\text{Si}_4\text{H}_{10}$  (two isomers), and even analogs of the cyclic saturated hydrocarbons, such as *cyclo*- $\text{Si}_5\text{H}_{10}$  and *cyclo*- $\text{Si}_6\text{H}_{12}$ . However, they are very different from the carbon compounds in their reactivity. The silanes are explosively flammable in air. In their reactivity, the silanes more resemble the boranes (see Chapter 13, Section 13.4).

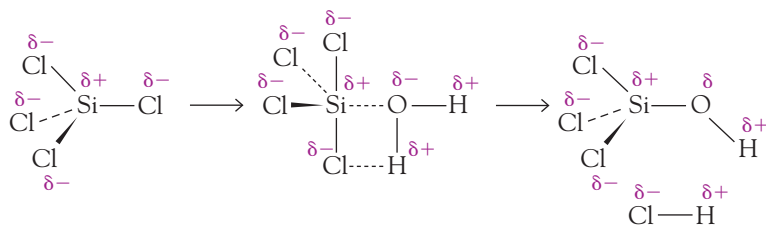
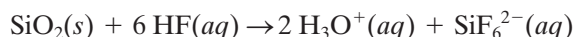
### Silicon Tetrahalides

The silicon-boron similarities were discussed in the context of the diagonal relationship in Chapter 9, Section 9.7. Such a resemblance extends to silicon tetrachloride, which, like boron trichloride, is a volatile reactive liquid. Silicon tetrachloride reacts violently with water to give silicic acid and hydrogen chloride gas in an analogous manner to the reaction of boron trichloride with water (see Chapter 13, Section 13.5).



In fact, we postulate a parallel mechanism for the process (Figure 14.16).

Again, like its boron analog, silicon tetrafluoride is comparatively unreactive. Just as boron trifluoride forms an aqueous-stable tetrafluoroborate ion,  $\text{BF}_4^-$ , so silicon tetrafluoride forms the hexafluorosilicate ion,  $\text{SiF}_6^{2-}$ . Fluoro-silicic acid is produced when silicon dioxide is reacted with hydrofluoric acid:



**FIGURE 14.16** First step of the postulated mechanism of hydrolysis of silicon tetrachloride.

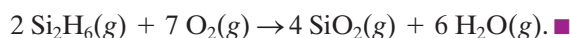
The reaction with hydrofluoric acid is used to etch designs on glass. The acid can be neutralized to give an ionic metal compound such as sodium hexafluorosilicate,  $\text{Na}_2\text{SiF}_6$ .

### WORKED EXAMPLE 14.5

Write a balanced equation for the reaction of gaseous  $\text{Si}_2\text{H}_6$  with air.

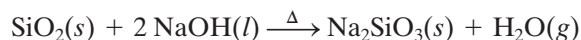
#### Answer

In parallel to the boron hydrides, the silanes should give the oxide and water vapor when oxidized. So then only balancing the equation is needed:



## 14.14 Silicon Dioxide

The most common crystalline form of silicon dioxide,  $\text{SiO}_2$ , commonly called *silica*, is the mineral quartz. Most sands consist of particles of silica that usually contain impurities such as iron oxides. Silicon dioxide is very unreactive; it reacts with molten sodium hydroxide to form sodium silicate:



Silicon dioxide is mainly used as an optical material. It is hard, strong, and transparent to visible and ultraviolet light, and it has a very low coefficient of expansion. Thus, lenses constructed from it do not warp as the temperature changes.

### Silica Gel

Silica gel is a hydrated form of silicon dioxide,  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ . It is used as a desiccant (drying agent) in the laboratory and also for keeping electronics and even prescription drugs dry. These packets or vials of silica gel keep the product dry even in humid climates. Commercial silica gel contains about 4 percent water by mass, but it will absorb very high numbers of water molecules over the crystal surface. And it has the particular advantage that it can be reused after heating for several hours; the high temperature drives off the water molecules, enabling the gel to function effectively once more.

### Aerogels

In the 1930s, an American chemist, Samuel Kistler, devised a way of drying wet silica gel without causing it to shrink and crack like mud on a dried riverbank. At the time, there was little interest in the product. Furthermore, the procedure required extremely high pressures, and one laboratory was destroyed by an explosion during the preparation of this material. Now, more than 70 years later, chemists have discovered new and safer synthetic routes to this rediscovered family of materials, called *aerogels*. The basic aerogel is silicon dioxide in

which a large number of pores exist—so many, in fact, that 99 percent of an aerogel block consists of air. As a result, the material has an extremely low density, yet is quite strong. The translucent solid is also an excellent thermal insulator, and it promises to be a useful fireproof insulating material. Aerogels also have some unique properties. For example, sound travels through aerogels more slowly than through any other medium. Chemists have now prepared aerogels that incorporate other elements, a technique that enables the chemists to vary the characteristics of the aerogels.

## Glasses

Glasses are noncrystalline materials. The cooling of molten glass results in an increasingly viscous liquid until it finally becomes infinitely viscous at its solidification point without change into an ordered crystalline structure. Glass has been used as a material for at least 5000 years. It is difficult to obtain a precise figure of current annual production, but it must be about 100 million tonnes.

Almost all glass is silicate glass; it is based on the three-dimensional network of silicon dioxide. Quartz glass is made simply by heating pure silicon dioxide above 2000°C and then pouring the viscous liquid into molds. The product has great strength and low thermal expansion, and it is highly transparent in the ultraviolet region. However, the high melting point precludes the use of quartz glass for most everyday glassware.

The properties of the glass can be altered by mixing in other oxides. The compositions of three common glasses are shown in Table 14.5. About 90 percent of glass used today is soda-lime glass. It has a low melting point, so it is very easy to form soda-lime glass into containers, such as soft-drink bottles. In the chemistry laboratory, we need a glass that will not crack from thermal stress when heated; borosilicate glass (discussed in Chapter 13, Section 13.2) is used for this purpose. Lead glasses have a high refractive index; as a result, cut glass surfaces sparkle like gemstones, and these glasses are used for fine glassware. The element lead is a strong absorber of radiation; hence, a very different use for lead glass is in radiation shields, such as those over cathode ray tubes.

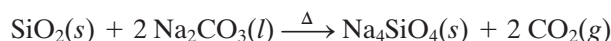
**TABLE 14.5** Approximate compositions of common glasses

Component	Composition (%)		
	Soda-lime glass	Borosilicate glass	Lead glass
SiO <sub>2</sub>	73	81	60
CaO	11	—	—
PbO	—	—	24
Na <sub>2</sub> O	13	5	1
K <sub>2</sub> O	1	—	15
B <sub>2</sub> O <sub>3</sub>	—	11	—
Other	2	3	>1

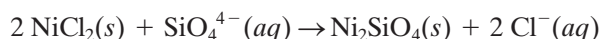


## 14.15 Silicates

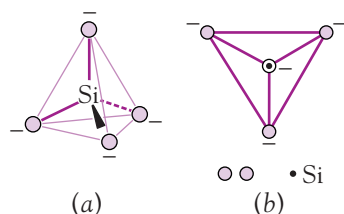
About 95 percent of the rocks of the Earth's crust are silicates, and there is a tremendous variety of silicate minerals. The simplest silicate ion has the formula  $\text{SiO}_4^{4-}$ ; zirconium silicate,  $\text{ZrSiO}_4$ , the gemstone zircon, being one of the few minerals to contain this ion. Silicates are generally very insoluble, as one might expect of rocks that have resisted rain for millions of years. The one common exception is sodium silicate, which can be prepared by reacting solid silicon dioxide with molten sodium carbonate:



A concentrated solution of sodium (ortho)silicate is called water glass, and it is extremely basic as a result of hydrolysis reactions of the silicate anion. The sodium silicate solution is used in the “crystal garden” home science experiment kit. In the experiment, addition of crystals of colored transition metal salts results in the formation of the appropriate insoluble silicate. For example, adding a crystal of nickel(II) chloride gives a large green “plume” of nickel(II) silicate:

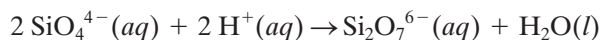


This is not the total extent of silicate chemistry. Oxygen atoms can be shared by different silicon atoms. To show these different structures, silicate chemists depict the units in a manner different from that used in conventional molecular geometry. We can illustrate the approach with the silicate ion itself. Most chemists look at an ion from the side, a perspective giving the arrangement depicted in Figure 14.17a. Silicate chemists look down on a silicate ion, sighting along the axis of a Si—O bond (Figure 14.17b). The corner spheres represent three of the oxygen atoms, the central black dot represents the silicon atom, and the circle around the black dot represents the oxygen atom vertically above it. Instead of covalent bonds, the edges of the tetrahedron are marked with solid lines.

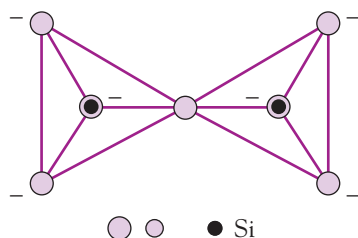


**FIGURE 14.17** Depiction of the tetrahedral shape of the silicate ion in the conventional (a) and silicate chemistry (b) forms.

When a small amount of acid is added to the (ortho)silicate ion, the pyrosilicate ion,  $\text{Si}_2\text{O}_7^{6-}$ , is formed:

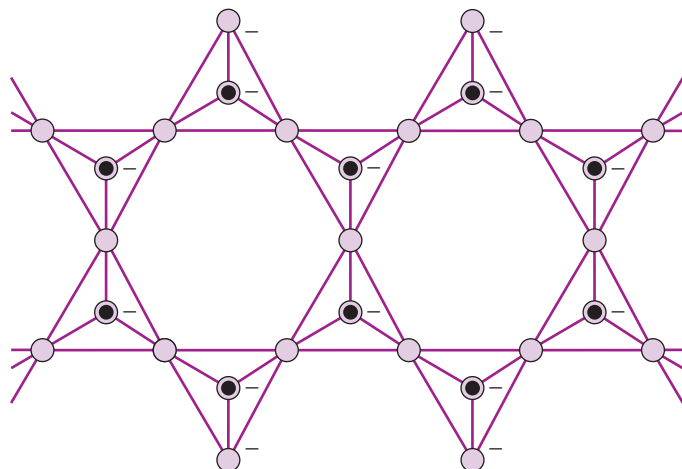


In the pyrosilicate ion, the two silicate ions are linked together by one shared oxygen atom (Figure 14.18). This ion is itself not of great importance. However, these silicate units can join to form long chains, and they can cross-link to form a double chain.



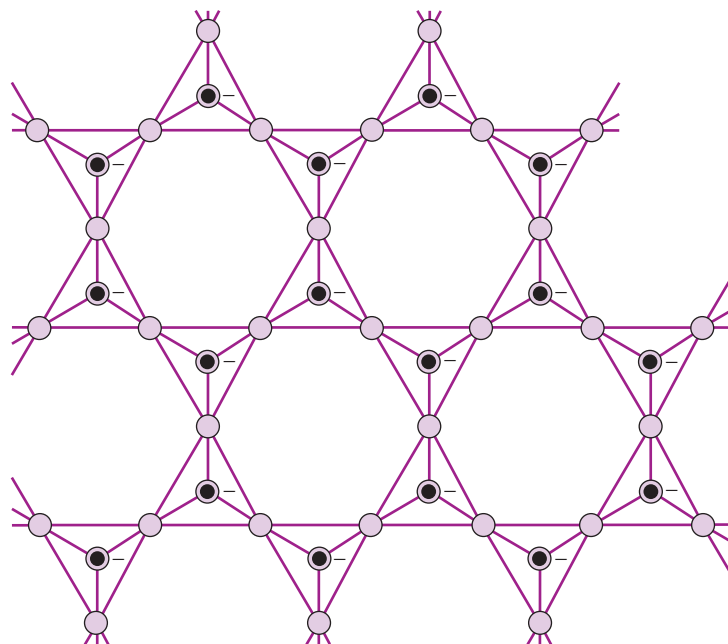
**FIGURE 14.18** Depiction of the  $\text{Si}_2\text{O}_7^{6-}$  ion.

A polymeric structure with an empirical formula of  $\text{Si}_4\text{O}_{11}^{6-}$  is formed in this way (Figure 14.19). The double chain is an important structure, and it gives rise to a whole family of minerals called the *amphiboles*. The cations that are packed in among these chains determine the identity of the mineral formed. For example,  $\text{Na}_2\text{Fe}_3(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$  is the mineral crocidolite, more commonly known as *blue asbestos*.



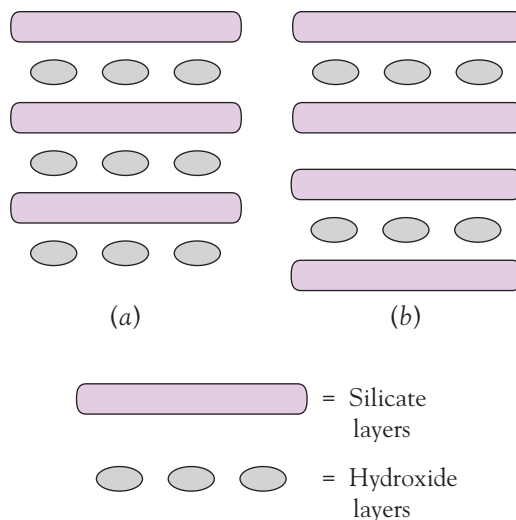
**FIGURE 14.19** Depiction of a section of the  $\text{Si}_4\text{O}_{11}^{6-}$  repeating double chain.

The double chains of silicate units can link side-by-side to give sheets of empirical formula  $\text{Si}_2\text{O}_5^{2-}$  (Figure 14.20). One of the sheet silicates is  $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ , chrysotile. This compound, also known as *white asbestos*, has alternating layers of silicate ions and hydroxide ions, with magnesium ions filling in available holes. Asbestos has been used for thousands of years. For example, the ancient Greeks used it as wicks for their lamps, and the European king Charlemagne astounded his guests in about 1200 years ago by throwing his dirty asbestos tablecloth into a fire and retrieving it unburned and clean. The use of asbestos is declining rapidly now that we are aware of the health risks from embedded asbestos fibers on the lung surface.



**FIGURE 14.20** Depiction of a section of the sheet silicate  $\text{Si}_2\text{O}_5^{2-}$ .

**FIGURE 14.21** The layer structures of (a) white asbestos and (b) talc.



Very few nonchemists realize that there are two common forms of this fibrous mineral and that they have very different chemical structures and different degrees of hazard. In fact, about 95 percent of asbestos currently used is the less harmful white asbestos and only about 5 percent is the more dangerous blue asbestos. Asbestos is a very convenient and inexpensive fireproof material, and it has been extremely difficult for chemists to find hazard-free replacements for all 3000 uses of asbestos. In fact, there is still a significant consumption of asbestos for products such as brake linings, engine gaskets, and even as a filter material for wine.

It is fascinating how minor changes in structure can cause major changes in properties. If, instead of alternating layers of magnesium silicate and magnesium hydroxide, we have a layer of hydroxide ions sandwiched between pairs of layers of silicate ions, we get a different formula,  $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ , and a different name, *talc* (Figure 14.21). Because each sandwich is electrically neutral, it is almost as slippery as graphite (but white instead of black). Talc is used on a very large scale—about 8 million tonnes worldwide—for ceramics, fine paper, paint, and the cosmetic product talcum powder.

### 14.16 Aluminosilicates

At first thought, one might consider that aluminum, a metal, and silicon, a metalloid, have little in common. However, in a large number of mineral structures aluminum partially replaces silicon. This should not be too surprising, for as we showed in Chapter 5, Section 5.5, aluminum and silicon fit in similar-size cation lattice sites. Of course, this is presuming the bonding is ionic. In fact, it is equally valid—and often more useful—to look at these compounds as charged polymeric covalent clusters with cations fitting in the lattice interstices.

The large range of aluminosilicates is actually derived from the basic silicon dioxide structure of a three-dimensional array of  $\text{SiO}_4$  units linked by the corner oxygen atoms. In silicon dioxide, the structure will be neutral. Then  $\text{Al}^{3+}$  is substituted for  $\text{Si}^{4+}$ ; the lattice acquires one net negative charge for every replacement. For example, replacement of one-fourth of the silicon atoms by aluminum results in an anion of empirical formula  $[\text{AlSi}_3\text{O}_8]^-$ ; replacement of one-half of the silicon atoms gives the formula  $[\text{Al}_2\text{Si}_2\text{O}_8]^{2-}$ . The charge is counterbalanced by Group 1 or 2 cations. This particular family of minerals comprises the *feldspars*, components of granite. Typical examples are orthoclase,  $\text{K}[\text{AlSi}_3\text{O}_8]$ , and anorthite,  $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ .

## Zeolites

One three-dimensional aluminosilicate structure has open channels throughout the network. Compounds with this structure are known as *zeolites*, and their industrial importance is skyrocketing. A number of zeolites exist in nature, but chemists have mounted a massive search for zeolites with novel cavities throughout their structures.

There are four major uses for zeolites:

- 1. Zeolites are used as ion exchangers.** If “hard” water (water high in calcium and magnesium ion concentration) is passed through a column containing pellets of a sodium ion zeolite, the Group 2 ions push out the sodium ions. The “soft” water emerging from the column requires less detergent for washing purposes and produces less solid deposit (scum) when soap is used. When the cation sites have been fully exchanged, passage of a saturated salt solution through the column pushes out the alkaline earth metal ions by a process based on the Le Châtelier principle.
- 2. Zeolites can act as adsorption agents.** The pores in a zeolite are just about the right size for holding small covalent molecules, so one major application is the use of zeolite to dry organic liquids. The water molecule is small enough to fit into a cavity of the zeolite, so it remains in the zeolite, which has effectively “dried” the organic liquid. Strong heating of the “wet” zeolite causes expulsion of the water, so the zeolite can be used again. Use of a zeolite with a particular pore size can make the process quite specific for the removal of certain molecules. These zeolites are called *molecular sieves*. For example, the zeolite of formula  $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O}$  has pores that are 400 pm in diameter; pores of this size can accommodate small molecules. The zeolite of formula  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot x\text{H}_2\text{O}$  has holes that are 800 pm in diameter and can accommodate larger molecules.
- 3. Zeolites can be used for gas separation.** Zeolites are very selective in their absorption of gases. In particular, they have a total preference for dinitrogen over dioxygen; 1 L of a typical zeolite contains about 5 L of nitrogen gas. This gas is released when the zeolite is heated. The selective absorption of dinitrogen makes zeolites of great use in the inexpensive separation of the two major components of the atmosphere. For example, a major cost in sewage treatment and steelworks has been the provision of oxygen-enriched air.

Traditionally, the only route to oxygen enrichment was liquefying the air and distilling the components. Now, by cycling air through beds of zeolites, the components can be separated inexpensively.

Why is dinitrogen selectively absorbed? After all, both dioxygen and dinitrogen are nonpolar molecules of about the same size. To answer this question, we have to look at the atomic nuclei rather than at the electrons. Nuclei can be spherical or ellipsoidal. If they are ellipsoidal (football shaped), like odd-odd nitrogen-14, then the nuclei possess an unevenly distributed nuclear charge, known as an electric quadrupole moment. Even-even oxygen-16, however, contains spherical nuclei and thus does not have an electric quadrupole moment. The interior of a zeolite cavity contains an extremely high electric charge, which attracts nuclei with electric quadrupole moments, such as those in the dinitrogen molecule. The effect is much smaller than the electron dipole moment and, apart from this instance, is of little importance in terms of chemical properties.

**4. Zeolites are vital as industrial catalysts.** The modern oil industry depends on zeolites. Crude oil from the ground does not meet many of our modern requirements. It has a high proportion of long-chain molecules, whereas the fuels we need are short-chain molecules with low boiling points. Furthermore, the long-chain molecules in crude oil have straight chains, which is fine for diesel engines, but the gasoline engine needs branched-chain molecules for optimum performance. Zeolite catalysts can, under specific conditions, convert straight-chain molecules to branched-chain isomers. The cavities in the zeolite structure act as molecular templates, rearranging the molecular structure to match the cavity shape. In addition to the oil industry, several industrial organic syntheses employ zeolite catalysts to convert a starting material to a very specific product. Such “clean” reactions are rare in conventional organic chemistry; in fact, side reactions giving unwanted products are very common.

One of the most important catalysts is  $\text{Na}_3[(\text{AlO}_2)_3(\text{SiO}_2)] \cdot x\text{H}_2\text{O}$ , commonly called ZSM-5. This compound does not occur in nature; it was first synthesized by research chemists at Mobil Oil. It is higher in aluminum than most naturally occurring zeolites, and its ability to function depends on the high acidity of water molecules bound to the high-charge-density aluminum ions. In fact, the hydrogen in ZSM-5 is as strong a Brønsted-Lowry acid as that in sulfuric acid.

## Ceramics

The term *ceramics* describes nonmetallic, inorganic compounds that are prepared by high-temperature treatment. The properties of ceramic materials are a function not only of their chemical composition but also of the conditions of their synthesis. Typically, the components are finely ground and mixed to a paste with water. The paste is then formed into the desired shape and heated to about 900°C. At these temperatures, all the water molecules are lost, and numerous high-temperature chemical reactions occur. In particular, long needle crystals of mullite,  $\text{Al}_6\text{Si}_2\text{O}_{13}$ , are formed. These make a major contribution to the strength of the ceramic material.

Conventional ceramics are made from a combination of quartz with two-dimensional silicates (clays) and three-dimensional silicates (feldspars). Thus, a stoneware used for household plates will have a composition of about 45 percent clay, 20 percent feldspar, and 35 percent quartz. By contrast, a dental ceramic for tooth caps is made from about 80 percent feldspar, 15 percent clay, and 5 percent quartz.

As the search for new materials intensifies, boundaries between compound classifications are disappearing. *Glassy ceramics* are glasses in which a carefully controlled proportion of crystals has been grown. One example of a compound that can be formed into glassy ceramics is lithium aluminum silicate,  $\text{Li}_2\text{Al}_2\text{Si}_4\text{O}_{12}$ . Such materials are nonporous and are known for their extreme resistance to thermal shock. That is, they can be heated to red heat and then be plunged into cold water without shattering. The major use of this material is in cooking utensils and heat-resistant cooking surfaces. Many of these glassy ceramics are produced by Corning.

### WORKED EXAMPLE 14.6

Magnesium aluminum silicate,  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_x$ , is another compound which can be formed into a glassy ceramic. Deduce the number of oxygen ions in this compound.

#### Answer

$$2[N_{\text{ox}}(\text{Mg})] + 4[N_{\text{ox}}(\text{Al})] + 5[N_{\text{ox}}(\text{Si})] + x[N_{\text{ox}}(\text{O})] = 0$$

Assigning normal oxidation numbers:  $\text{Mg} = +2$ ;  $\text{Al} = +3$ ,  $\text{Si} = +4$ ,  $\text{O} = -2$ . Then:

$$2(+2) + 4(+3) + 5(+4) + x(-2) = 0$$

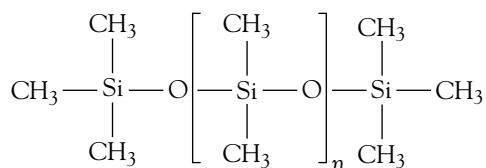
$$x(-2) = -36$$

$$x = 18$$

The compound must have the formula:  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ . ■

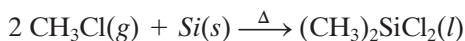
## 14.17 Silicones

Silicones, more correctly called *polysiloxanes*, constitute an enormous family of polymers, and they all contain a chain of alternating silicon and oxygen atoms. Attached to the silicon atoms are pairs of organic groups, such as the methyl group,  $\text{CH}_3$ . The structure of this simplest silicone is shown in Figure 14.22, where the number of repeating units,  $n$ , is very large.

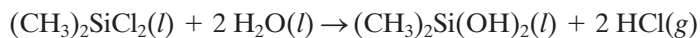


**FIGURE 14.22** The structure of the simplest silicone, catena-poly-[(dimethylsilicon)- $\mu$ -oxo]. The number of repeating units,  $n$ , is very large.

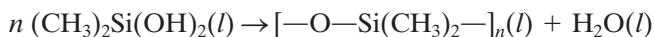
To synthesize this compound, chloromethane,  $\text{CH}_3\text{Cl}$ , is passed over a copper-silicon alloy at  $300^\circ\text{C}$ . A mixture of compounds is produced, including  $(\text{CH}_3)_2\text{SiCl}_2$ :



Water is added, causing hydrolysis:



The hydroxo compound then polymerizes, with loss of water:



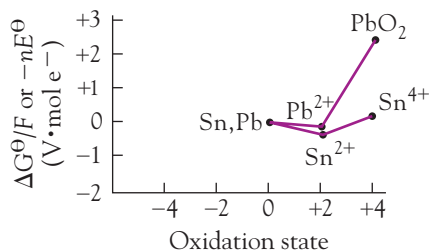
Silicones are used for a wide variety of purposes. The liquid silicones are more stable than hydrocarbon oils. In addition, their viscosity changes little with temperature, whereas the viscosity of hydrocarbon oils changes dramatically with temperature. Thus, silicones are used as lubricants and wherever inert fluids are needed; for example, in hydraulic braking systems. Silicones are very hydrophobic (nonwetting); hence, they are used in water-repellent sprays for shoes and other items.

By the cross-linking of chains, silicone rubbers can be produced. Like the silicone oils, the rubbers show great stability to high temperature and to chemical attack. Their multitudinous uses include the face-fitting edges for snorkel and scuba masks. The rubbers also are very useful in medical applications, such as transfusion tubes. However, silicone gels have attained notoriety in their role as a breast implant material. While sealed in a polymer sack, they are believed to be harmless. The major problem arises when the container walls leak or break. The silicone gel can then diffuse into surrounding tissues. The chemical inertness of silicones turns from a benefit to a problem because the body has no mechanism for breaking down the polymer molecules. Many medical personnel believe that these alien gel fragments trigger the immune system, thereby causing a number of medical problems.

The advantages of the silicone polymers over carbon-based polymers result from several factors. First, the silicon-oxygen bond in the backbone of the molecule is stronger than the carbon-carbon bond in the organic polymers ( $452 \text{ kJ}\cdot\text{mol}^{-1}$  compared to about  $346 \text{ kJ}\cdot\text{mol}^{-1}$ ), making the silicon-based polymers more resistant to oxidation at high temperatures. It is for this reason that high-temperature oil baths always utilize silicone oils, not hydrocarbon oils. The absence of substituents on the oxygen atoms in the chain and the wider bond angle ( $\text{Si}-\text{O}-\text{Si}$  is  $143^\circ$  compared with  $109^\circ$  for  $\text{C}-\text{C}-\text{C}$ ) results in the greater flexibility of a silicone polymer.

### 14.18 Tin and Lead

Tin and lead exist in two oxidation states, +4 and +2. It is possible to explain the existence of the +2 oxidation state in terms of the inert-pair effect, as we did for the +1 oxidation state of thallium in Chapter 9, Section 9.8. The



**FIGURE 14.23** Frost diagram for tin and lead.

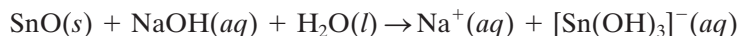
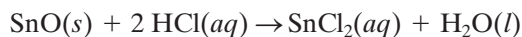
formation of ions of these metals is rare. Tin and lead compounds in which the metals are in the +4 oxidation state are covalent, except for a few solid-phase compounds.

Even when in the +2 oxidation state, tin generally forms covalent bonds, with ionic bonds only being present in compounds in the solid phase. Lead, on the other hand, forms the  $2+$  ion in solid *and* in solution, with the +4 state being strongly oxidizing, as the comparative Frost diagram (Figure 14.23) illustrates. As the charge density for  $\text{Pb}^{2+}$  is relatively low ( $32 \text{ C}\cdot\text{mm}^{-3}$ ), compounds are ionic, whereas that for the theoretical  $4+$  ion, the charge density is high ( $196 \text{ C}\cdot\text{mm}^{-3}$ )—high enough to cause the formation of covalent bonds with all but the least polarizable anion, fluoride.

## Tin

Tin forms two common allotropes: the shiny metallic allotrope, which is thermodynamically stable above  $13^\circ\text{C}$ , and the gray, nonmetallic diamond-structure allotrope, which is stable below that temperature. The change at low temperatures to microcrystals of the gray allotrope is slow at first but accelerates rapidly. This transition is a particular problem in poorly heated museums, where priceless historical artifacts can crumble into a pile of tin powder. The effect can spread from one object to another in contact with it, and this lifelike behavior has been referred to as “tin plague” or “museum disease.” The soldiers of Napoleon’s army had tin buttons fastening their clothes, and they used tin cooking utensils. It is believed by some that, during the bitterly cold winter invasion of Russia, the crumbling of buttons, plates, and pans contributed to the low morale and hence to the ultimate defeat of the French troops.

The existence of both a metallic and a nonmetallic allotrope identifies tin as a real “borderline” or weak metal. Tin is also amphoteric, another of its weak metallic properties. Thus, tin(II) oxide reacts with acid to give (covalent) tin(II) salts and with bases to form the stannite ion,  $[\text{Sn}(\text{OH})_3]^-$ :

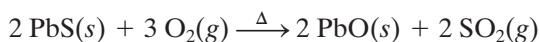


Tin(IV) oxide,  $\text{SnO}_2$ , is the more stable oxide of tin and it is incorporated in glazes used in the ceramics industry. About 3500 tonnes are used annually for this purpose.



## Lead

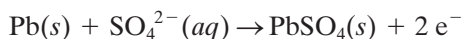
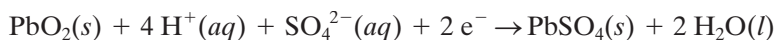
Lead, the more economically important of the two metals, is a soft, gray-black, dense solid found almost exclusively as lead(II) sulfide, the mineral galena. To obtain metallic lead, lead(II) sulfide is heated with air to oxidize the sulfide ions to sulfur dioxide. The lead(II) oxide can then be reduced with coke to lead metal:



## Lead Oxides

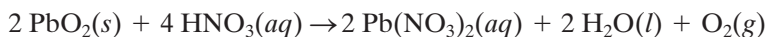
Lead(II) oxide, PbO, is the stable oxide of lead. It exists in two crystalline forms, one yellow (massicot) and the other red (litharge). There is also a mixed oxide of lead, Pb<sub>3</sub>O<sub>4</sub> (red lead), which behaves chemically as PbO<sub>2</sub>·2PbO; hence, its systematic name is lead(II) lead(IV) oxide. Red lead, Pb<sub>3</sub>O<sub>4</sub>, has been used on a large scale as a rust-resistant surface coating for iron and steel. Mixed metal oxides, such as calcium lead(IV) oxide, CaPbO<sub>3</sub>, are now being used as an even more effective protection against salt water for steel structures. The perovskite structure of CaPbO<sub>3</sub> is discussed in Chapter 5, Section 5.6.

The chocolate brown lead(IV) oxide, PbO<sub>2</sub>, is quite stable, and it is a strong oxidizing agent. The consumption of lead(II) oxide is much higher, of the order of 250 000 tonnes annually, because it is used to make lead glass and for the production of the electrode surfaces in lead-acid batteries. In these batteries, both electrodes are formed by pressing lead(II) oxide into a frame of lead metal. The cathode is formed by oxidizing lead(II) oxide to lead(IV) oxide, and the anode is produced by reducing lead(II) oxide to lead metal. The electric current arises when lead(IV) oxide is reduced to insoluble lead(II) sulfate in the sulfuric acid electrolyte, while the lead metal is oxidized to lead(II) sulfate on the other electrode:



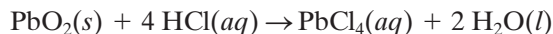
These two half-reactions are reversible. Hence, the battery can be recharged by applying an electric current in the reverse direction. In spite of a tremendous quantity of research, it has been very difficult to develop a low-cost, lead-free, heavy-duty battery that can perform as well as the lead-acid battery.

As mentioned in Section 14.18, the Pb<sup>4+</sup> ion is too polarizing to exist in aqueous solution. Oxide ion can often be used to stabilize the highest oxidation number of an element in the solid phase, and this phenomenon is true for lead. Lead(IV) oxide is an insoluble solid in which the Pb<sup>4+</sup> ions are stabilized in the lattice by the high lattice energy. Even then, one can argue that there is considerable covalent character in the structure. Addition of an acid, such as nitric acid, gives immediate reduction to the lead(II) ion and the production of oxygen gas:



In the cold, lead(IV) oxide undergoes a double-replacement reaction with concentrated hydrochloric acid to give covalently bonded lead(IV) chloride. When

warmed, the unstable lead(IV) chloride decomposes to give lead(II) chloride and chlorine gas:



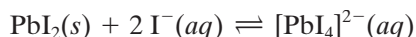
### Lead Halides

Lead(IV) chloride is a yellow oil that decomposes in the presence of moisture and explodes when heated. Lead(IV) bromide and iodide do not exist because the oxidation potential of these two halogens is sufficient to reduce lead(IV) to lead(II).

The lead(II) chloride, bromide, and iodide are all water-insoluble solids. Bright yellow crystals of lead(II) iodide are formed when colorless solutions of lead(II) ion and iodide ion are mixed:



Addition of a large excess of iodide ion causes the precipitate to dissolve, forming a solution of the tetraiodoplumbate(II) ion:

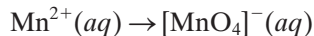
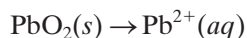


### WORKED EXAMPLE 14.7

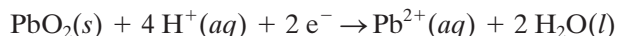
Lead(IV) oxide will oxidize a solution of manganese(II) ion to permanganate ion in acidic solution. Write a balanced chemical equation for the reaction.

#### Answer

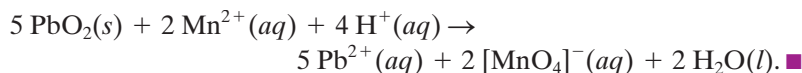
We start with the two skeletal half reactions:



Following the usual steps, the following half reactions are obtained:



Multiplying the first half-reaction by five, and the second by two, gives:



## 14.19 Biological Aspects

### The Carbon Cycle

There are many biogeochemical cycles on this planet. The largest-scale process is the carbon cycle. Of the  $2 \times 10^{16}$  tonnes of carbon, most of it is “locked away” in the Earth’s crust as carbonates, coal, and oil. Only about  $2.5 \times 10^{12}$  tonnes

are available as carbon dioxide. Every year, about 15 percent of this total is absorbed by plants and algae in the process of photosynthesis, which uses energy from the Sun to synthesize complex molecules such as sucrose.

Some plants are eaten by animals (such as humans), and a part of the stored chemical energy is released during their decomposition to carbon dioxide and water. These two products are returned to the atmosphere by the process of respiration. However, the majority of the carbon dioxide incorporated into plants is returned to the atmosphere only after the death and subsequent decomposition of the plant organisms. Another portion of the plant material is buried, thereby contributing to the soil humus or the formation of peat bogs. The carbon cycle is partially balanced by the copious output of carbon dioxide by volcanoes.

The demand for energy has led to the burning of coal and oil, which were formed mainly in the Carboniferous era. This combustion adds about  $2.5 \times 10^{10}$  tonnes of carbon dioxide to the atmosphere each year in addition to that from natural cycles. Although we are just returning to the atmosphere carbon dioxide that came from there, we are doing so at a very rapid rate, and many scientists are concerned that the rate of return will overwhelm the Earth's absorption mechanisms. This topic is currently being studied in many laboratories.

### The Essentiality of Silicon

Silicon is the second most abundant element in the Earth's crust, yet its biological role is limited by the low water solubility of its common forms, silicon dioxide and silicic acid,  $\text{H}_4\text{SiO}_4$ . At about neutral pH, silicic acid is uncharged and has a solubility of about  $2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ . As the pH decreases, polysilicic acids predominate, then colloidal particles of hydrated silicon dioxide. Although the solubility of silicic acid is low, on the global scale it is enormous, with about  $2 \times 10^{11}$  tonnes of silicic acid entering the sea per year. It is the continuous supply of silicic acid into the sea that enables marine organisms such as diatoms and radiolaria to construct their exoskeletons of hydrated silica.

On a smaller scale, plants require the absorption of about 600 L of water to form about 1 kg of dry mass; thus, plants consist of about 0.15 percent silicon. The silica is used by the plants to stiffen leaves and stalks. In some plants, it is also used for defense. Farther up the food chain, herbivores ingest considerable amounts of silica. A sheep consumes about 30 g of silicon per day, although almost all is excreted. Humans are estimated to consume about 30 mg of silicon per day; about 60 percent from breakfast cereal and 20 percent from water and drinks. It is the water-dissolved silicic acid that is bioavailable to our bodies.

The question obviously arose as to the function of the silicon. Chemical studies showed that silicic acid did not react or bind with organic molecules. Thus, incorporation into some essential biosynthetic pathway seemed highly unlikely. The answer seems to lie with its inorganic chemistry. As we saw in Chapter 13, Section 13.11, aluminum is ubiquitous in the environment and this

element is highly toxic to organisms. Addition of silicic acid to a saturated neutral solution of aluminum ion causes almost complete precipitation of the aluminum in the form of insoluble hydrated aluminosilicates.

Evidence that silicon does act in a preventative role was provided by a study of young salmon. Those in water containing aluminum ion died within 48 hours. Those in water containing the same concentration of aluminum plus silicic acid thrived. It is now generally accepted that indeed silicon is essential to our diet to inhibit the toxicity of the naturally present aluminum in our foodstuffs.

### The Toxicity of Tin

Although the element and its simple inorganic compounds have a fairly low toxicity, its organometallic compounds are very toxic. Compounds such as hydroxotributyltin,  $(C_4H_9)_3SnOH$ , are effective against fungal infections in potatoes, grapevines, and rice plants. For many years, organotin compounds were incorporated into the paints used on ships' hulls. The compound would kill the larvae of mollusks, such as barnacles, that tend to attach themselves to a ship's hull, slowing the vessel considerably. However, the organotin compound slowly leaches into the surrounding waters, where, particularly within the confines of a harbor, it destroys other marine organisms. For this reason, its marine use has been curtailed.

### The Severe Hazard of Lead

Why is there such concern about lead poisoning? For many elements the levels to which we are naturally exposed is many times smaller than toxic levels. For lead, however, there is a relatively small safety margin between unavoidable ingestion from our food, water, and air and the level at which toxic symptoms become apparent. Lead is ubiquitous in our environment. Plants absorb lead from the soil, and water dissolves traces of lead compounds.

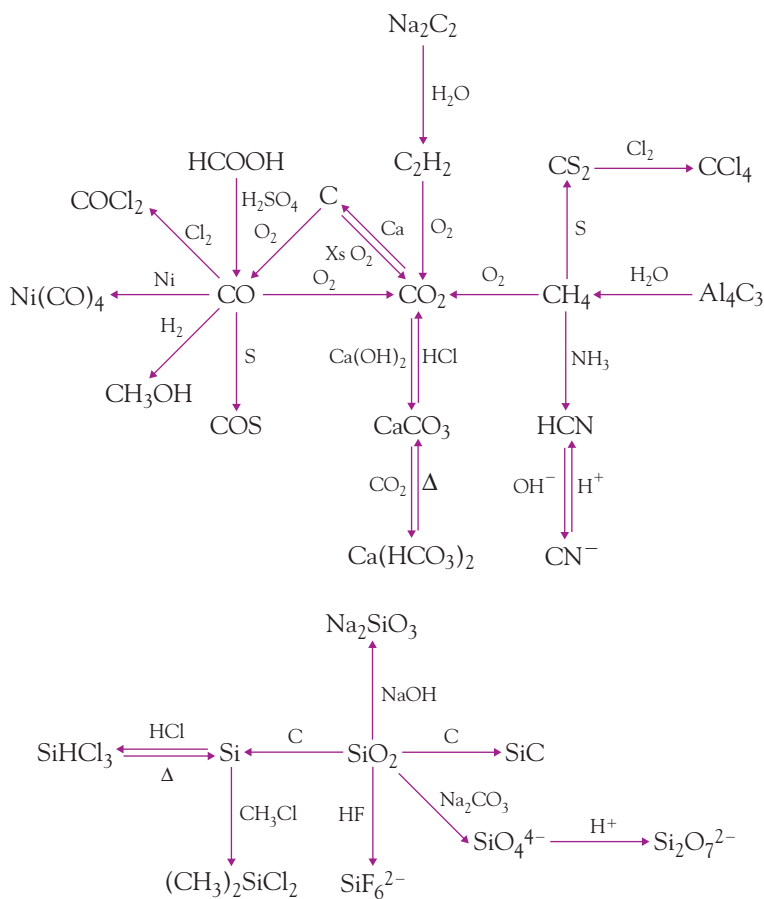
In addition to what our environment contains, humans have used lead products throughout history. Basic lead carbonate,  $Pb_3(CO_3)_2(OH)_2$ , was one of the few easily obtainable white substances. Thus, it was used until recently as a paint pigment, and many old houses have unacceptably high levels of lead resulting from the use of lead-based paints on the walls and ceilings. The same compound was used by women as a cosmetic. The factories producing the lead compound were known as "white cemeteries." Working in such a plant was a last resort. Yet circumstances of illness or death in the family or idleness or drunkenness by a husband gave some women little option even though it was a virtual death sentence.

About 95 percent of absorbed lead substitutes for calcium in the hydroxyapatite of bone. This can be explained as the lead(II) ion is only slightly larger than and has a similar charge density to that of calcium. Thus, the body "stores" lead. In the bone, the half-life is about 25 years, so lead poisoning is a very long-term problem. Lead interferes with the synthesis of hemoglobin and so can indirectly cause anemia. At high concentrations, kidney failure, convulsions, brain

damage, and then death ensue. There is also strong evidence of neurological effects, including reduced IQ in children exposed to more than minimal lead levels. As part of a program to minimize the hazard, playgrounds built on old industrial sites are checked for lead levels and, if necessary, closed or resurfaced.

## 14.20 Element Reaction Flowcharts

Flowcharts are shown for both carbon and silicon.



### KEY IDEAS

- Carbon has an extensive chemistry resulting from its ability to catenate.
- There are three classes of carbides.
- The two oxides of carbon have very different properties.
- Silicates have a wide variety of structures.
- Tin and lead have weakly metallic properties.

## EXERCISES

**14.1** Write balanced chemical equations corresponding to the following chemical reactions:

- (a) solid lithium dicarbide( $2-$ ) with water
- (b) silicon dioxide with carbon
- (c) copper(II) oxide heated with carbon monoxide
- (d) calcium hydroxide solution with carbon dioxide (two equations)
- (e) methane with molten sulfur
- (f) silicon dioxide with molten sodium carbonate
- (g) lead(IV) oxide with concentrated hydrochloric acid (two equations)

**14.2** Write balanced chemical equations corresponding to the following chemical reactions:

- (a) solid beryllium carbide with water
- (b) carbon monoxide with dichlorine
- (c) hot magnesium metal with carbon dioxide
- (d) solid sodium carbonate with hydrochloric acid
- (e) heating barium carbonate
- (f) carbon disulfide gas with chlorine gas
- (g) tin(II) oxide with hydrochloric acid

**14.3** Define the following terms: (a) catenation; (b) aerogel; (c) ceramic; (d) silicone.

**14.4** Define the following terms: (a) glass; (b) molecular sieves; (c) glassy ceramic; (d) galena.

**14.5** Contrast the properties of the three main allotropes of carbon—diamond, graphite, and  $C_{60}$ .

**14.6** Explain why (a) diamond has a very high thermal conductivity; (b) high pressure and temperature are required for the traditional method of diamond synthesis.

**14.7** Why are fullerenes soluble in many solvents even though both graphite and diamond are insoluble in all solvents?

**14.8** Explain why catenation is common for carbon but not for silicon.

**14.9** Compare and contrast the three classes of carbides.

**14.10** Calcium carbide forms a NaCl structure with a density of  $2.22 \text{ g}\cdot\text{cm}^{-3}$ . Assuming the carbide ion is spherical and taking the ionic radius of calcium as 114 pm, what is the radius of the carbide ion?

**14.11** Write the chemical equation for the reaction used in the commercial production of silicon carbide. Is it enthalpy or entropy driven? Explain your reasoning. Calculate the values of  $\Delta H^\ominus$  and  $\Delta S^\ominus$  for the process to confirm your deduction, then calculate  $\Delta G^\ominus$  at  $2000^\circ\text{C}$ .

**14.12** In compounds of carbon monoxide with metals, it is the carbon atom that acts as a Lewis base. Show why this is expected using a formal charge representation of the carbon monoxide molecule.

**14.13** Carbon dioxide has a negative enthalpy of formation, whereas that of carbon disulfide is positive. Using bond energy data, construct a pair of enthalpy of formation diagrams and identify the reason(s) for such different values.

**14.14** Contrast the properties of carbon monoxide and carbon dioxide.

**14.15** Discuss the bonding in carbon disulfide in terms of hybridization theory.

**14.16** From data tables in Appendix 1 of  $\Delta_f H^\ominus$  and  $S^\ominus$  values, show that the combustion of methane is a spontaneous process.

**14.17** Explain why silane burns in contact with air, whereas methane requires a spark before it will combust.

**14.18** Describe why the CFCs were once thought to be ideal refrigerants.

**14.19** Why is HFC-134a a less than ideal replacement for CFC-12?

**14.20** What would be the chemical formula of HFC-134b?

**14.21** Why does methane represent a particular concern as a potential greenhouse gas?

**14.22** Contrast the properties of carbon dioxide and silicon dioxide and explain these differences in terms of the bond types. Suggest an explanation as to why the two oxides adopt such dissimilar bonding.

**14.23** The ion  $\text{CO}_2^-$  can be prepared using ultraviolet irradiation. Whereas the carbon dioxide molecule is linear, this ion is V shaped, with a bond angle of about  $127^\circ$ . Use an electron-dot diagram to aid your explanation of this. Also, estimate an average carbon-oxygen bond order for the ion and contrast to that in the carbon dioxide molecule.

**14.24** Draw the electron-dot diagram for the symmetrical cyanamide ion,  $\text{CN}_2^{2-}$ . Then deduce the bond angle in the ion.

**14.25** What geometry would you expect for the ion  $:\text{C}(\text{CN})_3^-$ ? In fact, it is trigonal planar. Construct one of the three resonance forms to depict the probable electron arrangement and deduce an average carbon-carbon bond order.

**14.26** Ultramarine, the beautiful blue pigment used in oil-based paints, has the formula  $\text{Na}_x[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_2$ , where the

sulfur is present as the disulfide ion,  $S_2^{2-}$ . Determine the value of  $x$ .

**14.27** In crocidolite,  $Na_2Fe_5(Si_4O_{11})_2(OH)_2$ , how many of the iron ions must have a 2+ charge and how many a 3+ charge?

**14.28** Describe the difference in structure between white asbestos and talc.

**14.29** Describe the major uses of zeolites.

**14.30** If the water in a zeolite is expelled by strong heating, must the absorption of water by the zeolite be an endothermic or exothermic process?

**14.31** What advantage of silicone polymers becomes a problem when they are used as breast implants?

**14.32** Contrast the properties of the oxides of tin and lead.

**14.33** Construct the electron-dot structures of tin(IV) chloride and gaseous tin(II) chloride. Draw the corresponding molecular shapes.

**14.34** Lead(IV) fluoride melts at 600°C, whereas lead(IV) chloride melts at 215°C. Interpret the values in relation to the probable bonding in the compounds.

**14.35** To form the electrodes in the lead-acid battery, the cathode is produced by oxidizing lead(II) oxide to lead(IV) oxide, and the anode is produced by reducing the lead(II) oxide to lead metal. Write half-equations to represent the two processes.

**14.36** Suggest the probable products formed when  $CaCS_3$  is heated.

**14.37** Write the formulas of two carbon-containing species that are isoelectronic with the  $C_2^{2-}$  ion.

**14.38** There are two carbides that appear to contain the  $C^{4-}$  ion. What are they and how are they related?

**14.39** Discuss why inorganic polymer chemistry is much less developed than organic polymer chemistry.

**14.40** Discuss the introduction of tetraethyllead and why its use in gasoline continues today.

**14.41** Write balanced chemical equations corresponding to each transformation in the element reaction flowcharts for carbon and silicon (page 374).

## BEYOND THE BASICS

**14.42** Show from the standard reduction potentials from online Appendix 9 that lead(IV) iodide would not be thermodynamically stable in aqueous solution.

**14.43** It is contended that the ancient Romans sweetened their wine with “sugar of lead” a water-soluble compound of lead. The evidence comes from examination of skeletons. Suggest why the lead ions would be present in bone tissues.

**14.44** What are the main sources of lead in the environment today?

**14.45** Conventional soda glass, when washed frequently in hot water, tends to become opaque and rough, while pure silica ( $SiO_2$ ) glass does not lose its brilliance. Suggest an explanation.

**14.46** One route for the formation of the trace atmospheric gas carbonyl sulfide is hydrolysis of carbon disulfide. Write a chemical equation for this reaction. How would a water molecule attack a molecule of carbon disulfide? Draw a transition state for the attack, showing the bond polarities. Thus, deduce a possible intermediate for the reaction and suggest why it is feasible.

**14.47** There is a trimeric silicate ion,  $Si_3O_9^{6-}$ .

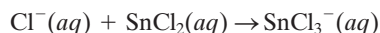
(a) Draw a probable structure for the ion.

(b) Phosphorus forms an isoelectronic and isostructural ion. What would be its formula?

(c) Another element forms an isoelectronic and isostructural neutral compound. What would be its formula?

**14.48** Methyl isocyanate,  $H_3CNCO$ , has a bent  $C-N-C$  bond, whereas silyl isocyanate,  $H_3SiNCO$ , has a linear  $Si-N-C$  bond. Suggest an explanation for the difference.

**14.49** In the following reaction, identify which is the Lewis acid and which the Lewis base. Give your reasoning.



**14.50** Tin reacts with both acids and bases. With dilute nitric acid, the metal gives a solution of tin(II) nitrate and ammonium nitrate; with concentrated sulfuric acid, solid tin(II) sulfate and gaseous sulfur dioxide; with potassium hydroxide solution, a solution of potassium hexahydroxostannate(IV),  $K_2Sn(OH)_6$ , and hydrogen gas. Write balanced net ionic equations for these reactions.

**14.51** Silicon dioxide is a weaker acid than carbon dioxide. Write a balanced chemical equation to show how silicate rocks, such as  $Mg_2SiO_4$ , might, in the presence of “carbonic acid,” be a partial sink for atmospheric carbon dioxide.

**14.52** When aqueous solutions of aluminum ion and carbonate ion are mixed, a precipitate of aluminum hydroxide is formed. Suggest an explanation using net ionic equations.



**14.53** A flammable gas (A) is reacted at high temperature with a molten yellow element (B) to give compounds (C) and (D). Compound (D) has the odor of rotten eggs. Compound (C) reacts with a pale green gas (E) to give as a final product compound (F) and element (B). Compound (F) can also be produced by the direct reaction of (A) with (E). Identify each species and write balanced chemical equations for each step.

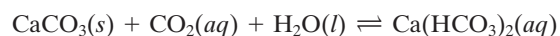
**14.54** Magnesium silicide,  $\text{Mg}_2\text{Si}$ , reacts with hydronium ion to give magnesium ion and a reactive gas (X). A mass of 0.620 g of gas (X) occupied a volume of 244 mL at a temperature of  $25^\circ\text{C}$  and a pressure of 100 kPa. The sample of gas decomposed in aqueous hydroxide ion solution to give 0.730 L of hydrogen gas and 1.200 g of silicon dioxide. What is the molecular formula of (X)? Write a balanced chemical equation for the reaction of (X) with water.

**14.55** Tin(IV) chloride reacts with an excess of ethyl magnesium bromide,  $(\text{C}_2\text{H}_5)\text{MgBr}$ , to give two products, one of which is a liquid (Y). Compound (Y) contains only carbon, hydrogen, and tin. 0.1935 g of (Y) was oxidized to give 0.1240 g of tin(IV) oxide. Heating 1.41 g of (Y) with 0.52 g of tin(IV) chloride gives 1.93 g of liquid (Z). When 0.2240 g

of (Z) was reacted with silver nitrate solution, 0.1332 g of silver chloride was formed. Oxidation of 0.1865 g of (Z) gave 0.1164 g of tin(IV) oxide. Deduce the empirical formulas of (Y) and (Z). Write a balanced chemical equation for the reaction of (Y) with tin(IV) chloride to give (Z).

**14.56** The solid compound aluminum phosphate,  $\text{AlPO}_4$ , adopts a quartz-like structure. Suggest why this occurs.

**14.57** Use thermodynamic calculations to show that decomposition of calcium hydrogen carbonate is favored at  $80^\circ\text{C}$ :



**14.58** Suggest why the density of moissanite is slightly less than that of diamond, even though the atomic mass of silicon is much greater than that of carbon.

**14.59** Use bond energy values to determine the energy available for transfer to a phosphor dye molecule when a mole of dicarbon tetroxide forms two moles of carbon dioxide.

**14.60** What is the oxidation number of each carbon atom in dicarbon tetroxide?

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)





# THE GROUP 15 ELEMENTS:

## The Pnictogens

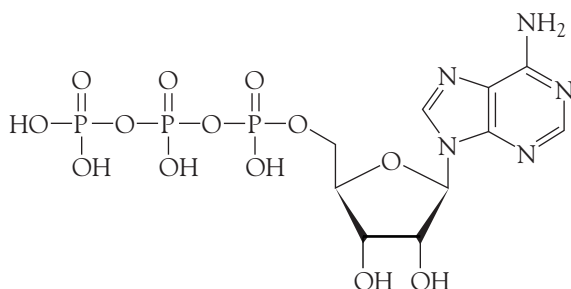
## CHAPTER 15

N
P
As
Sb
Bi

Two of the most dissimilar nonmetallic elements are in the same group: reactive phosphorus and unreactive nitrogen. Of the other members of the group, arsenic is really a semimetal and a metalloid, and the two lower members of the group, antimony and bismuth, exhibit weakly metallic behavior.

### Context: The Essential Phosphorus-Oxygen Bond

Living organisms need energy. For life on Earth, it is the phosphorus-oxygen bond which is our energy-transfer agent. Without this, life as we know it would be impossible. The energy is derived from the molecule adenosine triphosphate (ATP) (see following).

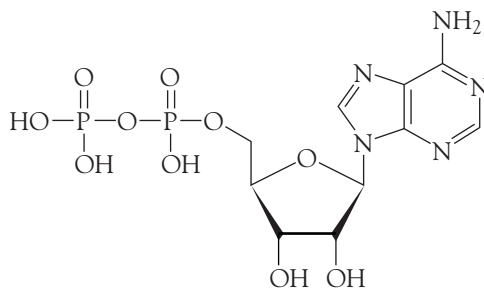


The structure of ATP.

The energy-releasing process is the hydrolysis of ATP to adenosine diphosphate (ADP), releasing inorganic phosphate.

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 15.1** Group Trends
- 15.2** Contrasts in the Chemistry of Nitrogen and Phosphorus
- 15.3** Overview of Nitrogen Chemistry
- 15.4** Nitrogen
- 15.5** Nitrogen Hydrides
- 15.6** Nitrogen Ions
- 15.7** The Ammonium Ion
- 15.8** Nitrogen Oxides
- 15.9** Nitrogen Halides
- 15.10** Nitrous Acid and Nitrites
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- 15.12** Overview of Phosphorus Chemistry
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- 15.14** Phosphine
- 15.15** Phosphorus Oxides
- 15.16** Phosphorus Chlorides
- 15.17** Phosphorus Oxoacids and Phosphates
- 15.18** The Pnictides
- 15.19** Biological Aspects
- 15.20** Element Reaction Flowcharts



The structure of ADP.

The hydrolysis involves breaking P—O covalent bonds (bond energy,  $335 \text{ kJ}\cdot\text{mol}^{-1}$ ; see Section 15.2) and making O—H bonds (bond energy,  $459 \text{ kJ}\cdot\text{mol}^{-1}$ ). The additional stability of the products arises from the multiple resonance structures of the phosphate. At typical blood pH, the phosphate exists as an equilibrium mixture of the monohydrogen phosphate ion,  $\text{HPO}_4^{2-}$ , and the dihydrogen phosphate ion,  $\text{H}_2\text{PO}_4^-$  (Section 15.17). It is this equilibrium which provides a pH buffer of blood.

The typical human body contains around 250 g of ATP but produces, consumes, and re-forms its own body weight of it each day. ATP releases energy in this way during reactions such as respiration, fermentation, and photosynthesis. The conversion of ADP back to ATP happens in two general ways. Plants, or more precisely, phototrophs, use light energy for this purpose, other organisms (such as ourselves) are chemotrophs, obtaining energy from the oxidation of foodstuffs. The reverse pathway is energetically possible because the P—O bond is atypically strong for a single bond. Thus, the external energy required, that is, the difference in energy between the O—H bond to be broken and the P—O bond to be re-formed, is feasible from visible light or carbohydrate sources. In this way, ATP and ADP are continuously inter-converted.

## 15.1 Group Trends

As of 2005, the International Union of Pure and Applied Chemistry (IUPAC)–approved name for this group is the pnictogens (pronounced *nikt-o-gens*). The original name was the pnigogens, from the Greek for “choking,” but a *t* somehow became incorporated, although a significant proportion of chemists still use *pnicogen*.

The first two members of Group 15, nitrogen and phosphorus, are nonmetals; the remaining three members, arsenic, antimony, and bismuth, have some metallic characteristics. Scientists like to categorize things, but in this group, their efforts are frustrated because there is no clear division of properties between nonmetals and metals. Two characteristic properties that we can study are the electrical resistivity of the elements and the acid-base behavior of the oxides (Table 15.1).

Nitrogen and phosphorus are both nonconductors of electricity, and both form acidic oxides, so they are unambiguously classified as nonmetals. The problems start with arsenic. Even though the common allotrope of arsenic looks metallic, subliming and recondensing the solid produce a second allotrope

**TABLE 15.1** Properties of the Group 15 elements

Element	Appearance at SATP	Electrical resistivity ( $\mu\Omega\cdot\text{cm}$ )	Acid-base properties of oxides
Nitrogen	Colorless gas	—	Acidic and neutral
Phosphorus	White, waxy solid	$10^{17}$	Acidic
Arsenic	Brittle, metallic solid	33	Amphoteric
Antimony	Brittle, metallic solid	42	Amphoretic
Bismuth	Brittle, metallic solid	120	Basic

**TABLE 15.2** Melting and boiling points of the Group 15 elements

Element	Melting point ( $^{\circ}\text{C}$ )	Boiling point ( $^{\circ}\text{C}$ )
N <sub>2</sub>	−210	−196
P <sub>4</sub>	44	281
As	Sublimes at 615	
Sb	631	1387
Bi	271	1564

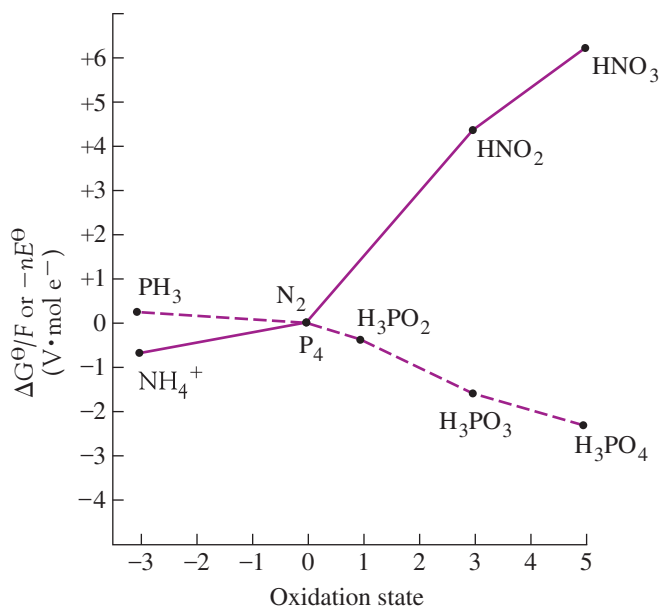
that is a yellow powder. Because it has both metallic-looking and nonmetallic allotropes and forms amphoteric oxides, arsenic can be classified as a metalloid. However, much of its chemistry parallels that of phosphorus, so there is a good case for considering it as a nonmetal.

Antimony and bismuth are almost as borderline as arsenic. Their electrical resistivities are much higher than those of a “true” metal, such as aluminum ( $2.8\ \mu\Omega\cdot\text{cm}$ ), and even higher than a typical “weak” metal, such as lead ( $22\ \mu\Omega\cdot\text{cm}$ ). Generally, however, these two elements are categorized as metals. All three of these borderline elements form covalent compounds almost exclusively.

If we want to decide where to draw the vague border between metals and metalloids, the melting and boiling points are as good an indicator as any. In Group 15, these parameters increase as we descend the group, except for a decrease in melting point from antimony to bismuth (Table 15.2). As noted for the alkali metals, the melting points of main group metals tend to decrease down a group, whereas those of nonmetals tend to increase down a group. (We will encounter the latter behavior most clearly with the halogens.) Thus, the increase-decrease pattern shown in Table 15.2 indicates that the lighter members of Group 15 follow the typical non-metal trend, and the shift to the metallic decreasing trend starts at bismuth.

## 15.2 Contrasts in the Chemistry of Nitrogen and Phosphorus

Although they are vertical neighbors in the periodic table, the redox behavior of nitrogen and phosphorus could not be more different (Figure 15.1). Whereas the higher oxidation states of nitrogen are strongly oxidizing in acidic solution,



**FIGURE 15.1** Frost diagram comparing the stability of the oxidation states of phosphorus and nitrogen in acidic solution.

those of phosphorus are quite stable. In fact, the highest oxidation state of phosphorus is the most thermodynamically stable and the lowest oxidation state, the least stable—the converse of nitrogen chemistry.

### The Thermodynamic Stability of Dinitrogen

If we look at the bond energies, we can see why different species are preferred for the two elements. Dinitrogen, N $_2$ , is the stable form for the element, and it is a common product from nitrogen-containing compounds in chemical reactions. This is, in large part, due to the very high strength of the nitrogen-nitrogen triple bond compared to the single (or double) bonds (Table 15.3). For phosphorus, there is a much smaller difference between the single and triple bond energies. Thus, elemental phosphorus contains groups of singly bonded phosphorus atoms. In fact, the strong phosphorus-oxygen single bond becomes a dominant feature of phosphorus chemistry. For example, as we will see below, whereas the element nitrogen is very stable to oxidation, elemental phosphorus reacts vigorously with oxygen to give oxides.

**TABLE 15.3** A comparison of approximate nitrogen and phosphorus bond energies

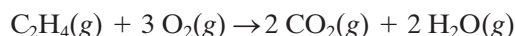
Nitrogen bonds	Bond energy (kJ·mol $^{-1}$ )	Phosphorus bonds	Bond energy (kJ·mol $^{-1}$ )
N—N	247	P—P	200
N $\equiv$ N	942	P $\equiv$ P	481
N—O	201	P—O	335

**TABLE 15.4** A comparison of nitrogen and carbon bond energies

Nitrogen bonds	Bond energy (kJ·mol <sup>-1</sup> )	Carbon bonds	Bond energy (kJ·mol <sup>-1</sup> )
N—N	247	C—C	346
N≡N	942	C≡C	835

The triple nitrogen-nitrogen bond energy is greater even than that for the triple carbon-carbon bond (Table 15.4). Conversely, the single bond between two nitrogen atoms is much weaker than the carbon-carbon single bond. It is this large difference between N≡N and N—N bond strengths (695 kJ·mol<sup>-1</sup>) that contributes to the preference in nitrogen chemistry for the formation of the dinitrogen molecule in a reaction rather than chains of nitrogen-nitrogen single bonds, as occurs in carbon chemistry. Furthermore, the fact that dinitrogen is a gas means that an entropy factor also favors the formation of the dinitrogen molecule in chemical reactions.

We can see the difference in behavior between nitrogen and carbon by comparing the combustion of hydrazine, N<sub>2</sub>H<sub>4</sub>, to that of ethene, C<sub>2</sub>H<sub>4</sub>. The nitrogen compound burns to produce dinitrogen, whereas the carbon compound gives carbon dioxide:

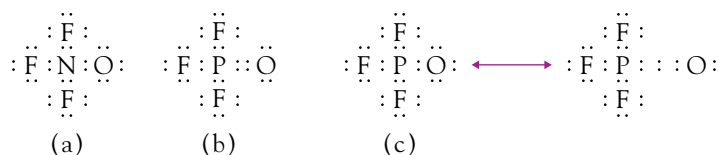


Curiously, in Groups 15 and 16, it is the second members—phosphorus and sulfur—that are prone to catenation.

### The Bonding Limitations of Nitrogen

Nitrogen forms only a trifluoride, NF<sub>3</sub>, whereas phosphorus forms two common fluorides, the pentafluoride, PF<sub>5</sub>, and the trifluoride, PF<sub>3</sub>. It is argued that the nitrogen atom is simply too small to accommodate more than the three fluorine atoms around it, while the (larger) lower members of the group can manage five (or even six) nearest neighbors. These molecules, such as phosphorus pentafluoride, in which the octet is exceeded for the central atom, are sometimes called *hypervalent compounds*. Traditionally, the bonding model for these compounds assumed that the 3d orbitals of the phosphorus played a major role in the bonding. Theoretical studies now suggest that participation of d orbitals is much less than that formerly assumed. A molecular orbital approach to the bonding very easily accommodates 10 or 12 valence electrons without having to involve d orbitals. However, in a course such as this, many chemists continue to explain the bonding in hypervalent compounds in terms of d-orbital involvement.

The pair of compounds NF<sub>3</sub>O and PF<sub>3</sub>O also illustrate the difference in bonding behavior between nitrogen and phosphorus. The former contains a weak nitrogen-oxygen bond, whereas the latter contains a fairly strong phosphorus-oxygen bond. For the nitrogen compound, we assume the oxygen is bonded

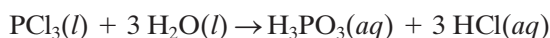
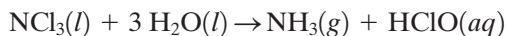


**FIGURE 15.2** Electron-dot representations of the bonding in  $\text{NF}_3\text{O}$  (a) and in  $\text{PF}_3\text{O}$  (b) which is a combination of two resonance structures (c).

through a coordinate covalent bond, with the nitrogen donating its lone pair in an  $\text{sp}^3$  hybrid orbital to a p orbital of the oxygen atom (Figure 15.2a). From bond energies, the phosphorus-oxygen bond has some double bond character (Figure 15.2b) but theoretical studies show that the bonding is most likely the result of two resonance structures, one with a single bond and one with a triple bond (Figure 15.2c).

### The Electronegativity Difference of Nitrogen and Phosphorus

Nitrogen has a much higher electronegativity than the other members of Group 15. As a result, the polarity of the bonds in nitrogen compounds is often the reverse of that in phosphorus and the other heavier members of the group. For example, the different polarities of the  $\text{N}-\text{Cl}$  and  $\text{P}-\text{Cl}$  bonds result in different hydrolysis products of the respective trichlorides:

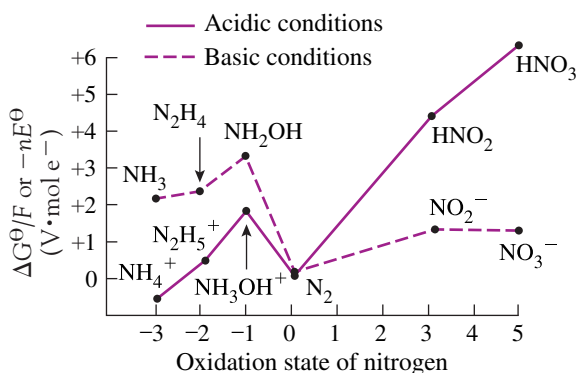


Because the nitrogen-hydrogen covalent bond is strongly polar, ammonia is basic, whereas the hydrides of the other Group 15 elements—phosphine,  $\text{PH}_3$ , arsine,  $\text{AsH}_3$ , and stibine,  $\text{SbH}_3$ —are essentially neutral.

## 15.3 Overview of Nitrogen Chemistry

Nitrogen chemistry is complex. For an overview, consider the oxidation-state diagram in Figure 15.3. The first thing we notice is that nitrogen can assume formal oxidation states that range from +5 to −3. Second, because it behaves

**FIGURE 15.3** Frost diagram for the common nitrogen species under acidic and basic conditions.



## The First Dinitrogen Compound

As we have said, dinitrogen is very unreactive, but this does not mean that it is totally unreactive. In Chapter 14, Section 14.6, we noted that carbon monoxide could bond to metals (a topic we discuss in more detail in Chapter 22). Dinitrogen is isoelectronic with carbon monoxide, although there is the important difference that dinitrogen is nonpolar, whereas carbon monoxide is polar. Nevertheless, the isoelectronic concept is useful for predicting the possible formation of a compound.

In early 1964, Caesar Senoff, a Canadian chemistry student at the University of Toronto, was working with compounds of ruthenium. He synthesized a brown compound whose composition he was unable to explain. Time passed, and in May 1965, during a discussion with another chemist, it dawned on him that the only feasible explanation was that the molecule contained the  $N_2$  unit bound to the metal in a manner analogous to the carbon monoxide–metal bond. Excitedly, he told his very skeptical supervisor, Bert Allen. After several months, Allen

finally agreed to submit the findings to a journal for publication. The manuscript was rejected—a common occurrence when a discovery contradicts accepted thought. After Allen and Senoff rebutted the criticisms, the journal sent the revised manuscript to 16 other chemists for comment and approval before publishing it. Finally, the article appeared in print, and the world of inorganic chemistry was changed yet again.

Since then, transition metal compounds containing the  $N_2$  unit have become quite well known, and some can be made by simply bubbling dinitrogen gas through the solution of a metal compound. (As a consequence, research chemists no longer use dinitrogen as an inert atmosphere for all their reactions.) Some of the compounds are of interest because they are analogs of compounds soil bacteria produce when they convert dinitrogen to ammonia. None of the compounds, however, has become of great practical significance, although they serve as a reminder to inorganic chemists to never say, “Impossible!”

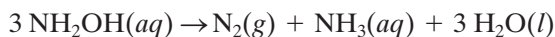
so differently under acidic and basic conditions, we can conclude that the relative stability of an oxidation state is very dependent on pH.

Let us look at some specific features of the chemistry of nitrogen.

1. Molecular dinitrogen is found at a deep minimum on the Frost diagram. Hence, it is a thermodynamically very stable species. In acidic solution, ammonium ion,  $NH_4^+$ , is slightly lower; thus, we might expect that a strong reducing agent would cause dinitrogen to be reduced to the ammonium ion. However, the diagram does not reveal anything about the kinetics of the process, and it is, in fact, kinetically very slow.
2. Species that have a high free energy to the left of  $N_2$  are strongly oxidizing. Thus, nitric acid,  $HNO_3$ , is a very strong oxidant, although the nitrate ion,  $NO_3^-$ , the conjugate base of nitric acid, is not significantly oxidizing.
3. Species that have a high free energy to the right of  $N_2$  tend to be strong reducing agents. Thus, in basic solution, hydroxylamine,  $NH_2OH$ , hydrazine,  $N_2H_4$ , and ammonia,  $NH_3$ , tend to be reducing in their chemical behavior.
4. Both hydroxylamine and its conjugate acid, the hydroxylammonium ion,  $NH_3OH^+$ , should readily disproportionate because they are at convex locations on the diagram. Experimentally, we find that they do disproportionate, but the products are not always those resulting in the greatest decrease in free



energy; instead kinetic factors select the products. Hydroxylamine disproportionates to give dinitrogen and ammonia, whereas the hydroxylammonium ion produces dinitrogen oxide and the ammonium ion:

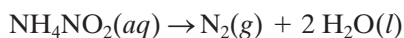


## 15.4 Nitrogen

The element nitrogen has only one allotrope: the colorless, odorless gas dinitrogen. Dinitrogen makes up 78 percent by moles of the dry atmosphere at the Earth's surface. Apart from its role in the nitrogen cycle, which we will discuss later, it is very important as an inert diluent for the highly reactive gas in our atmosphere, dioxygen. Without the dinitrogen, every spark in our atmosphere would cause a massive fire. The tragic deaths in 1967 of the astronauts Virgil ("Gus") I. Grissom, Edward H. White, and Roger B. Chaffee in an Apollo space capsule were a result of the use of a pure oxygen cabin atmosphere (since discontinued). An accidental electrical spark caused a raging inferno within seconds, killing all of the occupants.

Dinitrogen is not very soluble in water, although like most gases, its solubility increases rapidly with increasing pressure. This is a major problem for deep-sea divers. As they dive, additional dinitrogen dissolves in their bloodstream; as they return to the surface, the decreasing pressure brings the dinitrogen out of solution, and it forms tiny bubbles, particularly around the joints. Prevention of this painful and sometimes fatal problem—called "the bends"—required divers to return to the surface very slowly. In emergency situations, they were placed in decompression chambers, where the pressure was reapplied and then reduced carefully over hours or days. To avoid this hazard, oxygen-helium gas mixtures are now used for deep diving because helium has a much lower blood solubility than does dinitrogen.

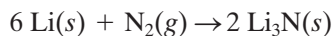
Industrially, dinitrogen is prepared by liquefying air and then slowly warming the liquid mixture. The dinitrogen boils at  $-196^\circ\text{C}$ , leaving behind the dioxygen, b.p.  $-183^\circ\text{C}$ . On a smaller scale, dinitrogen can be separated from the other atmospheric gases by using a zeolite, as discussed in Chapter 14, Section 14.16. In the laboratory, dinitrogen can be prepared by gently warming a solution of ammonium nitrite:



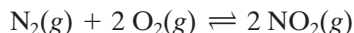
Dinitrogen does not burn or support combustion. It is extremely unreactive toward most elements and compounds. Hence, it is commonly used to provide an inert atmosphere when highly reactive compounds are being handled or stored. About 60 million tonnes of dinitrogen are used every year worldwide. A high proportion is used in steel production as an inert atmosphere and in oil refineries to purge the flammable hydrocarbons from the pipes and reactor vessels when they need maintenance. Liquid nitrogen is used as a safe refrigerant

where very rapid cooling is required. Finally, a significant proportion is employed in the manufacture of ammonia and other nitrogen-containing compounds.

There are few chemical reactions involving dinitrogen as a reactant. One example is the combination of dinitrogen on heating with the Group 2 metals and lithium to form ionic nitrides, containing the  $\text{N}^{3-}$  ion. The reaction with lithium is:

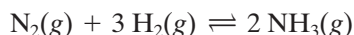


If a mixture of dinitrogen and dioxygen is sparked, nitrogen dioxide is formed:



On a large scale, this reaction takes place in lightning flashes, where it contributes to the biologically available nitrogen in the biosphere. However, it also occurs under the conditions of high pressure and sparking found in modern high-compression gasoline engines. Local concentrations of nitrogen dioxide may be so high that they become a significant component of urban pollution. The equilibrium position for this reaction actually lies far to the left, or, to express this idea another way, nitrogen dioxide has a positive free energy of formation. Its continued existence depends on its extremely slow decomposition rate. Thus, it is kinetically inert. It is one of the roles of the automobile catalytic converter to accelerate the rate of decomposition back to dinitrogen and dioxygen.

Finally, dinitrogen participates in an equilibrium reaction with hydrogen, one that under normal conditions does not occur to any significant extent because of the high activation energy of the reaction (in particular, a single-step reaction cannot occur because it would require a simultaneous four-molecule collision):



We will discuss this reaction in much more detail in Section 15.5.

## 15.5 Nitrogen Hydrides

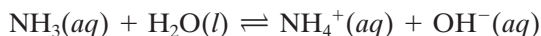
By far the most important hydride of nitrogen is ammonia, but in addition, there are two others, hydrazine,  $\text{N}_2\text{H}_4$ , and hydrogen azide,  $\text{HN}_3$ .

### Ammonia

Ammonia is a colorless, poisonous gas with a very strong characteristic smell. It is the only common gas that is basic. Ammonia condenses to a liquid at  $-35^\circ\text{C}$ . This boiling point is much higher than that of phosphine,  $\text{PH}_3$  ( $-134^\circ\text{C}$ ) because ammonia molecules form strong hydrogen bonds with their neighbors. Liquid ammonia is a good polar solvent, as we discussed in Chapter 7, Section 7.1.

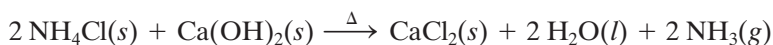
Ammonia dissolves readily in water: at room temperature, over 50 g of ammonia will dissolve in 100 g of water, giving a solution of density  $0.880 \text{ g}\cdot\text{mL}^{-1}$  (known as *880 ammonia*). The solution is most accurately called “aqueous

ammonia” but is often misleadingly called “ammonium hydroxide.” A small proportion does, in fact, react with the water to give ammonium and hydroxide ions:



This reaction is analogous to the reaction of carbon dioxide with water, and the equilibrium lies to the left. And, like the carbon dioxide and water reaction, evaporating the solution shifts the equilibrium farther to the left. Thus, there is no such thing as pure “ammonium hydroxide.”

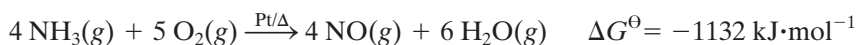
Ammonia is prepared in the laboratory by mixing an ammonium salt and a hydroxide; for example, ammonium chloride and calcium hydroxide:



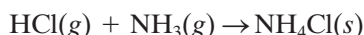
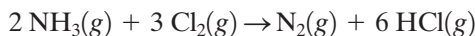
It is a reactive gas, burning in air when ignited to give water and nitrogen gas:



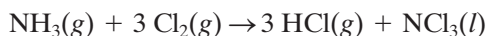
There is an alternative decomposition route that is thermodynamically less favored but in the presence of a platinum catalyst is kinetically preferred; that is, the (catalyzed) activation energy for this alternative route becomes lower than that for the combustion to nitrogen gas:



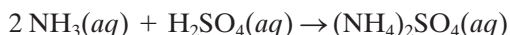
Ammonia acts as a reducing agent in its reactions with chlorine. There are two pathways. With excess ammonia, nitrogen gas is formed, and the excess ammonia reacts with the hydrogen chloride gas produced to give clouds of white, solid ammonium chloride:



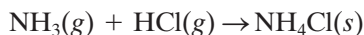
With excess chlorine, a very different reaction occurs. In this case, the product is nitrogen trichloride, a yellow, explosive, oily liquid:



As a base, ammonia reacts with acids in solution to give its conjugate acid, the ammonium ion. For example, when ammonia is mixed with sulfuric acid, ammonium sulfate is formed:



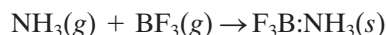
Ammonia reacts in the gas phase with hydrogen chloride to give a white smoke of solid ammonium chloride:



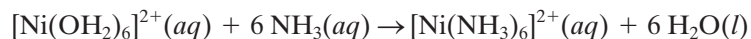
The formation of a white film over glass objects in a chemistry laboratory is usually caused by the reaction of ammonia escaping from reagent bottles with acid vapors, particularly hydrogen chloride.

With its lone electron pair, ammonia is also a strong Lewis base. One of the “classic” Lewis acid-base reactions involves that between the gaseous

electron-deficient boron trifluoride molecule and ammonia to give the white solid compound in which the lone pair on the ammonia is shared with the boron:



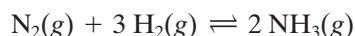
Ammonia also acts like a Lewis base when it coordinates to metal ions. For example, it will displace the six water molecules that surround a nickel(II) ion because it is a stronger Lewis base than water:



### The Industrial Synthesis of Ammonia

It has been known for hundreds of years that nitrogen compounds are essential for plant growth. Manure was once the main source of this ingredient for soil enrichment. But the rapidly growing population in Europe during the nineteenth century necessitated a corresponding increase in food production. The solution, at the time, was found in the sodium nitrate (Chile saltpeter) deposits in Chile. This compound was mined in vast quantities and shipped around Cape Horn to Europe. The use of sodium nitrate fertilizer prevented famine in Europe and provided Chile with its main income, turning it into an extremely prosperous nation. However, it was clear that the sodium nitrate deposits would one day be exhausted. Thus, chemists rushed to find some method of forming nitrogen compounds from the unlimited resource of unreactive nitrogen gas.

It was Fritz Haber, a German chemist, who showed in 1908 that at about 1000°C, traces of ammonia are formed when nitrogen gas and hydrogen gas are mixed:



In fact, the conversion of dinitrogen and dihydrogen into ammonia is exothermic and results in a decrease in gas volume and a resulting decrease in entropy. To “force” the reaction to the right, the Le Châtelier principle suggests that the maximum yield of ammonia would be at low temperature and high pressure. However, the lower the temperature, the slower the rate at which equilibrium is reached. A catalyst might help, but even then there are limits to the most practical minimum temperature. Furthermore, there are limits to how high the pressure can go, simply in terms of the cost of thick-walled containers and pumping systems.

Haber found that adequate yields could be obtained in reasonable time by using a pressure of 20 MPa (200 atm) and a temperature of 500°C. However, it took five years for a chemical engineer, Carl Bosch, to actually design an industrial-size plant for the chemical company BASF that could work with gases at this pressure and temperature. Unfortunately, completion of the plant coincided with the start of World War I. With Germany blockaded by the Allies, supplies of Chile saltpeter were no longer available; nevertheless, the ammonia produced was used for the synthesis of explosives rather than for

## Haber and Scientific Morality

It has been said that many scientists are amoral because they fail to consider the applications to which their work can be put. The life of Fritz Haber presents a real dilemma: should we regard him as a hero or as a villain? As discussed earlier, Haber devised the process of ammonia synthesis, which he intended to be used to help feed the world, yet the process was turned into a source of materials to kill millions. He cannot easily be faulted for this, but his other interest is more controversial. Haber argued that it was better to incapacitate the enemy during warfare than to kill them. Thus, he worked enthusiastically on poison gas research during World War I. His first wife, Clara Immerwahr Haber, a talented chemist, pleaded with him to desist, and when he did not, she committed suicide.

In 1918, Haber was awarded the Nobel Prize for his work on ammonia synthesis, but many chemists opposed the award on the basis of his poison gas research. After that war, Haber was a key figure in the rebuilding of

Germany's chemical research community. Then in 1933, the National Socialist (Nazi) government took power, and Haber, of Jewish origin himself, was told to fire all of the Jewish workers at his institute. He refused and resigned instead, bravely writing: "For more than 40 years I have selected my collaborators on the basis of their intelligence and their character and not on the basis of their grandmothers, and I am not willing to change this method which I have found so good."

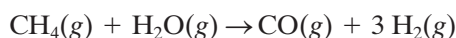
This action infuriated the Nazi leaders, but in view of Haber's international reputation, they did not act against him at that time. In 1934, the year after his death, the German Chemical Society held a memorial service for him. The German government was so angered by this tribute to someone who had stood up against their regime that they threatened arrest of all those chemists who attended. But their threat was hollow. The turnout of so many famous chemists for the event caused the Nazi authorities to back down.

crop production. Without the *Haber-Bosch process*, the German and Austro-Hungarian armies might well have been forced to capitulate earlier than 1918, simply because of a lack of explosives.

## The Modern Haber-Bosch Process

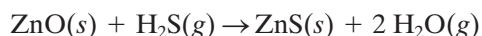
To prepare ammonia in the laboratory, we can simply take cylinders of nitrogen gas and hydrogen gas and pass them into a reaction vessel at appropriate conditions of temperature, pressure, and catalyst. But neither dinitrogen nor dihydrogen is a naturally occurring pure reagent. Thus, for the industrial chemist, obtaining the reagents inexpensively, on a large scale, with no useless by-products, is a challenge.

The first step is to obtain the dihydrogen gas. This is accomplished by the *steam re-forming process*, where a hydrocarbon, such as methane, is mixed with steam at high temperatures (about 750°C) and at high pressures (about 4 MPa). This process is endothermic, so high temperatures would favor product formation on thermodynamic grounds, but high pressure is used for kinetic reasons to increase the collision frequency (reaction rate). A catalyst, usually nickel, is present for the same reason:

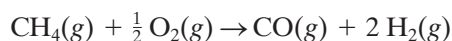


Catalysts are easily inactivated (*poisoned*) by impurities, and so it is crucial to remove impurities from the reactants (*feedstock*). Sulfur compounds

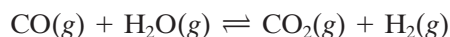
are particularly effective at reacting with the catalyst surface and deactivating it by forming a layer of metal sulfide. Thus, before the methane is used, it is pretreated to convert contaminating sulfur compounds to hydrogen sulfide. The hydrogen sulfide is then removed by passing the impure methane over zinc oxide:



Next, air is added to the mixture of carbon monoxide and dihydrogen, which still contains some methane—deliberately. The methane burns to give carbon monoxide, but, with control of how much methane is presented, the amount of dinitrogen left in the deoxygenated area should be that required to achieve the 1:3 stoichiometry of the Haber-Bosch reaction:



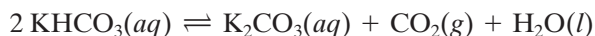
There is no simple way of removing carbon monoxide from the mixture of gases. For this reason, and to produce an additional quantity of hydrogen, the third step involves the oxidation of the carbon monoxide to carbon dioxide by using steam. This *water gas shift process* is performed at fairly low temperatures (350°C) because it is exothermic. Even though a catalyst of iron and chromium oxides is used, the temperature cannot be any lower without reducing the rate of reaction to an unacceptable level:



The carbon dioxide can be removed by a number of different methods. Carbon dioxide has a high solubility in water and in many other solvents. Alternatively, it can be removed by a chemical process such as the reversible reaction with potassium carbonate:

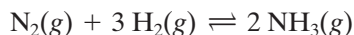


The potassium hydrogen carbonate solution is pumped into tanks where it is heated to generate pure carbon dioxide gas and potassium carbonate solution:

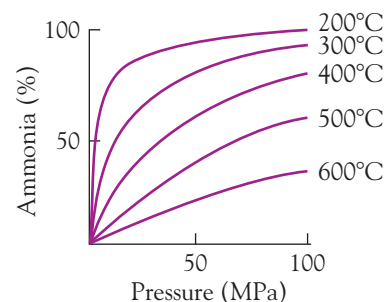


The carbon dioxide is liquefied under pressure and sold, and the potassium carbonate is returned to the ammonia processing plant for reuse.

Now that a mixture of the pure reagents of dinitrogen and dihydrogen gas has been obtained, the conditions are appropriate for the simple reaction that gives ammonia:



The practical thermodynamic range of conditions is shown in Figure 15.4. As mentioned earlier, to “force” the reaction to the right, high pressures are used. But the higher the pressure, the thicker the reaction vessels and piping required to prevent an explosion—and the thicker the containers, the higher the cost of construction.

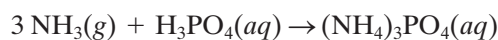
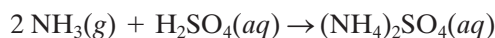


**FIGURE 15.4** Percentage yields of ammonia as a function of pressure, at various temperatures.

Today's ammonia plants utilize pressures between 10 and 100 MPa (100 and 1000 atm). There is a trade-off between kinetics and equilibrium: the lower the temperature, the higher the yield but the slower the rate. With current high-performance catalysts, the optimum conditions are 400°C to 500°C. The catalyst is the heart of every ammonia plant. The most common catalyst is specially prepared high-surface-area iron containing traces of potassium, aluminum, calcium, magnesium, silicon, and oxygen. About 100 tonnes of catalyst are used in a typical reactor vessel, and, provided all potential "poisons" are removed from the incoming gases, the catalyst will have a working life of about 10 years. The mechanism of the reaction is known to involve the dissociation of dinitrogen to atomic nitrogen on the crystal face of the iron catalyst, followed by reaction with atomic hydrogen, similarly bonded to the iron surface.

After leaving the reactor vessel, the ammonia is condensed. The remaining dinitrogen and dihydrogen are then recycled back through the plant to be mixed with the fresh incoming gas. A typical ammonia plant produces about 1000 tonnes per day. The most crucial concern is to minimize energy consumption. A traditional Haber-Bosch plant consumed about 85 GJ·tonne<sup>-1</sup> of ammonia produced, whereas a modern plant, built to facilitate energy recycling, uses only about 30 GJ·tonne<sup>-1</sup>.

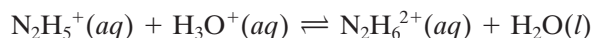
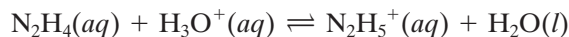
Even today, the most important use of ammonia itself is in the fertilizer industry. The ammonia is often applied to fields as ammonia gas. Ammonium sulfate and ammonium phosphate also are common solid fertilizers. These are simply prepared by passing the ammonia into sulfuric acid and phosphoric acid, respectively:



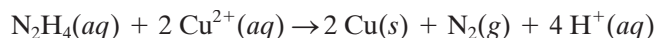
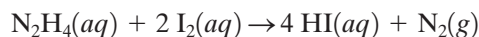
Ammonia is also used in a number of industrial syntheses, particularly that of nitric acid, as we will discuss in Section 15.11.

## Hydrazine

Hydrazine is a fuming, colorless liquid. It is a weak base, forming two series of salts, in which it is either monoprotonated or diprotonated:

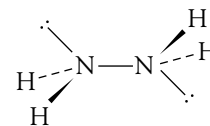


However, hydrazine is a strong reducing agent, reducing iodine to hydrogen iodide and copper(II) ion to copper metal:



Most of the 20 000 tonnes produced worldwide annually are used as the reducing component of a rocket fuel, usually in the form of asymmetrical dimethylhydrazine, (CH<sub>3</sub>)<sub>2</sub>NNH<sub>2</sub>. Another derivative, dinitrophenylhydrazine,

$\text{H}_2\text{NNHC}_6\text{H}_5(\text{NO}_2)_2$ , is used in organic chemistry to identify carbon compounds containing the  $\text{C}=\text{O}$  grouping. The structure of hydrazine is like that of ethane, except that two ethane hydrogens are replaced by lone pairs of electrons, with one pair on each nitrogen atom (Figure 15.5).



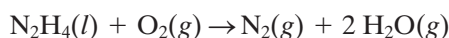
**FIGURE 15.5** The shape of the hydrazine molecule.

### WORKED EXAMPLE 15.1

Dimethylhydrazine,  $\text{N}_2\text{H}_2(\text{CH}_3)_2$  [ $\Delta_f H^\ominus = +42.0 \text{ kJ}\cdot\text{mol}^{-1}$ ], is used as a rocket fuel. By writing the corresponding combustion reactions and using additional thermodynamic values from Appendix 1, predict whether dimethylhydrazine is a more efficient fuel than hydrazine in terms of  $\text{kJ}\cdot\text{g}^{-1}$  fuel used.

#### Answer

The combustion reactions are:



The more efficient fuel will release the most energy per gram, so we need to calculate the enthalpy of combustion for each  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{H}_2(\text{CH}_3)_2$  and then convert to a per mass basis. This can be calculated from the difference between the enthalpies of formation of the products and reactants using the following data:

$\Delta_f H^\ominus/\text{kJ}\cdot\text{mol}^{-1}$	
$\text{N}_2\text{H}_4(l)$	+51.0
$\text{N}_2\text{H}_2(\text{CH}_3)_2(l)$	+42.0
$\text{CO}_2(g)$	-393.5
$\text{H}_2\text{O}(g)$	-241.8

For  $\text{N}_2\text{H}_4$ ,  $\Delta_{\text{comb}} H^\ominus = [2(-241.8) - (+51.0)] \text{ kJ}\cdot\text{mol}^{-1} = -534.6 \text{ kJ}\cdot\text{mol}^{-1}$

For  $\text{N}_2\text{H}_2(\text{CH}_3)_2$ ,  $\Delta_{\text{comb}} H^\ominus = \{[4(-241.8) + 2(-393.5)] - (+42.0)\} \text{ kJ}\cdot\text{mol}^{-1} = -1796.2 \text{ kJ}\cdot\text{mol}^{-1}$

Mass is important for rocket fuels so if we convert to  $\text{kJ}\cdot\text{g}^{-1}$  by dividing by the molar mass:

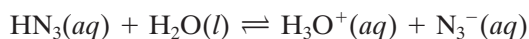
For  $\text{N}_2\text{H}_4$ ,  $\Delta_{\text{comb}} H^\ominus = -16.69 \text{ kJ}\cdot\text{g}^{-1}$

For  $\text{N}_2\text{H}_2(\text{CH}_3)_2$ ,  $\Delta_{\text{comb}} H^\ominus = -29.90 \text{ kJ}\cdot\text{g}^{-1}$ .

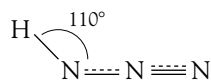
Therefore,  $\text{N}_2\text{H}_2(\text{CH}_3)_2$  is the preferable fuel. ■

### Hydrogen Azide

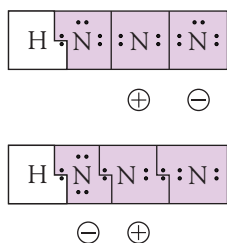
Hydrogen azide, a colorless liquid, is quite different from the other nitrogen hydrides. It is acidic, with a  $\text{p}K_a$  similar to that of acetic acid:



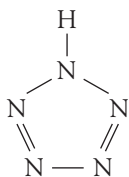




**FIGURE 15.6** The shape of the hydrogen azide molecule. The bond orders of the two nitrogen-nitrogen bonds are about 1.5 and 2.5.

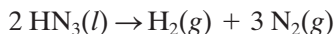


**FIGURE 15.7** The bonding in a hydrogen azide can be pictured as a resonance mixture of these two structures.



**FIGURE 15.8** The theoretical pentazole molecule.

The compound has a repulsive, irritating odor and is extremely poisonous. It is highly explosive, producing hydrogen gas and nitrogen gas:



The three nitrogen atoms in a hydrogen azide molecule are colinear, with the hydrogen at a  $110^\circ$  angle (Figure 15.6). The nitrogen-nitrogen bond lengths in hydrogen azide are 124 pm and 113 pm (the end N—N bond is shorter). A typical N=N bond is 120 pm, and the N≡N bond in the dinitrogen molecule is 110 pm. Thus, the bond orders in hydrogen azide must be approximately 1.5 and 2.5, respectively. The bonding can be pictured simply as an equal resonance mixture of the two electron-dot structures shown in Figure 15.7, one of which contains two N=N bonds and the other, a N—N bond and a N≡N bond.

## Pentazole

Does pentazole exist? If so, for how long? In this text, we have focused on chemical compounds which are known. Yet much of the excitement of inorganic chemistry is in the attempted synthesis of compounds which theoretically should exist, if only fleetingly. One such compound is the cyclic nitrogen-hydrogen compound,  $\text{N}_5\text{H}$  (Figure 15.8), and its corresponding pentazolide anion,  $\text{N}_5^-$ . Attempts have been made to synthesize this compound, but so far, there has been no conclusive evidence of its existence. Is it just a question of finding the synthetic route? Or are there errors in the theoretical calculations which suggest it could exist? Someday we will know who is correct.

## 15.6 Nitrogen Ions

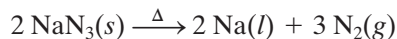
Besides the neutral nitrogen molecule, there is an anionic species, the azide ion,  $\text{N}_3^-$ , and a cationic species, the pentanitrogen ion,  $\text{N}_5^+$ .

### The Azide Anion

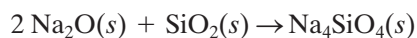
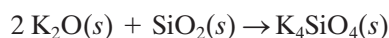
The azide ion,  $\text{N}_3^-$ , is isoelectronic with carbon dioxide, and it is presumed to have an identical electronic structure. The nitrogen-nitrogen bonds are of equal length (116 pm), an observation that reinforces the concept that the presence of the hydrogen atom in hydrogen azide causes the neighboring N=N bond to weaken (and lengthen to 124 pm) and the more distant one to strengthen (and shorten to 113 pm). In its chemistry, the azide ion behaves as a pseudo-halide ion (see Chapter 17, Section 17.12). For example, mixing a solution of azide ion with silver ion gives a precipitate of silver azide,  $\text{AgN}_3$ , analogous to silver chloride,  $\text{AgCl}$ . Azide ion also forms parallel complex ions to those of chloride ion, such as  $[\text{Sn}(\text{N}_3)_6]^{2-}$ , the analog of  $[\text{SnCl}_6]^{2-}$ .

It is interesting how so much of chemistry can be used either destructively or constructively. The azide ion is now used to save lives—by the automobile air bag. It is crucial that an air bag inflate extremely rapidly, before the victim is thrown forward after impact. The only way to produce such a fast response is through a controlled chemical explosion that produces a large volume of gas.

For this purpose, sodium azide is preferred: it is about 65 percent nitrogen by mass, can be routinely manufactured to a high purity (at least 99.5 percent), and decomposes cleanly to sodium metal and dinitrogen at 350°C:



In an air bag, this reaction takes place in about 40 ms. Obviously, we would not want the occupants to be saved from a crash and then have to face molten sodium metal. There are a variety of reactions that can be used to immobilize the liquid product. One of these involves the addition of potassium nitrate and silicon dioxide to the mixture. The sodium metal is oxidized by the potassium nitrate to sodium oxide, producing more nitrogen gas. The alkali metal oxides then react with the silicon dioxide to give inert glassy metal silicates:

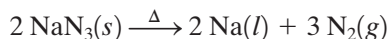


Lead(II) azide is important as a detonator: it is a fairly safe compound unless it is impacted, in which case it explosively decomposes. The shock wave produced is usually sufficient to detonate a more stable explosive such as dynamite:



### WORKED EXAMPLE 15.2

What volume of nitrogen would be produced by detonation of 1 g of sodium azide.



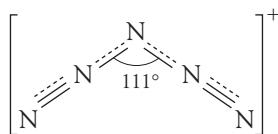
#### Answer

According to the equation above, 3 moles of  $\text{N}_2$  are produced for every 2 moles of  $\text{NaN}_3$ . 1 g of  $\text{NaN}_3$  is equivalent to 0.0154 mole. So there are  $(3/2 \times 0.0154 \text{ mol}) = 0.0231 \text{ mole } \text{N}_2$ . The volume of 1 mole of a gas at 298 K and 100 kPa is 24.8 L, so the reaction would produce 0.572 L of  $\text{N}_2$ . ■

### The Pentazenium Cation

Although most simple inorganic compounds have been known for over 100 years, new compounds are still being discovered. One of the most interesting is the pentazenium (also called *pentanitrogen*) cation,  $\text{N}_5^+$ , the first known stable cation of the element and only the third all-nitrogen species known. A salt of this cation was first synthesized in 1999 as part of a research program into high-energy materials at the Edwards Air Force Base in California. To stabilize the large cation, the large hexafluoroarsenate(V) anion was used. The actual synthesis reaction was:





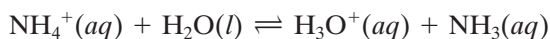
**FIGURE 15.9** The shape of the pentazenium ion.

The pentazenium ion is an extremely strong oxidizing agent and will explosively oxidize water to oxygen gas. The structure of the ion is shown in Figure 15.9. The bonds to the terminal nitrogen atoms are strong, indicating that they are between double and triple bonds in strength, while the central N—N bonds are closer to single-bond strengths.

## 15.7 The Ammonium Ion

The colorless ammonium ion is the most common nonmetallic cation used in the chemistry laboratory. As we discussed in Chapter 11, Section 11.14, this tetrahedral polyatomic ion can be thought of as a pseudo-alkali-metal ion, and is close in size to the potassium ion. Having covered the similarities with alkali metals in the forementioned section, here we will focus on the unique features of the ion. In particular, unlike the alkali metal ions, the ammonium ion does not always remain intact: it can be hydrolyzed, dissociated, or oxidized.

The ammonium ion is hydrolyzed in water to give its conjugate base, ammonia:



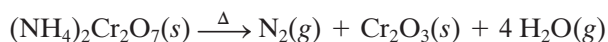
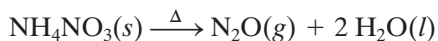
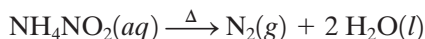
As a result, solutions of ammonium salts of strong acids, such as ammonium chloride, are slightly acidic.

Ammonium salts can volatilize (vaporize) by dissociation. The classic example of this is ammonium chloride:



If a sample of ammonium chloride is left open to the atmosphere, it will “disappear.” It is this same decomposition reaction that is used in “smelling salts.” The pungent ammonia odor, which masks the sharper smell of the hydrogen chloride, has a considerable effect on a semicomatose individual (although it should be noted that the use of smelling salts except by medical personnel is now deemed to be unwise and potentially dangerous).

Finally, the ammonium ion can be oxidized by the anion in the ammonium salt. These are reactions that occur when an ammonium salt is heated, and each one is unique. The three most common examples are the thermal decomposition of ammonium nitrite, ammonium nitrate, and ammonium dichromate:



The reaction of ammonium dichromate is often referred to as the “volcano” reaction. A source of heat, such as a lighted match, will cause the orange crystals to decompose, producing sparks and a large volume of dark green chromium(III) oxide. Although this is a very spectacular decomposition reaction, it needs to be performed in a fume hood because a little ammonium dichromate dust usually is dispersed by the reaction, and this highly carcinogenic material can be absorbed through the lungs.

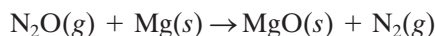
## 15.8 Nitrogen Oxides

Nitrogen forms a plethora of common oxides: dinitrogen oxide,  $\text{N}_2\text{O}$ ; nitrogen monoxide,  $\text{NO}$ ; dinitrogen trioxide,  $\text{N}_2\text{O}_3$ ; nitrogen dioxide,  $\text{NO}_2$ ; dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ ; and dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ . In addition, there is nitrogen trioxide,  $\text{NO}_3$ , commonly called the *nitrate radical*, which is present in tiny but essential proportions in the atmosphere. Each of the oxides is actually thermodynamically unstable with respect to decomposition to its elements, but all are kinetically stabilized.

### Dinitrogen Oxide

The sweet-smelling, gaseous dinitrogen oxide is also known as *nitrous oxide* or, more commonly, *laughing gas*. This name results from the intoxicating effect of low concentrations. It is sometimes used as an anesthetic, although the high concentrations needed to cause unconsciousness make it unsuitable for more than brief operations such as tooth extraction. Anesthetists have been known to become addicted to the narcotic gas. Because the gas is very soluble in fats, tasteless, and nontoxic, its major use is as a propellant in pressurized cans of whipped cream.

Dinitrogen oxide is a fairly unreactive, neutral gas, although it is the only common gas other than oxygen to support combustion. For example, magnesium burns in dinitrogen oxide to give magnesium oxide and nitrogen gas:



The standard method of preparation of dinitrogen oxide involves the thermal decomposition of ammonium nitrate. This reaction can be accomplished by heating the molten solid to about  $280^\circ\text{C}$ . An explosion can ensue from strong heating, however, so a safer route is to gently warm an ammonium nitrate solution that has been acidified with hydrochloric acid:



Dinitrogen oxide is isoelectronic with carbon dioxide and the azide ion. However, in dinitrogen oxide, the atoms are arranged asymmetrically, with a  $\text{N}-\text{N}$  bond length of 113 pm and a  $\text{N}-\text{O}$  bond length of 119 pm. The difference can be interpreted in terms of the central atom usually possessing the lower electronegativity. These values indicate a nitrogen-nitrogen bond order of close to 2.5 and a nitrogen-oxygen bond order close to 1.5 (Figure 15.10).

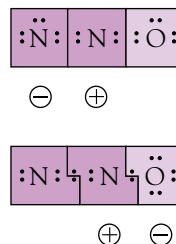
Like hydrogen azide, dinitrogen oxide can be pictured simply as a molecule that resonates between two electron-dot structures, one of which contains a  $\text{N}=\text{O}$  bond and a  $\text{N}=\text{N}$  bond and the other, a  $\text{N}-\text{O}$  bond and a  $\text{N}\equiv\text{N}$  bond (Figure 15.11).

### Nitrogen Monoxide

One of the most curious simple molecules is nitrogen monoxide, which is also called *nitric oxide*. It is a colorless, neutral, paramagnetic gas. The easiest

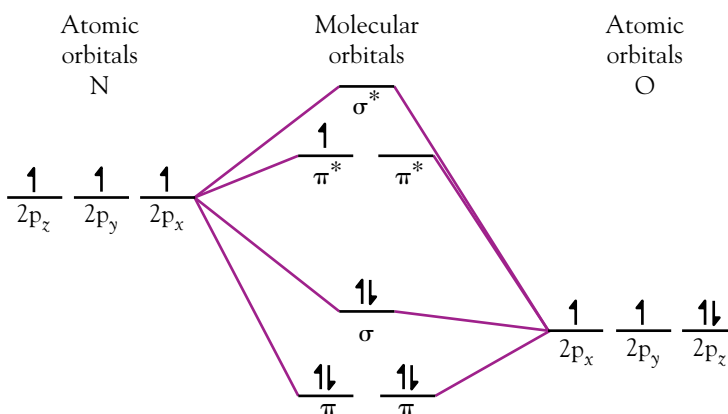


**FIGURE 15.10** The dinitrogen oxide molecule. The  $\text{N}-\text{N}$  bond order is about 2.5, and the  $\text{N}-\text{O}$  bond order is about 1.5.

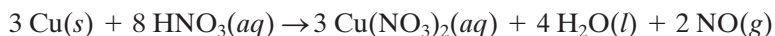


**FIGURE 15.11** The bonding in dinitrogen oxide can be pictured as a resonance mixture of these two structures.

**FIGURE 15.12** Molecular-orbital-energy-level diagram for the 2p atomic orbitals of the nitrogen monoxide molecule.



method for preparing the gas in the laboratory involves the reaction between copper and 50 percent nitric acid:



However, the product is always contaminated by nitrogen dioxide. This contaminant can be removed by bubbling the gas through water because the nitrogen dioxide reacts rapidly with water.

Its molecular orbital diagram resembles that of carbon monoxide but with one additional electron that occupies an antibonding orbital (Figure 15.12). Hence, the predicted net bond order is 2.5.

Chemists expect molecules containing unpaired electrons to be very reactive. Yet nitrogen monoxide in a sealed container is quite stable. Only when it is cooled to form the colorless liquid or solid does it show a tendency to form a dimer,  $\text{N}_2\text{O}_2$ , in which the two nitrogen atoms are joined by a single bond.

Consistent with the molecular orbital representation, nitrogen monoxide readily loses its electron from the antibonding orbital to form the nitrosyl ion,  $\text{NO}^+$ , which is diamagnetic and has a shorter N—O bond length (106 pm) than that of the parent molecule (115 pm). This triple-bonded ion is isoelectronic with carbon monoxide, and it forms many analogous metal complexes.

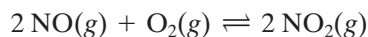
### WORKED EXAMPLE 15.3

Use a molecular orbital approach to demonstrate that the bond length in  $\text{NO}^+$  is shorter than that in NO.

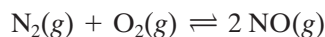
#### Answer

Using Figure 15.12, the filling of the molecular orbitals derived from the 2p atomic orbitals of NO is  $(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^1$ , giving a bond order  $(3 - \frac{1}{2}) = 2\frac{1}{2}$ . To form the cation, the single antibonding electron must be removed, giving the corresponding molecular orbital configuration for  $\text{NO}^+$  of  $(\pi_{2p})^4(\sigma_{2p})^2$ , giving a bond order  $(3 - 0) = 3$ . So we would expect  $\text{NO}^+$  to have a shorter bond than NO. ■

Nitrogen monoxide does show a high reactivity toward dioxygen, and once a sample of colorless nitrogen monoxide is opened to the air, brown clouds of nitrogen dioxide form:



The molecule is an atmospheric pollutant, commonly formed as a side reaction in high-compression internal combustion engines when dinitrogen and dioxygen are compressed and sparked:

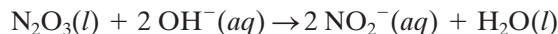
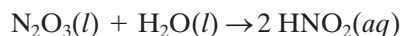


### Dinitrogen Trioxide

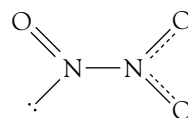
Dinitrogen trioxide, the least stable of the common oxides of nitrogen, is a dark blue liquid that decomposes above 230°C. It is prepared by cooling a stoichiometric mixture of nitrogen monoxide and nitrogen dioxide:



Dinitrogen trioxide is the first of the acidic oxides of nitrogen. In fact, it is the acid anhydride of nitrous acid. Thus, when dinitrogen trioxide is mixed with water, nitrous acid is formed, and when it is mixed with hydroxide ion, the nitrite ion is produced:



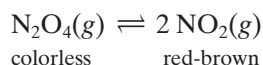
Although, simplistically, dinitrogen trioxide can be considered to contain two nitrogen atoms in the +3 oxidation state, the structure is asymmetrical, an arrangement that shows it to be a simple combination of the two molecules with unpaired electrons from which it is prepared (nitrogen monoxide and nitrogen dioxide). In fact, the nitrogen-nitrogen bond length in dinitrogen trioxide is abnormally long (186 pm) relative to the length of the single bond in hydrazine (145 pm). Bond length data indicate that the single oxygen is bonded to the nitrogen with a double bond, whereas the other two oxygen-nitrogen bonds each have a bond order of about  $1\frac{1}{2}$ . This value is the average of the single and double bond forms that can be constructed with electron-dot formulas (Figure 15.13).



**FIGURE 15.13** The shape of the dinitrogen trioxide molecule.

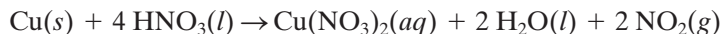
### Nitrogen Dioxide and Dinitrogen Tetroxide

These two toxic oxides coexist in a state of dynamic equilibrium. Low temperatures favor the formation of the colorless dinitrogen tetroxide, whereas high temperatures favor the formation of the dark red-brown nitrogen dioxide:

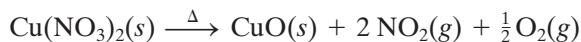


At the normal boiling point of  $-1^\circ\text{C}$ , the mixture contains 16 percent nitrogen dioxide, but the proportion of nitrogen dioxide rises to 99 percent at  $135^\circ\text{C}$ .

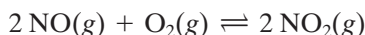
Nitrogen dioxide is prepared by reacting copper metal with concentrated nitric acid:



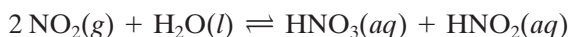
It is also formed by heating heavy metal nitrates, a reaction that produces a mixture of nitrogen dioxide and oxygen gases:



And, of course, it is formed when nitrogen monoxide reacts with dioxygen:

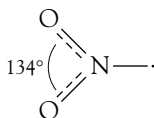


Nitrogen dioxide is an acid oxide, dissolving in water to give nitric acid and nitrous acid:

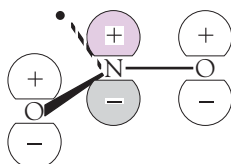


This potent mixture of corrosive, oxidizing acids is produced when nitrogen dioxide, formed from automobile pollution, reacts with rain. It is a major damaging component of urban precipitation.

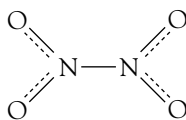
Nitrogen dioxide is a V-shaped molecule with an O—N—O angle of  $134^\circ$ , an angle slightly larger than the true trigonal planar angle of  $120^\circ$ . Because the third bonding site is occupied by a single electron rather than by a lone pair, it is not unreasonable for the bonding angle to be opened up (Figure 15.14). The oxygen-nitrogen bond length indicates a  $1\frac{1}{2}$  bond order, like that in the  $\text{NO}_2$  half of dinitrogen trioxide.



**FIGURE 15.14** The shape of the nitrogen dioxide molecule.



**FIGURE 15.15** Overlap of the p orbitals at right angles to the molecular plane of nitrogen dioxide.



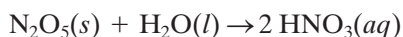
**FIGURE 15.16** The shape of the dinitrogen tetroxide molecule.

It is useful to compare the  $\pi$  bonding in nitrogen dioxide to that in carbon dioxide. The linear structure of carbon dioxide allows both sets of p orbitals that are at right angles to the bonding direction to overlap and participate in  $\pi$  bonding. In the bent nitrogen dioxide molecule, the p orbitals are still at right angles to the bonding direction, but in the plane of the molecule, they are skewed with respect to one another and cannot overlap to form a  $\pi$  system. As a result, the only  $\pi$  bond that can form is at right angles to the plane of the molecule (Figure 15.15). However, this single  $\pi$  bond is shared between two bonded pairs; hence, each pair has one-half a  $\pi$  bond.

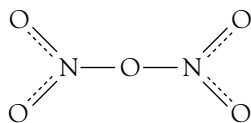
The O—N—O bond angle in the dinitrogen tetroxide molecule is almost identical to that in the nitrogen dioxide molecule (Figure 15.16). Although dinitrogen tetroxide has an abnormally long (and hence weak) nitrogen-nitrogen bond at 175 pm, it is not as weak as the N—N bond in dinitrogen trioxide. The N—N bond is formed by the combination of the weakly antibonding  $\sigma$  orbitals of the two  $\text{NO}_2$  units (overlap of the  $sp^2$  hybrid orbitals containing the “odd” electrons, in hybridization terminology). The resulting N—N bonding molecular orbital will have correspondingly weak bonding character. In fact, the N—N bond energy is only about  $60 \text{ kJ}\cdot\text{mol}^{-1}$ .

### Dinitrogen Pentoxide

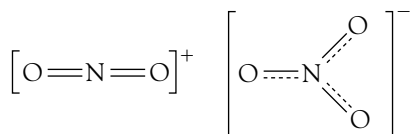
This colorless, solid, deliquescent oxide is the most strongly oxidizing of the nitrogen oxides. It is also strongly acidic, reacting with water to form nitric acid:







**FIGURE 15.17** The shape of the dinitrogen pentoxide molecule.



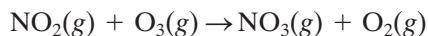
**FIGURE 15.18** The shape of the nitryl cation and nitrate anion present in solid-phase dinitrogen pentoxide.

In the liquid and gas phases, the molecule has a structure related to those of the other dinitrogen oxides,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_4$ , except that an oxygen atom links the two  $\text{NO}_2$  units (Figure 15.17). Once again, the two pairs of p electrons provide a half  $\pi$  bond to each oxygen-nitrogen pair. Of more interest, however, is the bonding in the solid phase. We have already seen that compounds of metals and nonmetals can be covalently bonded. Here we have a case of a compound of two nonmetals that contains ions! In fact, the crystal structure consists of alternating nitryl cations,  $\text{NO}_2^+$ , and nitrate anions,  $\text{NO}_3^-$  (Figure 15.18).

### Nitrogen Trioxide—The Nitrate Radical

Most people are aware that the Earth's atmosphere is predominantly dinitrogen and dioxygen and that trioxygen and carbon dioxide are also important atmospheric gases. What very few realize is the crucial role of certain trace gases, one of which is the nitrate radical,  $\text{NO}_3$ . This highly reactive free radical was first identified in the troposphere in 1980, where it is now known to play a major role in nighttime atmospheric chemistry.

The nitrate radical is formed by the reaction of nitrogen dioxide with ozone:



During the day, it is decomposed by light (photolyzed), the product depending on the wavelength of light:

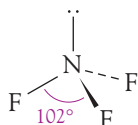


However, at night, the nitrate radical is the predominant oxidizing species on the Earth's surface, even though its concentration is usually in the 0.1 to 1 ppb range. This role is crucial in urban environments where there are high levels of hydrocarbons. Thus, it will remove a hydrogen atom from an alkane (represented as  $\text{RH}$  in the following equation) to give a reactive alkyl radical and hydrogen nitrate, the latter reacting with water to give nitric acid.



With alkenes, addition occurs to the double bond to form highly oxidizing and reactive organonitrogen and peroxy compounds, including the infamous peroxyacetyl nitrate,  $\text{CH}_3\text{COO}_2\text{NO}_2$ , known as PAN, a major eye irritant in the photochemical smog found in many city atmospheres.

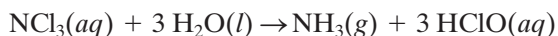




**FIGURE 15.19** The shape of the nitrogen trifluoride molecule.

## 15.9 Nitrogen Halides

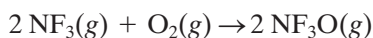
Nitrogen trichloride is a typical covalent chloride. It is a yellow, oily liquid that reacts with water to form ammonia and hypochlorous acid:



The compound is highly explosive when pure because it has a positive free energy of formation. However, nitrogen trichloride vapor is used quite extensively (and safely) to bleach flour.

By contrast, nitrogen trifluoride is a thermodynamically stable, colorless, odorless gas of low chemical reactivity. For example, it does not react with water at all. Such stability and low reactivity are quite common among covalent fluorides. Despite having a lone pair like ammonia (Figure 15.19), it is a weak Lewis base. The F—N—F bond angle in nitrogen trifluoride ( $102^\circ$ ) is significantly less than the tetrahedral angle. One explanation for the weak Lewis base behavior and the decrease in bond angle from  $109.5^\circ$  is that the nitrogen-fluorine bond has predominantly p orbital character (for which  $90^\circ$  would be the optimum angle), and the lone pair is in the nitrogen s orbital rather than in a more directional  $\text{sp}^3$  hybrid.

There is one unusual reaction in which nitrogen trifluoride does act as a Lewis base: it forms the stable compound nitrogen oxide trifluoride,  $\text{NF}_3\text{O}$ , when an electric discharge provides the energy for its reaction with oxygen gas at very low temperature:

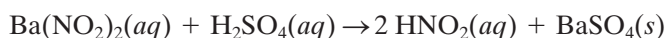


Nitrogen oxide trifluoride is often used as the classic example of a compound with a coordinate covalent bond between the nitrogen and oxygen atoms.

## 15.10 Nitrous Acid and Nitrites

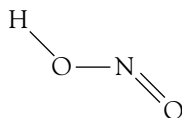
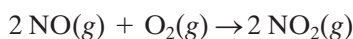
### Nitrous Acid

Nitrous acid is a weak acid that is unstable except in solution. It can be prepared by mixing a metal nitrite and a solution of a dilute acid at  $0^\circ\text{C}$  in a double-replacement reaction. Barium nitrite and sulfuric acid give a pure solution of nitrous acid because the barium sulfate that is formed has a very low solubility:



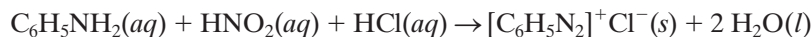
The shape of the nitrous acid molecule is shown in Figure 15.20.

Even at room temperature, disproportionation of aqueous nitrous acid occurs to give nitric acid and bubbles of nitrogen monoxide. The latter reacts rapidly with the oxygen gas in the air to produce brown fumes of nitrogen dioxide:



**FIGURE 15.20** The shape of the nitrous acid molecule.

Nitrous acid is used as a reagent in organic chemistry; for example, diazonium salts are produced when nitrous acid is mixed with an organic amine (in this case, aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ ):



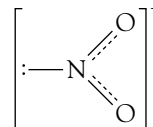
The diazonium salts are used, in turn, to synthesize a wide range of organic compounds.

### Nitrites

The nitrite ion is a weak oxidizing agent; hence, nitrites of metals in their lower oxidation states cannot be prepared. For example, nitrite will oxidize iron(II) ion to iron(III) ion and is simultaneously reduced to lower oxides of nitrogen.

The ion is V-shaped as a result of the lone pair on the central nitrogen (Figure 15.21), the bond angle being  $115^\circ$  compared with  $134^\circ$  for nitrogen dioxide (see Figure 15.14). The N—O bond length is 124 pm, longer than that in nitrogen dioxide (120 pm) but still much shorter than the N—O single bond (143 pm).

Sodium nitrite is a commonly used meat preservative, particularly in cured meats such as ham, hot dogs, sausages, and bacon. The nitrite ion inhibits the growth of bacteria, particularly *Clostridium botulinum*, an organism that produces the deadly botulism toxin. Sodium nitrite is also used to treat packages of red meat, such as beef. Blood exposed to the air rapidly produces a brown color, but shoppers much prefer their meat purchases to look bright red. Thus, the meat is treated with sodium nitrite; the nitrite ion is reduced to nitrogen monoxide, which then reacts with the hemoglobin to form a very stable bright red compound. It is true that the nitrite will prevent bacterial growth in this circumstance as well, but these days, the meat is kept at temperatures low enough to inhibit bacteria. To persuade shoppers to prefer brownish rather than red meat will require a lot of re-education. Now that all meats are treated with sodium nitrite, there is concern that the cooking process will cause the nitrite ion to react with amines in the meat to produce nitrosamines, compounds containing the —NNO functional group. These compounds are known to be carcinogenic. However, as long as preserved meats are consumed in moderation, it is generally believed that the cancer risk is minimal.

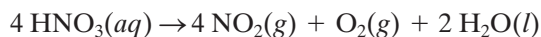


**FIGURE 15.21** The shape of the nitrite ion.

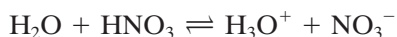
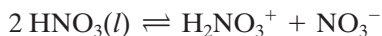
## 15.11 Nitric Acid and Nitrates

### Nitric Acid

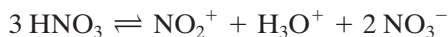
A colorless, oily liquid when pure, nitric acid is extremely hazardous. It is obviously dangerous as an acid, but as can be seen from the Frost diagram (see Figure 15.3), it is a very strong oxidizing agent, making it a potential danger in the presence of any oxidizable material. The acid, which melts at  $-42^\circ\text{C}$  and boils at  $83^\circ\text{C}$ , is usually slightly yellow as a result of a light-induced decomposition reaction:



When pure, liquid nitric acid is almost completely nonconducting. A small proportion ionizes as follows (all species exist in nitric acid solvent):



giving an overall reaction of

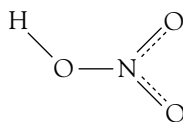


The nityl cation is important in the nitration of organic molecules; for example, in the conversion of benzene,  $\text{C}_6\text{H}_6$ , to nitrobenzene,  $\text{C}_6\text{H}_5\text{NO}_2$ , an important step in numerous organic industrial processes.



Concentrated nitric acid is actually a 70 percent solution in water (corresponding to a concentration of about  $16 \text{ mol}\cdot\text{L}^{-1}$ ), whereas “fuming nitric acid,” an extremely powerful oxidant, is a red solution of nitrogen dioxide in pure nitric acid. Even when dilute, it is such a strong oxidizing agent that the acid rarely evolves hydrogen when mixed with metals; instead, a mixture of nitrogen oxides is produced and the metal is oxidized to its cation.

The terminal O—N bonds are much shorter (121 pm) than the O—N bond attached to the hydrogen atom (141 pm). This bond length indicates multiple bonding between the nitrogen and the two terminal oxygen atoms. In addition to the electrons in the  $\sigma$  system, there are four electrons involved in the O—N—O  $\pi$  system, two in a bonding orbital and two in a nonbonding orbital, a system giving a bond order of 1.5 for each of those nitrogen-oxygen bonds (Figure 15.22).



**FIGURE 15.22** The shape of the nitric acid molecule.

Whereas nitrous acid is a weakish acid, nitric acid is a strong acid (Table 15.5). As discussed in Chapter 7, Section 7.3, an additional oxygen atom bonded to the central nitrogen atom withdraws more electron density from the O—H bond, hence weakening the O—H bond further and making ionization more favorable.

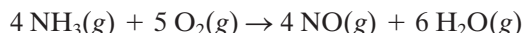
### The Industrial Synthesis of Nitric Acid

The three-step *Ostwald process* for nitric acid synthesis utilizes much of the ammonia produced by the Haber process. The Ostwald process is performed in three steps. First, a mixture of ammonia and dioxygen (or air) is passed through a platinum metal gauze. This is a very efficient, highly exothermic process that causes the gauze to glow red-hot. Contact time with the catalyst is limited to

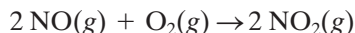
**TABLE 15.5** A comparison of the acid strengths of nitrous acid and nitric acid

	Very Acidic	Acidic	Basic	Very Basic
Nitrate	$\text{NO}_3^-(aq)$			
Nitrite	$\text{HNO}_2(aq)$	$\text{NO}_2^-(aq)$		

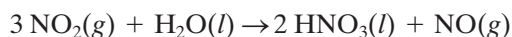
about 1 ms to minimize unwanted side reactions. The step is performed at low pressures to take advantage of the entropy effect; that is, the formation of 10 gas moles from 9 gas moles (an application of the Le Châtelier principle) to shift the equilibrium to the right:



Additional oxygen is added to oxidize the nitrogen monoxide to nitrogen dioxide. To improve the yield of this exothermic reaction, heat is removed from the gases, and the mixture is placed under pressure:

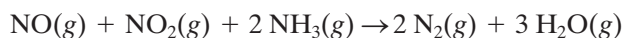


Finally, the nitrogen dioxide is mixed with water to give a solution of nitric acid:



This reaction also is exothermic. Again, cooling and high pressures are used to maximize yield. The nitrogen monoxide is returned to the second stage for re-oxidation.

Pollution used to be a major problem for nitric acid plants. The older plants were quite identifiable by the plume of yellow-brown gas—escaping nitrogen dioxide. State-of-the-art plants have little trouble in meeting the current emission standards of less than 200 ppm nitrogen oxides in their flue gases. Older plants now mix stoichiometric quantities of ammonia into the nitrogen oxides, a mixture producing harmless dinitrogen and water vapor:

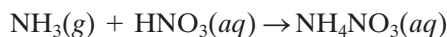


Worldwide, about 80 percent of the nitric acid is used in fertilizer production. This proportion is only about 65 percent in the United States because about 20 percent is required for explosives production.

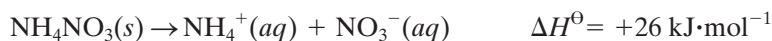
## Nitrates

Nitrates of almost every metal ion in its common oxidation states are known, and of particular note, all are water soluble. For this reason, nitrates tend to be used whenever a solution of a cation is required. Although nitric acid is strongly oxidizing, the colorless nitrate ion is not under normal conditions (see Figure 15.3). Hence, one can obtain nitrates of metals in their lower oxidation states, such as iron(II).

The most important nitrate is ammonium nitrate; in fact, this one chemical accounts for the major use of nitric acid. About  $1.5 \times 10^7$  tonnes is produced annually worldwide. It is prepared simply by the reaction of ammonia with nitric acid:

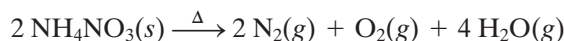


One of the common cold packs utilizes solid ammonium nitrate and water. When the dividing partition is broken, ammonium nitrate solution forms. This process is highly endothermic:



The endothermicity must be a result of comparatively strong cation-anion attractions in the crystal lattice and comparatively weak ion-dipole attractions to the water molecules in solution. If the enthalpy factor is positive but the compound is still very soluble, the driving force must be a large increase in entropy. In fact, there is such an increase:  $+110 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . In the solid, the ions have a low entropy, whereas in solution, the ions are mobile. At the same time, the large ion size and low charge result in little ordering of the surrounding water molecules. Thus, it is an increase in entropy that drives the endothermic solution process of ammonium nitrate.

Ammonium nitrate is a convenient and concentrated source of nitrogen fertilizer, although it has to be handled with care. At low temperatures, it decomposes to dinitrogen oxide, but at higher temperatures, explosive decomposition to dinitrogen, dioxygen, and water vapor occurs:



About 1955, the North American blasting explosives industry recognized the potential of an ammonium nitrate–hydrocarbon mixture. As a result, a mixture of ammonium nitrate with fuel oil has become very popular with the industry. It is actually quite safe because the ammonium nitrate and fuel oil can be stored separately until use, and a detonator is then employed to initiate the explosion. This mixture was put to more tragic use in the Oklahoma City, Oklahoma, terrorist bombing in 1995.

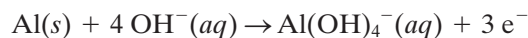
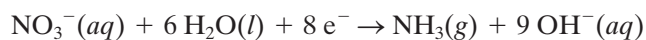
Other nitrates decompose by different routes when heated. Sodium nitrate melts, and then, when strongly heated, bubbles of oxygen gas are produced, leaving behind sodium nitrite:



Most other metal nitrates give the metal oxide, nitrogen dioxide, and oxygen. For example, heating blue crystals of copper(II) nitrate heptahydrate first yields a green liquid as the water of hydration is released and dissolves the copper(II) nitrate itself. Continued heating boils off the water, and the green solid then starts to release dioxygen and the brown fumes of nitrogen dioxide, leaving the black residue of copper(II) oxide:

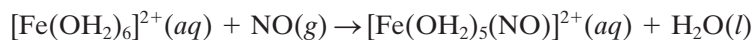
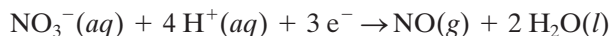


Both nitrates and nitrites can be reduced to ammonia in basic solution with zinc or Devarda's alloy (a combination of aluminum, zinc, and copper). This reaction is a common test for nitrates and nitrites because there is no characteristic precipitation test for this ion. The ammonia is usually detected by odor or with damp red litmus paper (which will turn blue):

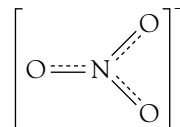


The accidental fire on a ship carrying wax-coated pellets of ammonium nitrate killed at least 500 people in Texas City, Texas, in 1947.

The “brown ring test” for nitrate involves the reduction of nitrate with iron(II) in very acidic solution, followed by replacement of one of the coordinated water molecules of the remaining iron(II) to give a brown complex ion:



The nitrate ion is trigonal planar and has short nitrogen-oxygen bonds (122 pm)—bonds slightly shorter than those in the nitrite ion. The nitrate ion is isoelectronic with the carbonate ion; thus, we assume similar partial bonding to give a bond order of  $1\frac{1}{3}$ . The partial bond representation of the nitrate ion is shown in Figure 15.23.

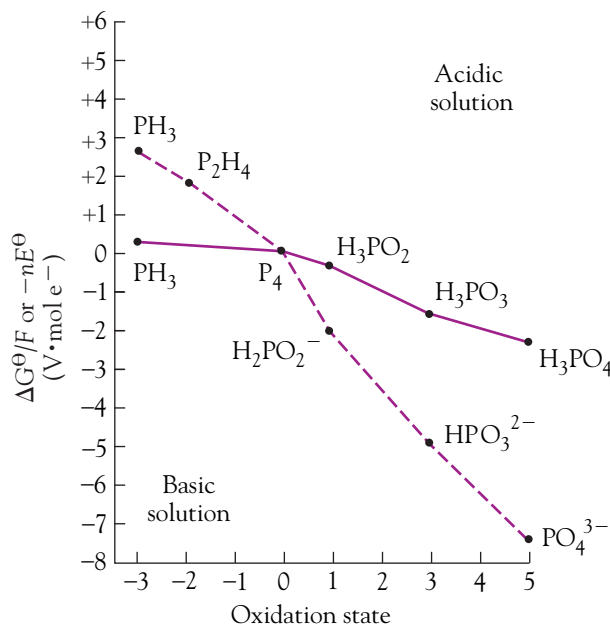


**FIGURE 15.23** The shape of the nitrate ion.

## 15.12 Overview of Phosphorus Chemistry

The Frost diagram for phosphorus species shows that under acidic conditions, the highest oxidation state, +5, is the most stable species, as phosphoric acid,  $\text{H}_3\text{PO}_4$ , and under basic conditions, the phosphate ion,  $\text{PO}_4^{3-}$ , is the most stable (Figure 15.24). In aqueous environments, these and the intervening acid anions are the predominant species.

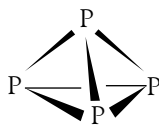
A unique feature of phosphorus chemistry is the stability of the tetrahedral  $\text{P}_4$  unit found in the white allotrope of phosphorus (see Section 15.13). For example, the common phosphorus oxides,  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$ , have structures based on the  $\text{P}_4$  framework (see Section 15.15), as do  $\text{P}_4\text{S}_{10}$  and the mixed oxide-sulfide compounds  $\text{P}_4\text{O}_6\text{S}_4$  and  $\text{P}_4\text{S}_6\text{O}_4$ .



**FIGURE 15.24** Frost diagram for the common phosphorus species under acidic and basic conditions.

### 15.13 Phosphorus

Phosphorus has several allotropes. Triply bonded  $P_2$  molecules which are analogous to  $N_2$  have been observed but they are very reactive and short lived. The common allotropes are white phosphorus (sometimes called *yellow phosphorus*) and red phosphorus. Curiously, the most thermodynamically stable form of phosphorus, black phosphorus, is the hardest to prepare. To make black phosphorus, white phosphorus is heated under pressures of about 1.2 GPa!

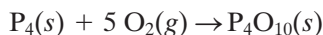


**FIGURE 15.25** The shape of the white phosphorus molecule.

#### White Phosphorus

White phosphorus, a very poisonous, white, waxy-looking substance, is formed when liquid phosphorus solidifies. This allotrope, having only weak dispersion forces between neighboring molecules, melts at  $44^\circ\text{C}$ . It is a tetratomic molecule with the phosphorus atoms at the corners of a tetrahedron (Figure 15.25). Because it is so reactive toward oxygen, white phosphorus has to be stored underwater. Although insoluble in hydrogen-bonding solvents such as water, it is extremely soluble in nonpolar organic solvents such as carbon disulfide.

The strained covalent bonds are probably the cause of tetraphosphorus being the least thermodynamically stable of the allotropes. It is an extremely reactive substance; for example, it burns vigorously in air to give tetraphosphorus decaoxide:



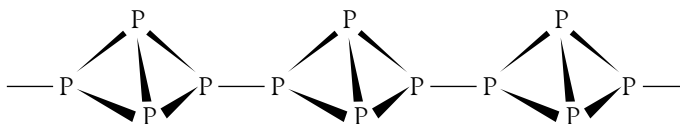
The oxide is formed in an electronically excited state, and as the electrons fall to the lowest energy state, visible light is released. In fact, the name *phosphorus* is derived from the phosphorescent glow when white phosphorus is exposed to air in the dark.

#### Red Phosphorus

When exposed to ultraviolet radiation (for example, from fluorescent lights), white phosphorus slowly turns to red phosphorus. In this allotrope, one of the bonds in the tetrahedral structure of white phosphorus has broken open and joined to a neighboring unit (Figure 15.26). Thus, red phosphorus is a polymer with bonds less strained than those of the white allotrope.

The more thermodynamically stable red phosphorus has properties that are completely different from those of the white allotrope. It is stable in air, reacting with the dioxygen in air only above about  $400^\circ\text{C}$ . The melting point of the red allotrope is about  $600^\circ\text{C}$ , at which temperature the polymer chains break to give the same  $P_4$  units contained in white phosphorus. As we would expect for a covalently bonded polymer, red phosphorus is insoluble in all solvents.

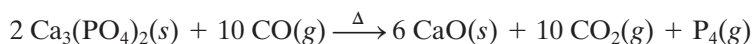
**FIGURE 15.26** The arrangement of atoms in red phosphorus.



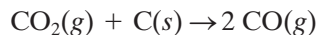
### The Industrial Extraction of Phosphorus

Phosphorus is such a reactive element that quite extreme methods have to be used to extract it from its compounds. The raw material is calcium phosphate. This compound is found in large deposits in central Florida, the Morocco-Sahara region, and the Pacific island of Nauru. The origins of these deposits are not well understood, although they may have been the result of the interaction of the calcium carbonate of coral reefs with the phosphate-rich droppings of seabirds over a period of hundreds of thousands of years.

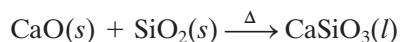
Processing of phosphate rock is highly dependent on electric energy. As a result, the ore is usually shipped to countries where electric power is abundant and inexpensive, such as North America and Europe. The conversion of phosphate rock to the element is accomplished in a very large electric furnace containing 60-tonne carbon electrodes. In this electrothermal process, the furnace is filled with a mixture of ore, sand, and coke, and a current of about 180 000 A (at 500 V) is applied across the electrodes. At the 1500°C operating temperature of the furnace, the calcium phosphate reacts with carbon monoxide to give calcium oxide, carbon dioxide, and gaseous tetraphosphorus:



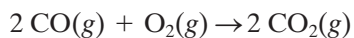
To condense the gaseous tetraphosphorus, it is pumped into a tower and sprayed with water. The liquefied phosphorus collects at the bottom of the tower and is drained into holding tanks. The average furnace produces about 5 tonnes of tetraphosphorus per hour. As to the other products, the carbon dioxide is then reduced back to carbon monoxide by the coke:



Some of the gas is reused, but the remainder escapes from the furnace. The calcium oxide reacts with silicon dioxide (sand) to give calcium silicate (slag):



The escaping carbon monoxide is burned and the heat is used to dry the three raw materials:



There are two common impurities in the phosphate ore. First, there are traces of fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , that react at the high temperatures to produce toxic and corrosive silicon tetrafluoride. This contaminant is removed from the effluent gases by treating them with sodium carbonate solution. The process produces sodium hexafluorosilicate,  $\text{Na}_2\text{SiF}_6$ , which is a commercially useful product. The second impurity is iron(III) oxide, which reacts with the tetraphosphorus to form ferrophosphorus (mainly  $\text{Fe}_2\text{P}$ , one of the several interstitial iron phosphides), a dense liquid that can be tapped from the bottom of the furnace below the liquid slag layer. Ferrophosphorus can be used in specialty steel products such as railroad brake shoes. The other by-product from the process, calcium silicate (slag), has little value apart



## Generating a Flame

In these days of pocket butane lighters, we forget how difficult it used to be to generate a flame. So in 1833, people were delighted to find how easily fire could be produced by using white phosphorus matches. This convenience came at a horrendous human cost, because white phosphorus is extremely toxic. The young women who worked in the match factories died in staggering numbers from phosphorus poisoning. This occupational hazard manifested itself as “phossy jaw,” a disintegration of the lower jaw, followed by an agonizing death.

In 1845, the air-stable red phosphorus was shown to be chemically identical to white phosphorus. The British industrial chemist Arthur Albright had been troubled by the enormous number of deaths in his match factory, so when he learned of this safer allotrope, he determined to produce matches bearing red phosphorus. But mixing the inert red phosphorus with an oxidizing agent gave an instant explosion. Prizes

were offered for the development of a safe match, and finally in 1848 some now-unknown genius proposed to put half the ingredients on the match tip and the remainder on a strip attached to the matchbox. Only when the two surfaces were brought into contact did ignition of the match head occur.

The modern design is slightly different. The head of the match consists of about 45–55% of the oxidant, potassium chlorate,  $\text{KClO}_3$ , together with a small proportion of sulfur and starch, inert material, and glue. Some match heads also contain antimony(III) sulfide,  $\text{Sb}_2\text{S}_3$ , to produce a more vigorous reaction. The striking surface is typically composed of about 50% red phosphorus, 25% powdered glass to provide the friction, and other minor components, including 4% carbon black. Despite the prevalence of cheap butane lighters, match consumption is still between  $10^{12}$  and  $10^{13}$  per year.

from road fill. The cost of this whole process is staggering, not only for its energy consumption but also for the total mass of materials. These are listed in Table 15.5.

The major pollutants from the process are dusts, flue gases, phosphorus-containing sludge, and process water from the cooling towers (Table 15.6). Older plants had very bad environmental records. In fact, the technology has changed to such an extent that it is now more economical to abandon an old plant and build a new one that will produce as little pollution as is possible using modern technology. However, the abandoned plant may become a severe

**TABLE 15.6** Materials consumed and produced in the extraction of 1 tonne of phosphorus

Required	Produced
10 tonnes calcium phosphate (phosphate rock)	1 tonne white phosphorus
3 tonnes silicon dioxide (sand)	8 tonnes calcium silicate (slag)
$1\frac{1}{2}$ tonnes carbon (coke)	$\frac{1}{4}$ tonne iron phosphides
14 MWh electrical energy	0.1 tonne filter dust
	2500 m <sup>3</sup> flue gas

environmental problem for the community in which it is located as a result of leaching from the waste material dumps.

The need for pure phosphorus is in decline because the energy costs of its production are too high to make it an economical source for most phosphorus compounds. Furthermore, demand for phosphate-based detergents has dropped because of ecological concerns. Nevertheless, elemental phosphorus is still the preferred route for the preparation of high-purity phosphorus compounds, such as phosphorus-based insecticides and match materials.

## 15.14 Phosphine

The analog of ammonia—phosphine,  $\text{PH}_3$ —is a colorless, highly poisonous gas. The two hydrides differ substantially because the  $\text{P—H}$  bond is much less polar than the  $\text{N—H}$  bond. Thus, phosphine is a very weak base, and it does not form hydrogen bonds. In fact, the phosphonium ion,  $\text{PH}_4^+$ , the equivalent of the ammonium ion, is difficult to prepare. Phosphine itself can be prepared by mixing a phosphide of a very electropositive metal with water:

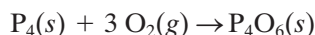


In phosphine, the  $\text{H—P—H}$  bond angle is only  $93^\circ$  rather than  $107^\circ$ , the angle of the  $\text{H—N—H}$  bond in ammonia. The phosphine angle suggests that the phosphorus atom is using  $p$  orbitals rather than  $\text{sp}^3$  hybrids for bonding.

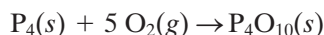
Although phosphine itself has few uses, substituted phosphines are important reagents in organometallic chemistry, as we will see in Chapter 22, Section 22.10. The most common of the substituted phosphines is triphenylphosphine,  $\text{P}(\text{C}_6\text{H}_5)_3$ , often abbreviated to  $\text{PPh}_3$ .

## 15.15 Phosphorus Oxides

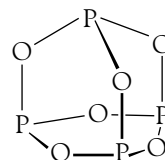
Phosphorus forms two oxides: tetraphosphorus hexaoxide,  $\text{P}_4\text{O}_6$ , and tetraphosphorus decaoxide,  $\text{P}_4\text{O}_{10}$ . They are both white solids at room temperature. Tetraphosphorus hexaoxide is formed when white phosphorus burns in an environment with a shortage of oxygen:



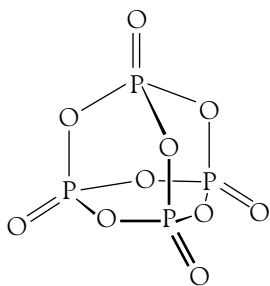
Conversely, tetraphosphorus decaoxide, the more common and more important oxide, is formed when white phosphorus burns in the presence of an excess of oxygen:



The structure of both these oxides is based on the tetrahedron of white phosphorus (tetraphosphorus) itself. In tetraphosphorus hexaoxide, oxygen atoms have inserted themselves in all the phosphorus-phosphorus bonds (Figure 15.27).



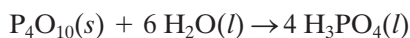
**FIGURE 15.27** The shape of the tetraphosphorus hexaoxide molecule.



**FIGURE 15.28** The shape of the tetraphosphorus decaoxide molecule.

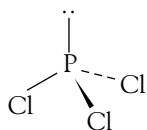
In tetraphosphorus decaoxide, four additional oxygen atoms form coordinate covalent bonds to the phosphorus atoms, extending out from the corners of the tetrahedron (Figure 15.28). These bonds are stronger than single P—O bonds, and so they must have some form of multiple bond character.

Tetraphosphorus decaoxide can be used as a dehydrating agent because it reacts vigorously with water in a number of steps to give, ultimately, phosphoric acid:



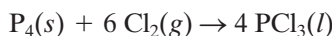
Many compounds are dehydrated by tetraphosphorus decaoxide; for example, nitric acid is dehydrated to dinitrogen pentoxide and organic amides,  $\text{RCONH}_2$ , to nitriles,  $\text{RCN}$ .

## 15.16 Phosphorus Chlorides

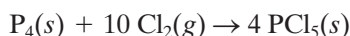


**FIGURE 15.29** The shape of the phosphorus trichloride molecule.

In parallel with the oxides, there are two chlorides: phosphorus trichloride,  $\text{PCl}_3$ , a colorless liquid, and phosphorus pentachloride,  $\text{PCl}_5$ , a white solid. Phosphorus trichloride is produced when chlorine gas reacts with an excess of phosphorus:

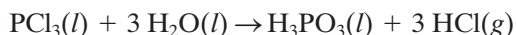


An excess of chlorine results in phosphorus pentachloride:



### Phosphorus Trichloride

Phosphorus trichloride reacts with water to give phosphonic acid,  $\text{H}_3\text{PO}_3$  (commonly called *phosphorous acid*), and hydrogen chloride gas (Figure 15.29):

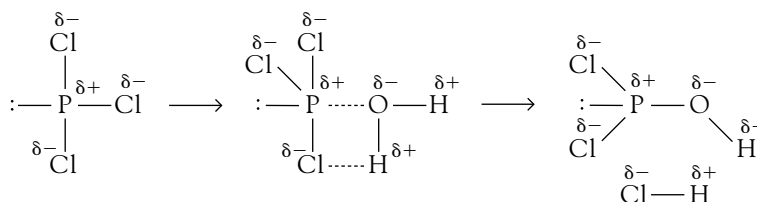


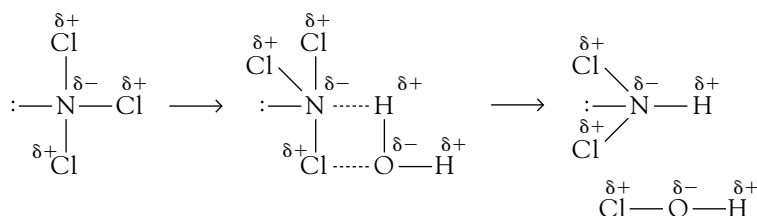
This behavior contrasts with that of nitrogen trichloride, which, as mentioned in Section 15.9, hydrolyzes to give ammonia and hypochlorous acid (Figure 15.30):



Trigonal phosphorus trichloride (Figure 15.31) is an important reagent in organic chemistry, and its worldwide production amounts to about 250 000 tonnes. For example, it can be used to convert alcohols to chloro

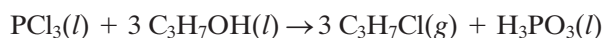
**FIGURE 15.30** The proposed mechanism for the first step in the reaction between phosphorus trichloride and water.





**FIGURE 15.31** The proposed mechanism for the first step in the reaction between nitrogen trichloride and water.

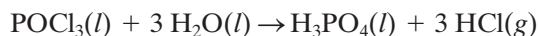
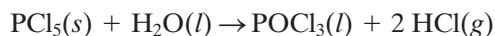
compounds. Thus, 1-propanol is converted to 1-chloropropane by phosphorus trichloride:



### Phosphorus Pentachloride

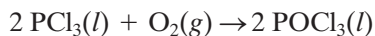
The structure of phosphorus pentachloride is interesting because it is different in the solid phase at room temperature from that in the gas phase at high temperatures. In the gas phase, phosphorus pentachloride is a trigonal bipyramidal covalent molecule (Figure 15.32), but in the solid phase, phosphorus pentachloride adopts the ionic structure  $(\text{PCl}_4)^+(\text{PCl}_6)^-$  (Figure 15.33).

Phosphorus pentachloride is also used as an organic reagent, but it is less important, with annual production being only about 20 000 tonnes worldwide. Like phosphorus trichloride, it reacts with water, but in a two-step process, the first step yielding phosphoryl chloride,  $\text{POCl}_3$ , also known as *phosphorus oxychloride*:

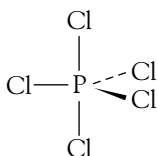


### Phosphoryl Trichloride

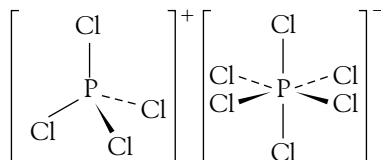
Commonly called *phosphoryl chloride*, phosphoryl trichloride,  $\text{POCl}_3$ , is one of the most important industrial phosphorus compounds. This dense toxic liquid, which fumes in moist air, is produced industrially by the catalytic oxidation of phosphorus trichloride:



An extensive range of chemicals is made from phosphoryl chloride. Tri-*n*-butyl phosphate,  $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$ , commonly abbreviated to TBP, is a useful selective solvent, such as for separating uranium and plutonium compounds. Similar



**FIGURE 15.32** The shape of the phosphorus pentachloride molecule in liquid and gas phases.



**FIGURE 15.33** The shape of the two ions present in solid-phase phosphorus pentachloride.

compounds are crucial to our lives as fire retardants that are sprayed on children's clothing, aircraft and train seats, curtain materials, and many more items that we encounter in our everyday lives.

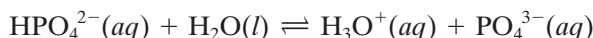
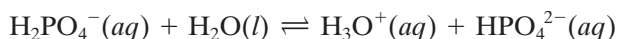
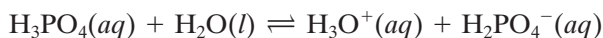
### 15.17 Phosphorus Oxoacids and Phosphates

There are three oxyacids of phosphorus that we will mention here: phosphoric acid,  $\text{H}_3\text{PO}_4$ ; phosphonic acid,  $\text{H}_3\text{PO}_3$  (commonly called *phosphorous acid*); and phosphinic acid,  $\text{H}_3\text{PO}_2$  (commonly called *hypophosphorous acid*). The first, phosphoric acid, is really the only oxyacid of phosphorus that is important. However, the other two acids are useful for making a point about the character of oxyacids.

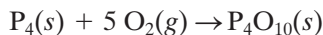
In an oxyacid, for the hydrogen to be significantly acidic, it must be attached to an oxygen atom—and this is normally the case. In general, as we progress through a series of oxyacids—for example, nitric acid,  $(\text{HO})\text{NO}_2$ , and nitrous acid,  $(\text{HO})\text{NO}$ —it is one of the terminal oxygen atoms that is lost as the oxidation state of the central element is reduced. Phosphorus is almost unique in that the oxygens linking a hydrogen to the phosphorus are the ones that are lost. Thus, phosphoric acid possesses three ionizable hydrogen atoms, phosphonic acid, two, and phosphinic acid, only one (Figure 15.34).

#### Phosphoric Acid

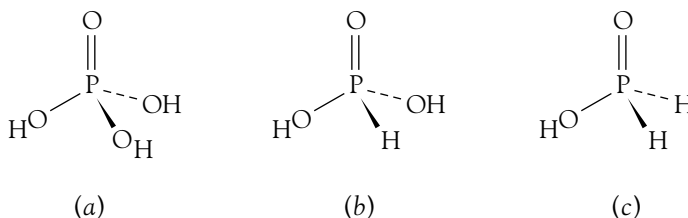
Pure (ortho)phosphoric acid is a colorless solid, melting at  $42^\circ\text{C}$ . A concentrated aqueous solution of the acid (85 percent by mass and having a concentration of  $14.7 \text{ mol}\cdot\text{L}^{-1}$ ) is called “syrupy” phosphoric acid, with its viscous nature being caused by extensive hydrogen bonding. As discussed earlier, the acid is essentially nonoxidizing. In solution, phosphoric acid is a weak acid, undergoing three ionization steps:



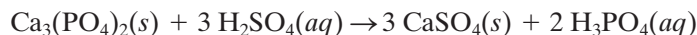
The pure acid is prepared by burning white phosphorus to give tetraphosphorus decaoxide, then treating the oxide with water:



**FIGURE 15.34** The bonding in the three common oxyacids of phosphorus: (a) phosphoric acid, (b) phosphonic acid, (c) phosphinic acid.



Such high purity is not required for most purposes, so where trace impurities can be tolerated, it is much more energy efficient to treat calcium phosphate with sulfuric acid to give a solution of phosphoric acid and a precipitate of calcium sulfate:



The only problem associated with this process (known as the “wet” process) is the disposal of the calcium sulfate. Some of this product is used in the building industry, but production of calcium sulfate exceeds the uses; hence, most of it must be dumped. Furthermore, when the phosphoric acid is concentrated at the end of the process, many of the impurities precipitate out. This “slime” must be disposed of in an environmentally safe manner.

Heating phosphoric acid causes a stepwise loss of water; in other words, the phosphoric acid molecules undergo condensation. The first product is pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ . As in phosphoric acid, each phosphorus atom is tetrahedrally coordinated (Figure 15.35). The next product is tripolyphosphoric acid,  $\text{H}_5\text{P}_3\text{O}_{10}$ :

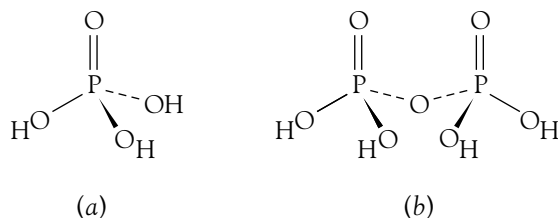


Subsequent condensations give products with even greater degrees of polymerization.

Most of the phosphoric acid is used for fertilizer production. Phosphoric acid also is a common additive to soft drinks; its weak acidity prevents bacterial growth in the bottled solutions. It often serves a second purpose in metal containers. Metal ions may be leached from the container walls, but the phosphate ions will react with the metal ions to give an inert phosphate compound, thus preventing any potential metal poisoning. Phosphoric acid is also used on steel surfaces as a rust remover, both in industry and for home automobile repairs.

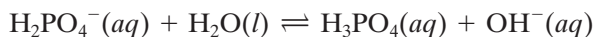
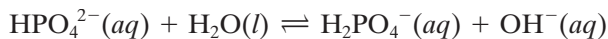
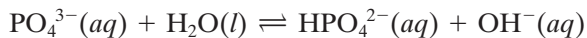
## Phosphates

With high lattice energies resulting from the high anion charge, most phosphates are insoluble. The alkali metals and ammonium phosphates are the only common exceptions to this rule. There are three series of phosphate salts: the phosphates, containing the  $\text{PO}_4^{3-}$  ion; the hydrogen phosphates, containing the  $\text{HPO}_4^{2-}$  ion; and the dihydrogen phosphates, containing the  $\text{H}_2\text{PO}_4^-$  ion. In



**FIGURE 15.35** The shape of (a) (ortho)phosphoric acid and (b) pyrophosphoric acid.

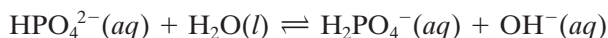
solution, there is an equilibrium between the three species and phosphoric acid itself. For example, a solution of phosphate ion will hydrolyze:



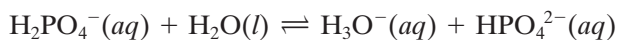
Each successive equilibrium lies more and more to the left. Thus, the concentration of actual phosphoric acid is minuscule. A solution of sodium phosphate, then, will be quite basic, almost entirely as a result of the first equilibrium. It is this basicity (good for reaction with greases) and the complexing ability of the phosphate ion that make a solution of sodium phosphate a common kitchen cleaning solution (known as *TSP*, trisodium phosphate).



Figure 15.36 shows how the proportions of the phosphate species depend on pH. A solution of sodium hydrogen phosphate,  $\text{Na}_2(\text{HPO}_4)$ , will be basic as a result of the second step of the preceding sequence:

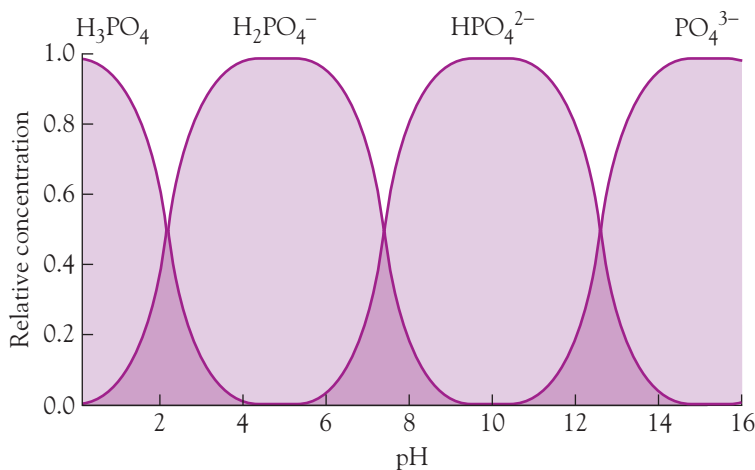


A solution of sodium dihydrogen phosphate,  $\text{Na}(\text{H}_2\text{PO}_4)$ , however, is slightly acidic as a result of the following reaction predominating:



Solid hydrogen phosphates and dihydrogen phosphates are only known for most of the monopositive cations (the alkali metals ions and the ammonium ion) and a few of the dipositive cations, such as calcium ion. As we have seen before, to stabilize a large low-charge anion, a low-charge-density cation is required. For most di-positive and all tri-positive metal ions, the metal ion precipitates the small proportion of phosphate ion from a solution of one of the acid ions. The Le Châtelier principle then drives the equilibria to produce more phosphate ion, causing additional metal phosphate to precipitate.

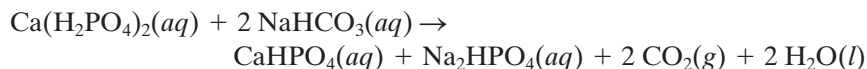
**FIGURE 15.36** The relative concentrations of phosphate species at different values of pH.



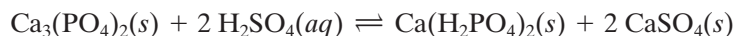
The phosphates have a tremendous range of uses. As mentioned earlier, trisodium phosphate is used as a household cleaner. Other sodium phosphates, such as sodium pyrophosphate,  $\text{Na}_4\text{P}_2\text{O}_7$ , and sodium tripolyphosphate,  $\text{Na}_5\text{P}_3\text{O}_{10}$ , are often added to detergents because they react with calcium and magnesium ions in the tap water to form soluble compounds, preventing the deposition of scum in the washing. However, when the phosphate-rich wastewater reaches lakes, it can cause a rapid growth of algae and other simple plant life. This formation of green, murky lakes is called *eutrophication*. Phosphates are also added to detergents as fillers. Fillers are required because we are used to pouring cupfuls of solid detergent into a washing machine. However, only small volumes of cleaning agents are actually needed, so most of the detergent is simply inert materials. In more frugal societies, such as Japan, people are used to adding spoonfuls of detergent—hence, less wasteful filler is required.

Disodium hydrogen phosphate is used in the preparation of pasteurized processed cheese, although even today, the reason why this ion aids in the cheese-making process is not well understood. The ammonium salts, diammonium hydrogen phosphate and ammonium dihydrogen phosphate, are useful nitrogen-phosphorus combination fertilizers. Ammonium phosphates also make excellent flame retardants for drapes, theater scenery, and disposable paper clothing and costumes.

The calcium phosphates are used in many circumstances. For example, “combination baking powder” relies on the reaction between calcium dihydrogen phosphate and sodium hydrogen carbonate to produce the carbon dioxide gas so essential for baking. The reaction can be simplistically represented as:



Finally, calcium dihydrogen phosphate is used as a fertilizer. The calcium phosphate rock is too insoluble to provide phosphate for plant growth, so it is treated with sulfuric acid to produce calcium dihydrogen phosphate:



This compound is only slightly soluble in water but soluble enough to release a steady flow of phosphate ions into the surrounding soil, where they can be absorbed by plant roots.

## 15.18 The Pnictides

Although the term *pnictogen* is used for all the members of Group 15, the corresponding anion term, *pnictides*, excludes nitrides. The reason for the exclusion is that phosphides, arsenides, antimonides, and bismuthides share behavior that is quite different from the behavior of nitrides. Many of these three-element pnictides, such as  $\text{LaSiP}_3$ ,  $\text{Eu}_2\text{Ga}_2\text{P}_6$ , and  $\text{K}_6\text{Bi}_2\text{Sn}_{23}$ , inhabit an ill-defined bonding area somewhere between ionic and covalent.



Such compounds are not just laboratory curiosities; many exhibit rare or unique properties. For example, passage of an electric current through a block of a module containing  $\text{Mo}_3\text{Sb}_5\text{Te}_2$ , a thermoelectric material, causes heat transfer, and so this compound has refrigeration potential. Mixed-metal pnictides exhibit other valuable properties; as another example, the iron pnictides, such as  $\text{SmFeAsO}_{0.82}\text{F}_{0.18}$ , are high-temperature superconductors.

## 15.19 Biological Aspects

### Nitrogen Monoxide: The Nerve Gas

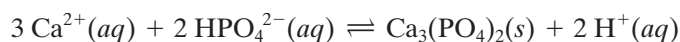
Until recently, a discussion of simple nitrogen monoxide chemistry would have ended here. Now we realize that this little molecule plays a vital role in our bodies and those of all mammals. In fact, the prestigious journal *Science* called it the 1992 Molecule of the Year. It has been known since 1867 that organic nitro compounds, such as nitroglycerine, can relieve angina, lower blood pressure, and relax smooth muscle tissue. Yet it was not until 1987 that Salvador Moncada and his team of scientists at the Wellcome Research Laboratories in Britain identified the crucial factor in blood vessel dilation as nitrogen monoxide gas. That is, organic nitro compounds are broken down to produce this gas in the organs.

Since this initial work, we have come to realize that nitrogen monoxide is crucial in controlling blood pressure. There is even an enzyme (nitric oxide synthase) whose sole task is the production of nitrogen monoxide. At this point, a tremendous quantity of biochemical research is concerned with the role of this molecule in the body. A lack of nitrogen monoxide is implicated as a cause of high blood pressure, whereas septic shock, a leading cause of death in intensive care wards, is ascribed to an excess of nitrogen monoxide. The gas appears to have a function in memory and in the stomach. Male erections have been proved to depend on production of nitrogen monoxide, and there are claims of important roles for nitrogen monoxide in female uterine contractions. One question still to be answered concerns the life span of these molecules, considering the ease with which they react with oxygen gas.

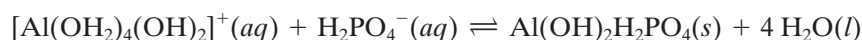
### Phosphorus: The Phosphorus Cycle

Just as there are carbon and nitrogen cycles, there is an active phosphorus cycle. Phosphorus is an essential element for plant growth, although its soil concentration is usually quite low—between 1 and  $0.001 \text{ mg} \cdot \text{L}^{-1}$ . One major difference from the carbon and nitrogen cycles is that phosphorus has no major gas-phase compound; thus, cycling is almost totally between aqueous and solid phases involving the phosphate ion. Organic phosphates are the most soluble in soils. These are phosphates covalently bound as phospholipids, nucleic acids, and inositol phosphates, where inositol is a sugar-like molecule,  $\text{C}_6\text{H}_6(\text{OH})_6$ .

At the normal pH range of soils, inorganic phosphate is present as the hydrogen phosphate and dihydrogen phosphate ions. However, the equilibrium is shifted by the presence of high-charge metal ions that force the equilibria toward insoluble and, hence, unavailable compounds. Of particular importance, calcium ion forms insoluble calcium phosphate. As the pH increases, so the equilibrium favors formation of the insoluble compound:



Solution availability of phosphate is also limited at the acid end of the scale. As we mentioned in Chapter 13, Section 13.6, aluminum ion becomes more soluble as the pH decreases. The solubilized aluminum ion species will then react with the phosphate species to give insoluble aluminophosphate compounds. For example:



As a result of these two reaction types, the level of inorganic phosphate in soils is very low except in a narrow window from pH 6 to pH 7.

### Arsenic: The Water Poisoner

Amazing as it may seem, arsenic also is an element essential to life. But we only need trace amounts of this element, whose role is still unknown. Anything more than a tiny amount of an inorganic compound of arsenic causes acute poisoning. In part, poisoning is believed to occur by the reaction of the soft-acid arsenic(III) with the soft-base sulfide of thio-amino acids, blocking the sulfur atoms from cross-linking to form disulfide bridges. In fact, one of the treatments for arsenic poisoning is the administration of thiol compounds to “mop up” the arsenite ions.

Many people believe that well water is, by definition, “pure” water. In fact, the composition of well water reflects the soluble (and possibly toxic) components of the water-laden strata. It is always important to check rural well-water supplies for trace elements such as arsenic. Arsenic poisoning from well water is now a serious health problem in the Asian country of Bangladesh. In rural Bangladesh, villagers had traditionally relied on disease-carrying surface ponds for their water supply. The government, together with many international aid agencies, carried out a highly successful campaign of drilling over 18 000 wells to provide safe, deep well water.

However, in their enthusiasm for nonsurface water, they did not check on the underlying geological strata. These happened to be high in leachable arsenic compounds. As a result, in many places, illness from waterborne diseases was replaced by illness and death from arsenic poisoning and arsenic-induced tumors. The immediate task was to identify which of the 18 000 wells exceeded the limit of 0.05 ppm. In a wealthy country such as the United States, the test samples would be rushed to a laboratory with state-of-the-art instrumentation. This is not an option for a poor country such as Bangladesh. Instead, a low-cost kit was developed by a Japanese company using the traditional Marsh test for

### Paul Ehrlich and His “Magic Bullet”

Arsenic has also been used as a lifesaver. In the nineteenth century, physicians had no means of combating infections, and patients usually died. The whole nature of medicine changed in 1863 when a French scientist, Antoine Béchamps, noticed that an arsenic compound was toxic to some microorganisms. A German, Paul Ehrlich, decided to synthesize new arsenic compounds, testing each one for its organism-killing ability. In 1909, with his 606th compound of arsenic, he found a substance that selectively killed the syphilis organism. At the time, syphilis was a feared and widespread disease for which there was no cure, only suffering, dementia, and death. Ehrlich’s arsenic compound, what he dubbed

a “magic bullet,” provided miraculous cures, and a search for other chemical compounds that could be used in the treatment of disease was launched. The story is recounted in the classic movie *Dr. Ehrlich’s Magic Bullet*, released in 1940.

This field, chemotherapy, has produced one of the most effective tools of controlling bacterial infections and those of many other microorganisms. Chemotherapy also provides one of the lines of attack against cancerous tissues. Despite its reputation, arsenic is a key element in this fight and there are now a growing number of arsenic-containing pharmaceuticals, known collectively as *arsenicals*.

arsenic. This kit could be carried by community health workers from village-to-village and used by relatively unskilled personnel. With the identification of the most hazardous wells, the next step is to find a low-cost method of arsenic removal. Some prototypes are in use and better use of surface water is also being implemented.

### Bismuth: The Medicinal Element

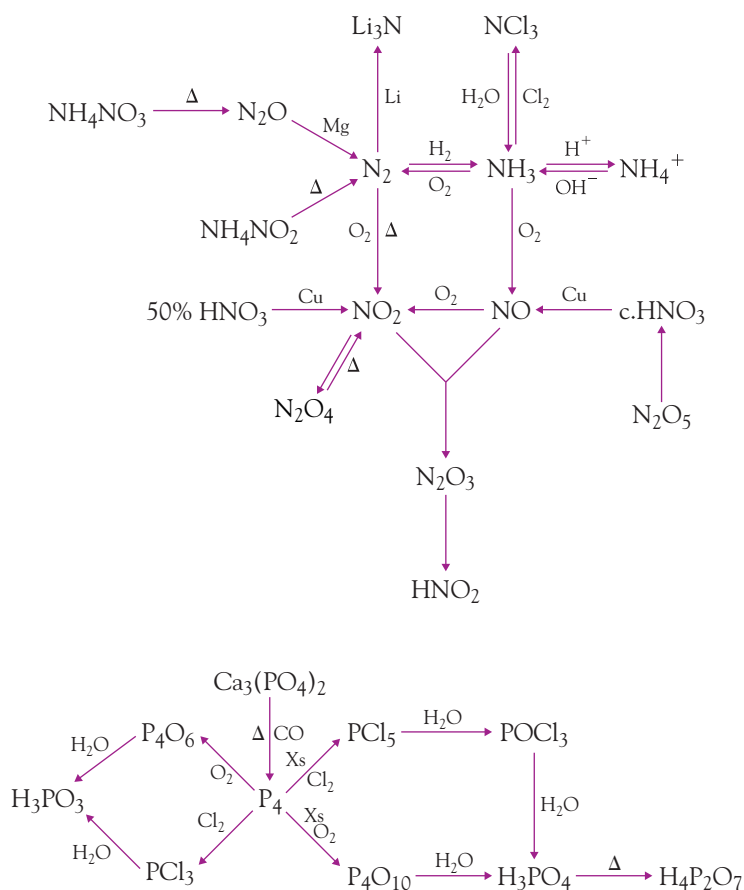
Although bismuth is not known to serve any essential role in biological systems, bismuth compounds have been used in the treatment of bacteria-related illnesses in Western medicine for over 250 years. Bismuth compounds are to be found in traditional Chinese medicine and in some medicinal plants (herbal remedies) that are bismuth accumulators.

Bismuth compounds are used in the treatment of syphilis and certain types of tumors; the major use of bismuth-containing compounds is in the treatment of gastrointestinal (stomach) disorders. Commercial preparations include Pepto-Bismol, which contains bismuth sub-salicylate (BSS), and De-Nol, which contains colloidal bismuth subcitrate (CBS). These compounds are antimicrobial but also appear to fortify the gastric mucus and stimulate cytoprotective processes. Both BSS and CBS are effective against the bacterium *Helicobacter pylori*, now known to be a causative factor of most types of gastroduodenal ulcers, and BSS is also effective against traveler’s diarrhea. In fact, Canadian health authorities advise visitors to regions of the world where bacterial food and water levels are high to take one or two BSS tablets before each meal as a preventative measure. (Although it doesn’t constitute a scientifically meaningful sample, one of the co-authors of this text has found this advice to be very effective.)

The efficacy of bismuth as a bacterial killer must relate to some unique aspect of its chemistry, which is defined by bismuth's weakly metallic properties. The predominant oxidation state of bismuth is +3, but the free cation does not exist and covalent behavior predominates. The only common ionic species of bismuth is  $\text{BiO}^+$ , known as the *bismuthyl ion*; its compounds are called *basic*, *oxy*-, or *sub*- salts. In fact, the aqueous chemistry of bismuth is dominated by the formation of clusters containing six bismuth and eight oxygen atoms, such as  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$ . Because of the complexity of its solution chemistry, even the stoichiometry of compounds such as BSS and CBS is variable, depending on the precise conditions of synthesis. Much research still is needed to discover how bismuth compounds function as bactericides.

## 15.20 Element Reaction Flowcharts

Flowcharts are shown for both nitrogen and phosphorus, the two key elements in Group 15.



## KEY IDEAS

- Several aspects of nitrogen chemistry are unique to that element.
- There are a large number of oxides of nitrogen.
- Phosphorus is a very reactive element.
- Phosphates and phosphoric acid are the most common compounds of phosphorus.

## EXERCISES

**15.1** Write balanced chemical equations for the following chemical reactions:

- arsenic trichloride with water
- magnesium with dinitrogen
- ammonia with excess chlorine
- methane with steam
- hydrazine and oxygen
- heating a solution of ammonium nitrate
- sodium hydroxide solution with dinitrogen trioxide
- heating sodium nitrate
- heating tetraphosphorus decaoxide with carbon

**15.2** Write balanced chemical equations for the following chemical reactions:

- heating a solution of ammonium nitrite
- solutions of ammonium sulfate with sodium hydroxide
- ammonia with phosphoric acid
- decomposition of sodium azide
- nitrogen monoxide and nitrogen dioxide
- heating solid lead nitrate
- tetraphosphorus with an excess of dioxygen
- calcium phosphide with water
- hydrazine solution and dilute hydrochloric acid

**15.3** Why is it hard to categorize arsenic as either a metal or a nonmetal?

**15.4** What are the factors that distinguish the chemistry of nitrogen from that of the other members of Group 15?

**15.5** Contrast the behavior of nitrogen and carbon by comparing the properties of: (a) methane and ammonia; (b) ethene and hydrazine.

**15.6** Contrast the bonding to oxygen in the two compounds  $\text{NF}_3\text{O}$  and  $\text{PF}_3\text{O}$ .

**15.7** (a) Why is dinitrogen very stable? (b) Yet why is dinitrogen not always the product during redox reactions involving nitrogen compounds?

**15.8** When ammonia is dissolved in water, the solution is often referred to as “ammonium hydroxide.” Discuss whether this terminology is appropriate.

**15.9** In the Haber process for ammonia synthesis, the recycled gases contain increasing proportions of argon gas. Where does the argon come from? Suggest how it might be removed.

**15.10** Why is it surprising that high pressure is used in the steam re-forming process during ammonia synthesis?

**15.11** Discuss the differences between the ammonium ion and the alkali metal ions.

**15.12** Using bond energies, calculate the heat released when gaseous hydrazine burns in air (oxygen) to give water vapor and nitrogen gas.

**15.13** Construct a possible electron-dot structure for the azide ion. Identify the location of the formal charges.

**15.14** Construct three possible electron-dot structures for the theoretical molecule  $\text{N—O—N}$ . By assignment of formal charges, suggest why the actual dinitrogen oxide molecule has its asymmetrical structure.

**15.15** Taking into account the nitrogen gas produced in both steps of the air bag reaction, calculate the mass of sodium azide needed to fill a 70-L air bag with dinitrogen at 298 K and 100 kPa pressure.

**15.16** Nitrogen monoxide can form an anion,  $\text{NO}^-$ . Calculate the bond order.

**15.17** Nitrogen trifluoride boils at  $-129^\circ\text{C}$ , whereas ammonia boils at  $-33^\circ\text{C}$ . Account for the difference in these values.

**15.18** Draw the shape of each of the following molecules: (a) dinitrogen trioxide; (b) dinitrogen pentoxide (solid and gas phases); (c) phosphorus pentafluoride.

**15.19** Draw the shape of each of the following molecules: (a) dinitrogen oxide; (b) dinitrogen tetroxide; (c) phosphorus trifluoride; (d) phosphonic acid.

**15.20** Describe the physical properties of: (a) nitric acid; (b) ammonia.

**15.21** Explain why, in the synthesis of nitric acid, the reaction of nitrogen monoxide with dioxygen is performed at high pressure and with cooling.

**15.22** Write balanced equations for the following reactions: (a) the reduction of nitric acid to the ammonium ion by zinc metal; (b) the reaction of solid silver sulfide with nitric acid to give silver ion solution, elemental sulfur, and nitrogen monoxide.

**15.23** Contrast the properties of the two common allotropes of phosphorus.

**15.24** Contrast the properties of ammonia and phosphine.

**15.25** Phosphine,  $\text{PH}_3$ , dissolves in liquid ammonia to give  $(\text{NH}_4)^+(\text{PH}_2)^-$ . What does this tell you about the relative acid-base strengths of the two Group 15 hydrides?

**15.26** In the “strike-anywhere” match, assume that the potassium chlorate is reduced to potassium chloride and the tetraphosphorus trisulfide is oxidized to tetraphosphorus decaoxide and sulfur dioxide. Write a balanced chemical equation for the process and identify the oxidation number changes that have occurred.

**15.27** A compound is known to have the formula  $\text{NOCl}$  (nitrosyl chloride).

(a) Construct an electron-dot diagram for the molecule and identify the oxidation number of nitrogen.

(b) What is the anticipated nitrogen-oxygen bond order?

(c) From the  $\Delta_f H^\ominus$  value for this compound of  $+52.6 \text{ kJ}\cdot\text{mol}^{-1}$  and appropriate bond energy data from Appendix 3, calculate the  $\text{N}-\text{O}$  bond energy in this compound. Compare it with values for  $\text{N}-\text{O}$  single and double bonds.

**15.28** (a) Construct an electron-dot structure for  $\text{POCl}_3$  (assume it to be similar to  $\text{PF}_3\text{O}$ ) and draw its molecular shape.

(b) According to the hybridization concept, what is the likely hybridization of the central phosphorus atom?

(c) The phosphorus-oxygen distance is very short. How would you explain this?

**15.29** Another compound of phosphorus and chlorine is  $\text{P}_2\text{Cl}_4$ . Construct an electron-dot structure for this compound and then draw its molecular shape.

**15.30** When gaseous dinitrogen tetroxide is bubbled into liquid nitric acid solvent, the  $\text{N}_2\text{O}_4$  ionizes to form a conducting solution. Suggest the identity of the products on the basis of known positive and negative ions containing only nitrogen and oxygen. Write a balanced equation for the reaction.

**15.31** In the solid phase,  $\text{PCl}_5$  forms  $(\text{PCl}_4)^+(\text{PCl}_6)^-$ . However,  $\text{PBr}_5$  forms  $(\text{PBr}_4)^+\text{Br}^-$ . Suggest a reason why the bromine compound has a different structure.

**15.32** The experimentally determined bond angles for arsine ( $\text{AsH}_3$ ), arsenic trifluoride, and arsenic trichloride are  $92^\circ$ ,  $96^\circ$ , and  $98.5^\circ$ , respectively. Offer explanations for the trends in the values.

**15.33** Figure 15.6 depicts the nitrogen-nitrogen bond orders in hydrogen azide, while Figure 15.7 shows the contributing resonance structures. How does the bonding differ in the azide ion,  $\text{N}_3^-$ ?

**15.34** Write the formula of two ions that are isoelectronic with the dinitrogen molecule.

**15.35** Hydroxylamine,  $\text{NH}_2\text{OH}$ , can be oxidized to nitrate ion by bromate ion,  $\text{BrO}_3^-$ , which is itself reduced to bromide ion. Write a balanced chemical equation for the reaction.

**15.36** Suggest why acidification promotes the decomposition of ammonium nitrate to dinitrogen oxide and water. *Hint:* Consult Figure 15.3.

**15.37** Gaseous  $\text{NOF}$  reacts with liquid  $\text{SbF}_5$  to give an electrically conducting solution. Write a balanced chemical equation for the reaction.

**15.38** A solution of the hydrogen phosphate ion is basic, whereas the dihydrogen phosphate ion is acidic. Write chemical equilibria for the predominant reactions that account for this difference in behavior.

**15.39** In Section 15.18, we mentioned pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ . What are the formulas of the equivalent isoelectronic acids of sulfur and silicon?

**15.40** There is an oxyanion of a transition metal that is isostructural with the pyrophosphate ion,  $\text{P}_2\text{O}_7^{4-}$ . Write the formula of the corresponding ion and explain your reasoning.

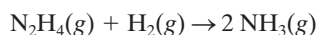
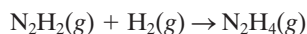
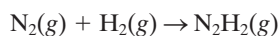
**15.41** Explain the terms (a) eutrophication; (b) symbiotic relationship; (c) chemotherapy; (d) apatite.

**15.42** Write balanced chemical equations corresponding to each transformation in the element reaction flowcharts for nitrogen and phosphorus (page 421).

## BEYOND THE BASICS

**15.43** When gaseous phosphine is bubbled into liquid hydrogen chloride, a conducting solution is formed. The product reacts with boron trichloride to give another ionic compound. Suggest the identity of each product. Write a balanced equation for each reaction and identify each reactant as a Lewis acid or base.

**15.44** A possible mechanism for the formation of ammonia is:



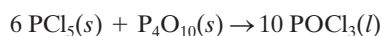
Use bond energy calculations to determine  $\Delta H$  for each step. Then suggest the major weakness with this possible route. Suggest another possible mechanism that would account for the slowness of the reaction. Determine the  $\Delta H$  value for the replacement step in the mechanism and show that it is indeed feasible.

**15.45** Deduce the shape of the nitrate radical. Suggest approximate values for the bond angles. What would be the expected average value of the N—O bond order?

**15.46** When phosphorus oxychloride fumes in moist air, what is the likely chemical reaction?

**15.47** Suggest a structure for the compound  $\text{P}_4\text{O}_6\text{S}_4$ .

**15.48** An alternative route for the synthesis of phosphorus oxychloride involves the reaction of phosphorus pentachloride with tetraphosphorus decoxide:



However, the reaction is usually performed by bubbling chlorine gas through a mixture of phosphorus trichloride and tetraphosphorus decoxide. Suggest the reason for this.

**15.49** Suggest why sodium azide is comparatively stable while heavy metal azides, such as copper(II) azide, are much more likely to explode.

**15.50** The nitrite ion is an ambidentate ion, bonding through oxygen or nitrogen. Which category of base (hard, borderline, soft) would you expect it to be in each of the two bonding types?

**15.51** The equilibrium constant,  $K$ , for a reaction can be found from the expression  $\Delta G^\ominus = -RT \ln K$ , where  $R$  is the ideal gas constant ( $8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ).

(a) Determine the equilibrium constant for the formation of ammonia from its elements at 298 K.

(b) Assuming  $\Delta H^\ominus$  and  $S^\ominus$  are temperature independent, calculate the equilibrium constant at 775 K.

(c) 775 K is a common operating temperature for the dinitrogen-dihydrogen reaction in an ammonia synthesis plant. In view of your answers to (a) and (b), why would such a high temperature be used for the reaction?

**15.52** The potentials of most nitrogen redox reactions cannot be measured directly. Instead, the values are obtained from free energy values. If  $\Delta_f G^\ominus (\text{NH}_3(\text{aq}))$  is  $-26.5 \text{ kJ} \cdot \text{mol}^{-1}$ , what is the standard potential for the  $\text{N}_2(\text{g})/\text{NH}_3(\text{aq})$  half-reaction in basic solution?

**15.53** Determine the N—N bond energy in the dinitrogen tetroxide molecule from appropriate thermodynamic data. Assume that the bonding within the  $\text{NO}_2$  units is the same as that in the nitrogen dioxide molecule itself.

**15.54** The energy needed to break a particular bond type differs from compound to compound. For example, the breaking of a nitrogen-chlorine bond requires much more energy for:



than for:



Suggest an explanation for this.

**15.55** Combinations of hydrogen phosphate and dihydrogen phosphate ions are often used as buffer mixtures. To prepare 1 L of a pH 6.80 buffer mixture, what masses of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  would be needed to give a total buffer concentration of  $0.10 \text{ mol} \cdot \text{L}^{-1}$ ? The  $\text{p}K_{\text{a}2}(\text{H}_3\text{PO}_4)$  is 7.21.

**15.56** Liquid phosphorus oxychloride is a useful nonaqueous solvent. Suggest the formulas of the cation and anion that would form on self-ionization. Identify which one would be the solvent's acid and which one the conjugate base.

**15.57** On warming, phosphorus pentachloride dissociates into phosphorus trichloride and dichlorine; however, phosphorus pentafluoride does not dissociate. Use bond energy arguments to explain the different behavior of the two pentahalides.

**15.58** One mole of phosphinic acid,  $\text{H}_3\text{PO}_2$ , requires 2 moles of diiodine to be oxidized to phosphoric acid, with the diiodine being reduced to iodide. Determine the formal oxidation number of phosphorus in phosphinic acid. By



comparison, what would be the oxidation number of phosphorus in phosphonic acid,  $\text{H}_3\text{PO}_3$ ?

**15.59** In this chapter, we mention that nitrogen only forms a trifluoride, whereas phosphorus forms both a trifluoride and a pentafluoride. However, nitrogen does form a compound of empirical formula  $\text{NF}_5$ . Suggest a possible structure for this compound.

**15.60** When nitrogen monoxide and air are mixed, dinitrogen tetroxide and nitrogen dioxide are formed. However, nitrogen monoxide produced in automobile exhausts at parts per million concentration only reacts very slowly with the dioxygen in the atmosphere. Suggest a possible mechanism for the reaction and explain why the reaction at low nitrogen monoxide concentrations is so slow.

**15.61** A red substance (A), when heated in the absence of air, vaporized and recondensed to give a yellow waxy substance (B). (A) did not react with air at room temperature, but (B) burned spontaneously to give clouds of a white solid (C). (C) dissolved exothermically in water to give a solution containing a triprotic acid (D). (B) reacted with a limited amount of chlorine to give a colorless fuming liquid (E), which in turn reacted further with chlorine to give a white solid (F). (F) gave a mixture of (D) and hydrochloric acid when treated with water. When water was added to (E), a diprotic acid (G) and hydrochloric acid were produced. Identify substances (A) to (G) and write equations for all reactions.

**15.62** When magnesium metal is heated in nitrogen gas, a pale gray compound (A) is formed. Reaction of (A) with water gives a precipitate of (B) and a gas (C). Gas (C) reacts with hypochlorite ion to form a colorless liquid (D) of empirical formula  $\text{NH}_2$ . Liquid (D) reacts in a 1:1 ratio with sulfuric acid to produce the ionic compound (E) of empirical formula  $\text{N}_2\text{H}_6\text{SO}_4$ . An aqueous solution of (E) reacts with nitrous acid to give a solution that, after neutralization with ammonia, produces a salt (F), with empirical formula  $\text{NH}$ . The compound (F) contains one cation and one anion per formula unit. The gas (C) reacts with heated sodium metal to give a solid (G) and hydrogen gas. When the solid (G) is heated with dinitrogen oxide in a 1:1 mole ratio, a solid (H) and water are produced. The anion in (H) is the same as that in (F). Identify substances (A) to (H).

**15.63** An alternative to the Haber process for the synthesis of ammonia is the reaction between lithium nitride and water. Write a balanced equation for this reaction and suggest why it is not commercially viable.

**15.64** Hydrogen azide reacts with diiodine in a 2:1 mole ratio. Deduce the products using a balanced chemical equation.

**15.65** There are numerous analogs between water and ammonia chemistry; for example, the base  $\text{K}^+(\text{NH}_2)^-$  in the ammonia system parallels  $\text{K}^+(\text{OH})^-$  in the water system. Deduce the ammonia-system analog for each of the following compounds:  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{CO}_3$ . *Hint:* Not all oxygen atoms need be replaced.

**15.66** Nitrogen forms two compounds with hydrogen and oxygen that are superficially similar: hydroxylamine,  $\text{NH}_2\text{OH}$ , and ammonium hydroxide,  $\text{NH}_4\text{OH}$ . However, the former is purely covalently bonded, while the latter consists of two separate ions. Use your knowledge of bonding to draw the shapes of each of these compounds.

**15.67** Nitrogen trichloride is an explosive compound. Write a balanced chemical equation for its decomposition to its constituent elements and use bond energy data from Appendix 3 to explain the exothermicity of the reaction.

**15.68** When methylammonium chloride,  $(\text{CH}_3\text{NH}_3)^+\text{Cl}^-$ , is dissolved in heavy water,  $\text{D}_2\text{O}$ , only half of the hydrogen atoms in the compound are replaced by deuterium. Explain why this happens.

**15.69** When phosphinic acid,  $\text{H}_3\text{PO}_2$ , is dissolved in heavy water,  $\text{D}_2\text{O}$ ,  $\text{HD}_2\text{PO}_2$  is formed. Suggest an explanation.

**15.70** If a strip of magnesium is ignited and placed in a container of dinitrogen oxide, it continues to burn brightly. Write a balanced chemical equation for the reaction. If the products are as you predict, how does this confirm the structure of the dinitrogen oxide molecule?

**15.71** The azide ion,  $\text{N}_3^-$ , is isoelectronic with carbon dioxide,  $\text{CO}_2$ . Deduce the formulas of two other nitrogen containing ions that are isoelectronic with them.

**15.72** Hyponitrous acid and nitroamide (nitramide) have the same formulas of  $\text{N}_2\text{O}_2\text{H}_2$ . Draw structures of these two compounds and contrast their acid-base behavior.

**15.73** The pentanitrogen hexafluoroarsenate(V) salt,  $(\text{N}_5)^+[\text{AsF}_6]^-$ , is only marginally stable at room temperature. Suggest how a more stable salt of this cation might be synthesized.

**15.74** Phosphorus and nitrogen form a polyatomic ion,  $(\text{P}_4\text{N}_{10})^{n-}$ . Deduce the charge,  $n-$ , on this ion.

**15.75** The azide ion can be considered as a pseudo-halide ion. Identify

- (a) an aqueous cation that would give a precipitate on addition to azide ion solution
- (b) the reaction of azide ion with water
- (c) a way in which azide ion does not resemble a halide ion



**15.76** The pentanitrogen ion,  $\text{N}_5^+$ , is V-shaped. Construct the electron-dot diagram and determine the bond order for each bond in the ion.

**15.77** Write a balanced chemical equation for the reaction of the explosive ADN,  $(\text{NH}_4)^+[\text{N}(\text{NO}_2)_2]^-$ , with aluminum powder. Explain the three main reasons why you would expect this reaction to be highly exothermic. What other aspect of the reaction would make it a good rocket propellant?

**15.78** An isomer of hydrazoic acid,  $\text{HN}_3$ , called *cyclotriazine*, contains a triangle of nitrogen atoms. Draw an electron-dot diagram for cyclotriazine. Do you expect all three nitrogen-nitrogen bond lengths to be equivalent? Give your reasoning.

**15.79** Research the traditional Marsh test used for arsenic. Write balanced chemical equations for each step in the procedure.

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# THE GROUP 16 ELEMENTS:

## The Chalcogens

## CHAPTER 16

O
S
Se
Te
Po

Again, the first two members of the group have the most significant chemistry: oxygen and sulfur. The differences between the first and second members that we saw for the Group 15 elements (nitrogen and phosphorus) are repeated in this group, except oxygen is the more reactive. Selenium and tellurium both possess some metalloid behavior, and only the radioactive element, polonium, can be said to exhibit metallic character.

### Context: Macular Degeneration and Singlet Oxygen

Elemental oxygen is, of course, essential for animal life on Earth through its involvement in respiration. However, oxygen is not always benign. As we will discuss in Section 16.3, one of the electrons in molecular oxygen,  $O_2$ , can be raised to an excited electronic energy state. There are several ways in which the excited state—called *singlet oxygen*—is formed, including exposure to ultraviolet radiation from the Sun. This singlet oxygen can cause significant cell damage as the energy is released and the molecule reverts to its ground state. Our

25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 16.1** Group Trends
- 16.2** Contrasts in the Chemistry of Oxygen and Sulfur
- 16.3** Allotropes of Oxygen
- 16.4** Oxygen and the Atmosphere
- 16.5** Bonding in Covalent Oxygen Compounds
- 16.6** Trends in Oxide Properties
- 16.7** Hydrogen Oxides
- 16.8** Hydroxides
- 16.9** Allotropes of Sulfur
- 16.10** Overview of Sulfur Chemistry
- 16.11** Hydrogen Sulfide
- 16.12** Sulfides
- 16.13** Sulfur Oxides
- 16.14** Sulfites
- 16.15** Sulfuric Acid
- 16.16** Sulfates and Hydrogen Sulfates
- 16.17** Other Oxosulfur Anions
- 16.18** Sulfur Halides
- 16.19** Sulfur-Nitrogen Compounds
- 16.20** Selenium
- 16.21** Biological Aspects
- 16.22** Element Reaction Flowcharts

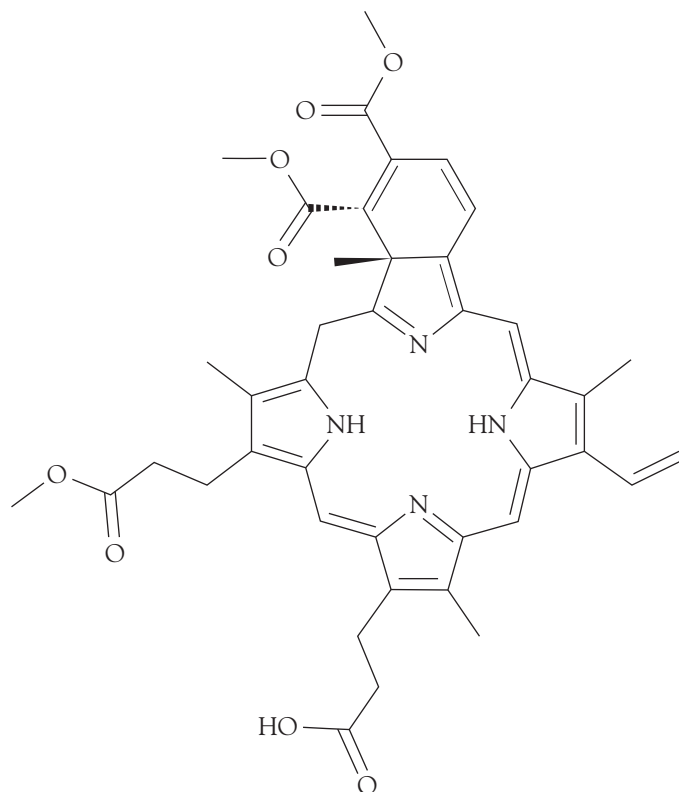
bodies rely on antioxidants to combat the effect of the rampaging high-energy oxygen molecules.

However, the destructive power of singlet oxygen can be harnessed for medical use. A common eye disease linked to aging is macular degeneration. Macular degeneration (the so-called “wet form”) results from the growth of abnormal blood vessels in the retina. For those affected, the central field of vision is lost and they have trouble recognizing faces and reading (see following figure).



Vision resulting from macular degeneration.

One form of treatment for wet macular degeneration is photodynamic therapy (PDT). In this treatment, singlet oxygen molecules are deliberately generated in these abnormal blood vessels and their destructive power damages these vessels and cuts off their blood supply. This procedure depends upon synthesizing a molecule which will first concentrate specifically in these blood vessels and second, upon input of energy, will catalyze the conversion of normal dioxygen to singlet dioxygen. One such molecule, known as *verteporfin*, is shown in the following figure. The center of the molecule is the same structure as the heme-ring of hemoglobin. After injection of a solution of verteporfin, red light of wavelength 693 nm is focused on the back of the patient's retina. The verteporfin absorbs the energy and transfers it to oxygen molecules. Singlet oxygen is produced, and the abnormal blood vessels severely damaged, preventing the disease from spreading further.



The verteporfin molecule.

## 16.1 Group Trends

This group is sometimes called the *chalcogens*. The common properties of these elements are shown in Table 16.1. Oxygen and sulfur are most definitely nonmetals, whereas polonium is a metal. Selenium and tellurium fall into an ambiguous area, just like arsenic in Group 15. The only crystalline form of tellurium consists of a network of spiral chains of atoms. The element has semiconductor properties and exhibits amphoteric behavior. Thus, a designation of metalloid is probably the most appropriate for tellurium.

**TABLE 16.1** Properties of the Group 16 elements

Element	Appearance at SATP	Electrical resistivity ( $\mu\Omega \cdot \text{cm}$ )	Acid-base properties of oxides
Oxygen	Colorless gas	—	—
Sulfur	White, waxy solid	$2 \times 10^{23}$	Acidic
Selenium	Red or gray	$10^6$	Acidic
Tellurium	Lustrous silvery solid	$4 \times 10^6$	Amphoteric
Polonium	Silvery metallic solid	43	Basic

**TABLE 16.2** Melting and boiling points of the Group 16 elements

Element	Melting point (°C)	Boiling point (°C)
O <sub>2</sub>	−219	−183
S <sub>8</sub>	119	445
Se <sub>8</sub>	221	685
Te	452	987
Po	254	962

Selenium illustrates the difficulty of artificial categorizations in that it has several allotropes. All but one are nonelectrically conducting red solids, consisting of ring structures analogous to those which we will discuss for sulfur. The nonred allotrope is a gray solid with a structure similar to that of tellurium, and, like tellurium, this allotrope of selenium is a semiconductor. Thus, selenium seems to teeter on the nonmetal-metalloid borderline. Most chemists choose to classify selenium as a third nonmetal member of the group. The melting and boiling points show the rising trend characteristic of nonmetals followed by the drop at metallic polonium (Table 16.2).

Except for oxygen, there are patterns in the oxidation states of the Group 16 elements. We find all of the even-numbered oxidation states from +6, through +4 and +2, to −2. The stability of the −2 and +6 oxidation states decreases down the group, whereas that of the +4 state increases. As happens in many groups, the trends are not as regular as we would like. For example, the +6 oxidation-state oxoacids have formulas: H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SeO<sub>4</sub>, however tellurium forms H<sub>6</sub>TeO<sub>6</sub>. Explanations can often be deduced in such cases. Here, if the acid formula is written according to its structure as (HO)<sub>2</sub>SO<sub>2</sub>, (HO)<sub>2</sub>SeO<sub>2</sub>, and (HO)<sub>6</sub>Te, we can surmise that possibly only tellurium is large enough to fit six hydroxido groups around the central atom.

## 16.2 Contrasts in the Chemistry of Oxygen and Sulfur

The contrast between the second period member and the third (and subsequent) period member found for the Group 15 elements (see Chapter 15, Section 15.2) is also found for the Group 16 elements. Thus, oxygen, like nitrogen, is limited to a maximum of four covalent bonds, whereas sulfur, like phosphorus, forms up to six covalent bonds. For example, oxygen forms only one normal oxide with fluorine, OF<sub>2</sub>, whereas sulfur forms several compounds with fluorine, including SF<sub>6</sub>.

Like nitrogen, the O=O bond is much stronger than the O—O bond. This large difference is in contrast to sulfur and the other members of the group, where the energy of two single bonds is greater than that of one double bond (Table 16.3). For this reason, multiple bonding is only common for oxygen.

**TABLE 16.3** A comparison of approximate oxygen and sulfur bond energies

Oxygen bonds	Bond energy (kJ·mol <sup>-1</sup> )	Sulfur bonds	Bond energy (kJ·mol <sup>-1</sup> )
O—O	142	S—S	268
O=O	494	S=S	425

In fact, compounds containing two oxygen atoms singly bonded together are usually strong oxidizing agents, and compounds containing three or more oxygen atoms bonded together are rare and tend to be highly explosive. Such behavior can be explained by the weakness of the O—O bond compared to its bonds to other elements (Table 16.4). Thus, oxygen will endeavor to bond to other elements rather than to itself. In particular, the covalent bond to hydrogen is very strong, and so the thermodynamically preferred outcome of a reaction involving oxygen is often water. Conversely, the S—S bond energy is only slightly lower than the energy of sulfur's bonds to other elements, thereby stabilizing catenation in sulfur compounds.

**TABLE 16.4** A comparison of approximate oxygen and sulfur bond energies with other elements

Oxygen bonds	Bond energy (kJ·mol <sup>-1</sup> )	Sulfur bonds	Bond energy (kJ·mol <sup>-1</sup> )
O—O	142	S—S	268
O—Cl	218	S—Cl	271
O—H	459	S—H	363

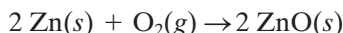
## 16.3 Allotropes of Oxygen

Gaseous oxygen exists in two allotropic forms: the common dioxygen and the less common trioxygen, commonly called *ozone*.

### Dioxygen

Dioxygen is a colorless, odorless gas that condenses to a pale blue liquid. Because it has a low molar mass and forms a nonpolar molecule, it has very low melting and boiling points. The gas does not burn, but it does support combustion. In fact, almost all elements will react with oxygen at room temperature or when heated. The main exceptions are the “noble” metals, such as platinum, and the noble gases. For a reaction to occur, the state of division of the reactant is often important: the smaller the particles, the greater the surface area and the greater the reactivity. In fact, very finely powdered metals

such as iron, zinc, and even lead will catch fire in air at room temperature. These finely divided forms of metals are sometimes called *pyrophoric*, a term reflecting their ability to catch fire. For example, zinc dust will inflame to give white zinc oxide:

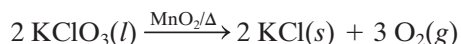


Dioxygen is not very soluble in water, about  $2 \times 10^{-5}$  mole fraction at 25°C compared to  $6 \times 10^{-4}$  for carbon dioxide. Nevertheless, the concentration of oxygen in natural waters is high enough to support marine organisms. The solubility of dioxygen decreases with increasing temperature; hence, it is the cold waters, such as the Labrador and Humboldt Currents, that are capable of supporting the largest fish stocks—and have been the focus of the most severe overfishing. Even though the solubility of dioxygen is low, it is twice that of dinitrogen. Hence, the gas mixture released by heating air-saturated water will actually be enriched in dioxygen.

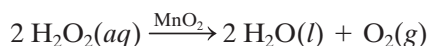
The measurement of dissolved oxygen (DO) is one of the crucial determinants of the health of a river or lake. Low levels of dissolved oxygen can be caused by eutrophication (excessive algae and plant growth) or an input of high-temperature water from an industrial cooling system. As a temporary expedient, air-bubbling river barges can be used to increase dissolved dioxygen levels. This has been done in London, England, to help bring back game fish to the River Thames. Almost the opposite of DO is BOD—biological oxygen demand—the measure that indexes the potential for oxygen consumption by aquatic organisms. Thus, a high BOD can indicate potential problems in a lake or river.

Dioxygen is a major industrial reagent; about  $10^9$  tonnes are used worldwide every year; mostly in the steel industry. Dioxygen is also employed in the synthesis of nitric acid from ammonia (see Chapter 15, Section 15.11). Almost all the oxygen is obtained by fractional distillation of liquid air. Dioxygen is consumed in large quantities by hospital facilities. In that context, it is mostly used to raise the dioxygen partial pressure in gas mixtures given to people with respiratory problems, making absorption of oxygen gas easier for poorly functioning lungs.

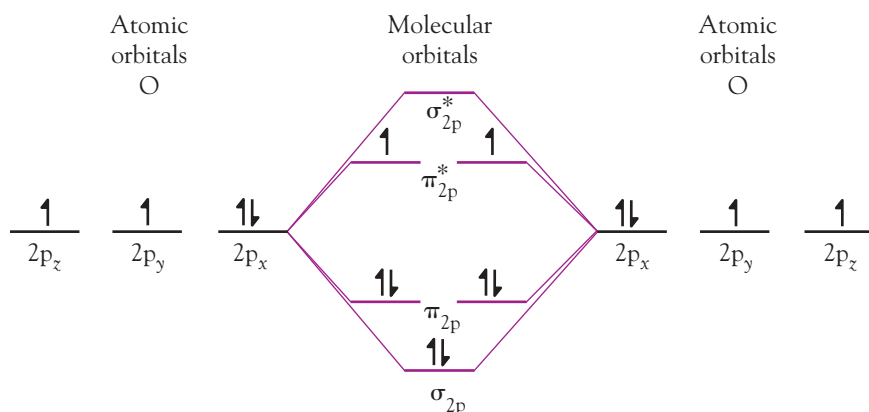
In the laboratory, there are a number of ways of making dioxygen gas. For example, strong heating of potassium chlorate in the presence of manganese(IV) oxide gives potassium chloride and oxygen gas:



However, a much safer route in the laboratory is the catalytic decomposition of aqueous hydrogen peroxide. Again, manganese(IV) oxide can be used as the catalyst:



As discussed in Chapter 3, Section 3.8, the molecular orbital model is the only representation of the bonding in dioxygen that fits with experimental evidence. Figure 16.1 indicates that the net bond order is 2 (six bonding electrons



**FIGURE 16.1** Molecular orbital energy level diagram showing the combination of the 2p atomic orbitals in the paramagnetic ground state of the dioxygen molecule.

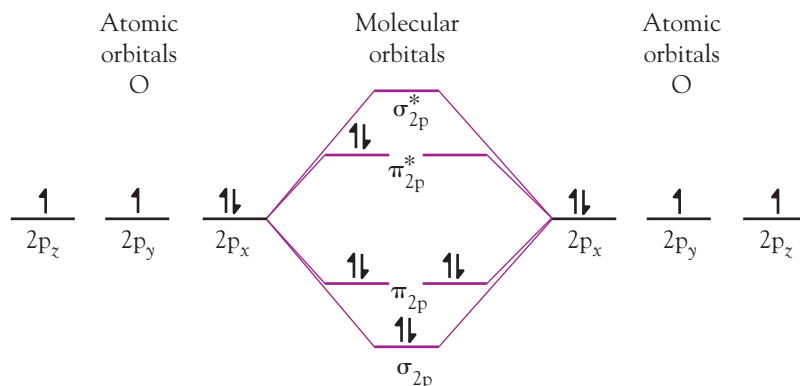
and two antibonding electrons), with the two antibonding electrons having parallel spins. The molecule, therefore, is paramagnetic.

However, an energy input of only  $95 \text{ kJ}\cdot\text{mol}^{-1}$  is required to cause one of the antibonding electrons to “flip” and pair with the other antibonding electron (Figure 16.2). This spin-paired (diamagnetic) form of dioxygen reverts to the paramagnetic form in seconds or minutes, depending on both the concentration and the environment of the molecule. The diamagnetic form can be prepared by the reaction of hydrogen peroxide with sodium hypochlorite:



Diamagnetic dioxygen is an important reagent in organic chemistry and gives products different from those of the paramagnetic form. Furthermore, diamagnetic oxygen, which is very reactive and formed by ultraviolet radiation, has been implicated in skin cancer induction. Diamagnetic oxygen is often referred to as *singlet oxygen*, and the paramagnetic form is called *triplet oxygen*.

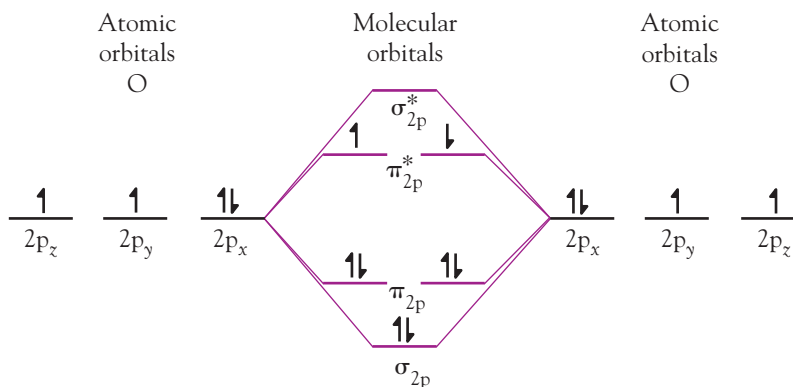
There is a second singlet form of dioxygen in which the spin of one electron is simply flipped over, so the resulting unpaired electrons have opposite spins (Figure 16.3). Surprisingly, this arrangement requires much more energy to attain; about  $158 \text{ kJ}\cdot\text{mol}^{-1}$ . As a result, this other singlet form is of little laboratory importance.



**FIGURE 16.2** Molecular orbital energy level diagram showing the combination of the 2p atomic orbitals in the lower-energy diamagnetic form of the dioxygen molecule.

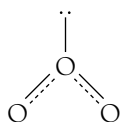


**FIGURE 16.3** Molecular orbital energy level diagram showing the combination of the 2p atomic orbitals in the higher-energy diamagnetic form of the dioxygen molecule.

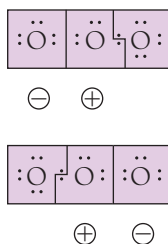


### Trioxxygen (Ozone)

Trioxxygen, a thermodynamically unstable allotrope of oxygen, is a diamagnetic gas with a strong odor. In fact, the “metallic” smell of ozone can be detected in concentrations as low as 0.01 ppm. The gas is extremely toxic; the maximum permitted concentration for extended exposure is 0.1 ppm. Ozone is produced in regions of high voltages; thus, heavily used photocopiers and laser printers have been responsible for high levels of ozone in many office environments.



**FIGURE 16.4** The ozone molecule.



**FIGURE 16.5** The bonding of trioxxygen can be interpreted as the mean of these two resonance structures.

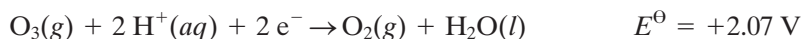
The trioxxygen molecule is V-shaped with a bond angle of  $117^\circ$ . Its O—O bonds are of equal length and have a bond order of about  $1\frac{1}{2}$  (Figure 16.4). Unsurprisingly, the bond angles and bond lengths of trioxxygen are very similar to those of the isoelectronic nitrite ion. The  $1\frac{1}{2}$  bond order can be simply understood in terms of the average of the two resonance structures shown in Figure 16.5. However, molecular orbital theory can provide a better picture of a  $\pi$ -system across all three atoms.

A convenient way to generate trioxxygen is to pass a stream of dioxygen through a 10 to 20 kV electric field. This field provides the energy necessary for the reaction:



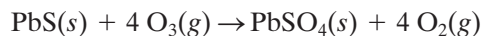
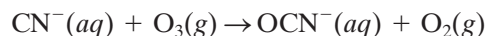
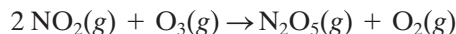
At equilibrium, the concentration of trioxxygen is about 10 percent. The trioxxygen slowly decomposes to dioxygen, although the rate of conversion depends on the phase (gas or aqueous solution).

Trioxxygen is a very powerful oxidizing agent, much more powerful than dioxygen, as can be seen from a comparison of reduction potentials in acid solution:



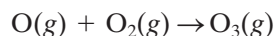
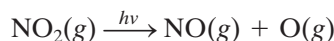
In fact, in acid solution, fluorine and the perxenate ion,  $\text{XeO}_6^{4-}$ , are the only common oxidizing agents that are stronger than trioxxygen. Its range of oxidizing

ability is illustrated by the following reactions—one in the gas phase, one in aqueous solution, and the third with a solid:



It is the strongly oxidizing nature of trioxygen that enables it to be used as a bactericide. For example, it is used to kill bacteria in bottled waters, and in France, particularly, it is used to kill organisms in municipal water supplies and public swimming pools. However, experts in North America have preferred the use of chlorine gas for water purification. There are advantages and disadvantages of both bactericides. Ozone changes to dioxygen over a fairly short period; thus, its bactericidal action is not long lasting. However, ozone is chemically innocuous in water supplies. Dichlorine remains in the water supply to ensure bactericidal action, but it reacts with any organic contaminants in the water to form hazardous organochlorine compounds (see Chapter 17, Section 17.13).

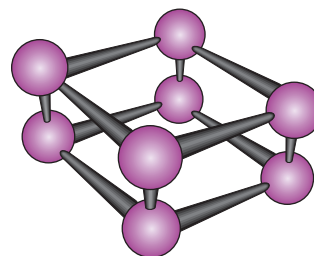
On the surface of the Earth, ozone is a dangerous compound, being a major atmospheric pollutant in urban areas. In addition to its damaging effect on lung tissue and even on exposed skin surfaces, ozone reacts with the rubber of tires, causing them to become brittle and crack. The ozone is produced by the photolysis of nitrogen dioxide, itself being formed mainly from internal combustion engines:



Ozone forms compounds with the alkali and alkaline earth metals. These compounds contain the trioxide(1−) ion,  $\text{O}_3^-$ . As we would expect from lattice stability arguments, it is the larger cations, such as cesium, that form the most stable trioxides. It has been shown that the trioxide(1−) is also V-shaped. Because the O—O bond length is 135 pm in the trioxide(1−) ion, slightly longer than the 128 pm bond in trioxygen itself, we can assume the additional electron is in an antibonding orbital.

### Octaoxygen

Dioxygen condenses to a light-blue liquid at 90 K and then solidifies to a light-blue solid at 54 K. There are several polymorphs of solid oxygen which are formed under increasing pressure. Above 10 GPa pressure, a different allotrope of oxygen,  $\text{O}_8$ , is formed. This allotrope, which was not predicted theoretically, is dark red in color and it is stable over a wide pressure range. The structure of octaoxygen has been conclusively shown to be a unique cube-like structure (Figure 16.6).



**FIGURE 16.6** The structure of the octaoxygen molecule.

## Oxygen Isotopes in Geology

Although we usually consider oxygen atoms to have eight neutrons (oxygen-16), there are in fact two other stable isotopes of the element. The isotopes and their abundances are:

Isotope	Abundance (%)
Oxygen-16	99.763
Oxygen-17	0.037
Oxygen-18	0.200

Thus, one oxygen atom in every 500 has a mass that is 12% greater than the other 499. This “heavy” oxygen will have slightly different physical properties, both as

the element and in its compounds. In particular,  $\text{H}_2^{18}\text{O}$  has a vapor pressure significantly lower than that of  $\text{H}_2^{16}\text{O}$ . Hence, in an equilibrium between liquid and gaseous water, the gas phase will be deficient in oxygen-18. Because the most evaporation occurs in tropical waters, those waters will have a higher concentration of oxygen-18. This increased proportion of oxygen-18 will be found in all the marine equilibria that involve oxygen.

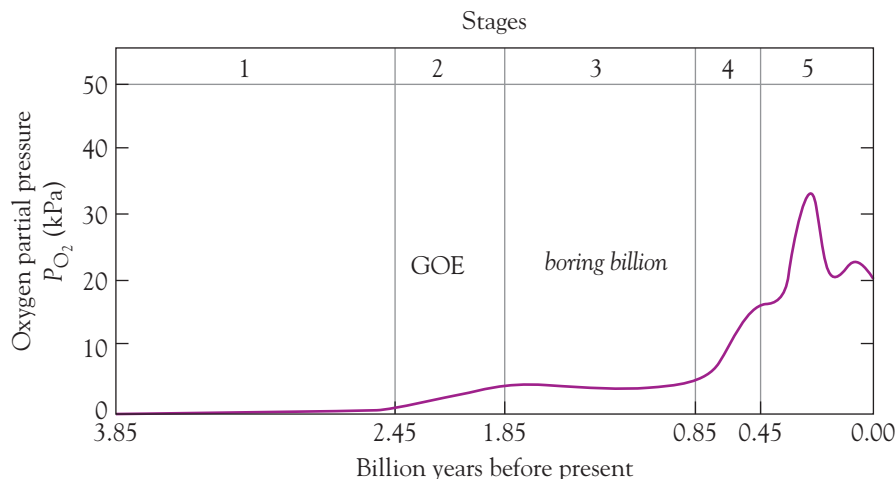
We can use the ratio of the two isotopes of oxygen to determine the temperature of the seas in which shells were formed millions of years ago simply by determining the oxygen isotopic ratio in the calcium carbonate of the shells. When the proportion of oxygen-18 is higher, the ancient seas were warmer.

## 16.4 Oxygen and the Atmosphere

### The Geological History of Dioxygen

Currently comprising 21% of Earth’s atmosphere, oxygen, an oxidizing gas, does not naturally occur in planetary atmospheres. The “normal” atmosphere of a planet is reducing, consisting mainly of the gases hydrogen, methane, ammonia, and carbon dioxide. As shown in Figure 16.7, from about 3.85 to 2.45 billion years ago the Earth’s atmosphere is believed to have contained nitrogen with some carbon dioxide, water vapour, and probably methane. It was cyanobacteria which were the first organisms to produce dioxygen gas from carbon dioxide.

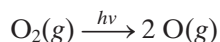
**FIGURE 16.7** The increase in atmospheric oxygen over geological time.



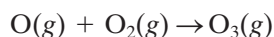
From 2.45 to 1.85 billion years B.P., atmospheric oxygen levels rose to between 2 and 4 kPa during the great oxygen event (GOE) as the rate of photosynthesis increased considerably. From 1.85 billion years to 0.85 billion years B.P., there seems to have been very little change in the atmospheric composition, and this stage became known as the *boring billion* years. Then from 0.85 billion years to 0.54 billion years B.P., the oxygen concentration rose until it reached close to the current level; somewhere between 10 and 20 kPa. Subsequently, it is widely believed that the oxygen level reached as high as 35 kPa during the Carboniferous period (0.36 billion years to 0.30 billion years B.P.) followed by a return to close to 20 kPa.

### The Ozone Layer

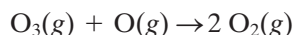
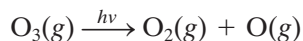
Until the dioxygen concentration in the atmosphere became significant, there was no ozone layer and the surface of the Earth was exposed to the life-destroying ultraviolet radiation from the Sun. As the dioxygen level increased, so the ozone layer commenced to form. The ozone cycle is quite complex, but the main steps are as follows. First, the shorter wavelength ultraviolet radiation reacts with dioxygen to produce atomic oxygen:



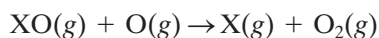
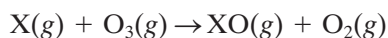
The atomic oxygen reacts with dioxygen to give trioxxygen:



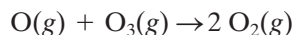
The trioxxygen absorbs longer-wavelength ultraviolet radiation and decomposes back to dioxygen:



Chemistry is rarely this simple, and the chemistry of the stratosphere is no exception. There are alternative routes for the destruction of ozone that involve trace components of the stratosphere, including hydrogen atoms, the hydroxyl radical, nitrogen monoxide, and chlorine atoms. These species, represented here by X, undergo a catalytic cycle for the decomposition of ozone without ultraviolet ray absorption:



to give the net reaction:



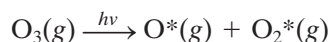
There is a particular reason why these four species act in this role—apart from the fact that they are known trace constituents of the upper atmosphere. Because there are equal numbers of gas molecules, entropy cannot be a significant driving factor for either reaction step; both steps must be exothermic. This places limits on X. Thus, for the first step, the X—O bond energy must be

greater than the difference between the  $\text{O}_3$  and  $\text{O}_2$  enthalpies of formation ( $107 \text{ kJ}\cdot\text{mol}^{-1}$ ). For the second step, the  $\text{X}-\text{O}$  bond energy must be less than the dioxygen bond energy ( $498 \text{ kJ}\cdot\text{mol}^{-1}$ ). And these conditions hold when  $\text{X}$  is  $\text{H}$ ,  $\text{OH}$ ,  $\text{NO}$ , or  $\text{Cl}$ .

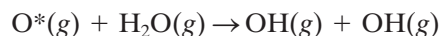
### The Hydroxyl Radical

Although we commonly regard tropospheric ozone as a nasty pollutant, it also serves a very important positive role in generating the “daytime detergent,” the hydroxyl radical. In Chapter 15, Section 15.8, we saw that the chemical reactions of the troposphere are dominated at night by the nitrate radical.

The hydroxyl radical is present in the troposphere during the day at concentrations of between  $10^5$  and  $10^6$  molecules $\cdot\text{cm}^{-3}$ . It is most commonly formed by the photodissociation of ozone by light of wavelengths less than 319 nm to give atomic and molecular oxygen (oxygen and dioxygen). The two species produced are in excited states, the atomic oxygen having two of its p electrons paired instead of the ground-state condition of all the p electrons being unpaired. The excited state can be indicated by an asterisk, \*, following the relevant chemical formula. Thus, the reaction is represented as



About 20 percent of the excited oxygen atoms collide with water molecules to form two hydroxyl radicals:



These hydroxyl radicals are potent oxidizing agents. On the whole, this is good, for they oxidize, fragment, and destroy gas-phase organic molecules. For example, methane is oxidized to methyl hydroperoxide,  $\text{CH}_3\text{OOH}$ , then to methanol,  $\text{HCHO}$ , and finally to carbon dioxide. Hydroxyl radicals oxidize atmospheric nitrogen dioxide to nitric acid and hydrogen sulfide to sulfur dioxide.

## 16.5 Bonding in Covalent Oxygen Compounds

### Bond Angles and the Bent Rule

An oxygen atom will usually form two single covalent bonds or one multiple bond, ordinarily a double bond. When two single bonds are formed, the angle between the bonds can be significantly different from the  $109.5^\circ$  tetrahedral angle. The traditional explanation for the bond angle of  $104.5^\circ$  in water asserts that the lone pairs occupy more space than bonding pairs, thus “squashing” the bond angle in the water molecule.

However, when we compare the two halogen-oxygen compounds—oxygen difluoride,  $\text{OF}_2$  (with a bond angle of  $103^\circ$ ), and dichlorine oxide,  $\text{Cl}_2\text{O}$  (with a bond angle of  $111^\circ$ )—we have to look for a different explanation. The best explanation relates to the degree of orbital mixing. In Chapter 3, Section 3.5, we introduced the hybridization model of bonding, where orbital characters mixed. Only integral values of mixing were described—for example, one s orbital

with three p orbitals to form four  $sp^3$  hybrid orbitals. However, there is no reason why the mixing cannot be fractional. Thus, some covalent bonds can have more s character and others, more p character. Also, beyond Period 2, we have to keep in mind that d orbitals might be mixed in as well. This approach of partial orbital mixing is, in fact, moving toward the more realistic molecular orbital representation of bonding.

It was Henry A. Bent who proposed an empirical rule—the *Bent rule*—to explain, among other things, the variation in bond angles of oxygen compounds. The rule states: More electronegative substituents “prefer” hybrid orbitals with less s character, and more electropositive substituents “prefer” hybrid orbitals with more s character. Thus, with fluorine (more electronegative), the bond angle tends toward the  $90^\circ$  angle of two “pure” p orbitals on the oxygen atom. Conversely, the angle for chlorine (less electronegative) is greater than that for an  $sp^3$  hybrid orbital, somewhere between the  $109.5^\circ$  angle of  $sp^3$  hybridization and the  $120^\circ$  angle of  $sp^2$  hybridization. An alternative explanation for the larger angle in dichlorine oxide is simply that there is a steric repulsion between the two large chlorine atoms, thus increasing the angle.

Oxygen can form coordinate covalent bonds either as a Lewis acid or as a Lewis base. The former is very rare; the compound  $NF_3O$  (mentioned in Chapter 15, Section 15.2) is one such case. However, oxygen readily acts as a Lewis base; for example, in the bonding of water molecules to transition metal ions through a lone pair on the oxygen (see Chapter 19).

There are other bonding modes of oxygen. In particular, oxygen can form three equivalent covalent bonds. The classic example is the hydronium ion, in which each bond angle is close to that of the tetrahedral value of  $109.5^\circ$  (Figure 16.8). However, such oxygen-containing molecules are not always tetrahedral. In the unusual cation  $[O(HgCl)_3]^+$ , the atoms are all coplanar and the  $Hg-O-Hg$  bond angle is  $120^\circ$  (Figure 16.9). To explain this, we must assume that the lone pair on the oxygen atom is not in its usual  $sp^3$  hybrid orbital but in a p orbital, where it can form a  $\pi$  bond with empty 6p orbitals of the mercury atom.

### Highest Oxidation States of Oxides

Oxygen often “brings out” a higher oxidation state than does fluorine. This may be a result of the ability of oxygen to form a  $\pi$  bond, using one of its own full p orbitals and an empty orbital on the other element, or it may simply be steric grounds. For example, osmium can fit four oxygen atoms to form  $OsO_4$  but not eight fluorine atoms to form  $OsF_8$  (Table 16.5).

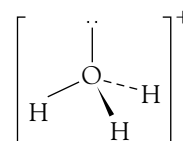


FIGURE 16.8 The hydronium ion.

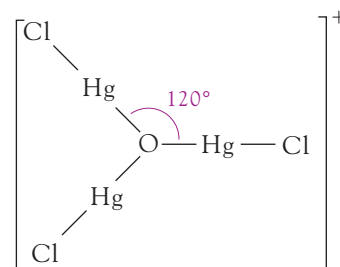


FIGURE 16.9 The  $[O(HgCl)_3]^+$  ion.

TABLE 16.5 Highest stable oxidation states of oxides and fluorides of three elements

Element	Highest oxide	Highest fluoride
Chromium	$CrO_3(+6)$	$CrF_5(+5)$
Xenon	$XeO_4(+8)$	$XeF_6(+6)$
Osmium	$OsO_4(+8)$	$OsF_7(+7)$

**WORKED EXAMPLE 16.1**

Sketch the electron-dot diagram for (a)  $\text{NF}_3\text{O}$  and (b)  $\text{CF}_2\text{O}$ .

**Answer**

(a) N is the central atom as it has the lowest electronegativity. There are a total of 32 electrons; 5 from N, 6 from O, and 7 from each F. As nitrogen cannot expand its octet, a  $\text{N}=\text{O}$  bond is necessary to give the best electron-dot diagram:

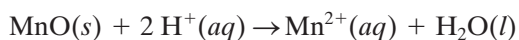


(b) C is the central atom as it has the lowest electronegativity. There are a total of 24 electrons; 4 from C, 6 from O, and 7 from each F. In this structure, a  $\text{C}=\text{O}$  bond is necessary to produce the best electron-dot diagram:

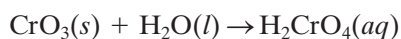
**16.6 Trends in Oxide Properties****Acid-Base Behavior of Metal Oxides**

The properties of an oxide depend on the oxidation number of the other element. For metal oxides, we find there is a transition in bonding types, as discussed in Chapter 9, Section 9.2. For example, chromium(III) oxide,  $\text{Cr}_2\text{O}_3$ , has a melting point of  $2266^\circ\text{C}$ , a value typical of ionic compounds, while chromium(VI) oxide,  $\text{CrO}_3$ , has a melting point of  $196^\circ\text{C}$ , a value typical of covalent compounds. The transition from ionic to covalent behavior can be linked to the increase in charge density of the metal ion.

This change in bonding type can be used to explain the difference in acid-base behavior among metal oxides. If the metal is in a low-oxidation state, typically +2, the oxide is basic (and sometimes reducing); for example, ionic manganese(II) oxide reacts with acid to give the aqueous manganese(II) ion:



If the metal is in the +3 oxidation state, the metal oxide is often amphoteric. Chromium(III) oxide, for example, reacts with acids to give the chromium(III) ion and with a strong base to give the chromite anion,  $\text{CrO}_2^-$ . The oxide of a high-oxidation-state metal is often acidic and oxidizing. Thus, covalently bonded chromium(VI) oxide reacts with water to give chromic acid:



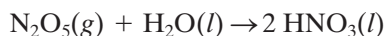
**TABLE 16.6** An approximate relationship between oxidation state and acid-base properties for metal oxides

Oxidation state	Properties	Examples
+1	Very basic	Na <sub>2</sub> O
+2	Basic	CaO, MnO
+3, +4, +5	Amphoteric	Al <sub>2</sub> O <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub> (not Fe <sub>2</sub> O <sub>3</sub> ), SnO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub>
+6, +7	Acidic	CrO <sub>3</sub> , Mn <sub>2</sub> O <sub>7</sub>

The typical properties of metal oxides are shown in Table 16.6.

### Acid-Base Behavior of Nonmetal Oxides

The oxides of nonmetals are always covalently bonded. Those with the element in a low-oxidation state tend to be neutral, whereas those with the element in the higher-oxidation states tend to be acidic. For example, dinitrogen oxide, N<sub>2</sub>O, is neutral, whereas dinitrogen pentoxide dissolves in water to give nitric acid:



The higher the oxidation state of the other element, the more acidic the properties. For example, sulfur dioxide is weakly acidic, while sulfur trioxide is a strongly acidic oxide. The typical properties of nonmetal oxides are shown in Table 16.7.

### Abnormal Oxidation States of Oxygen

It is always necessary to be cautious when assigning oxidation states in oxygen compounds for, as we have seen, there are oxygen ions in which oxygen itself has an abnormal oxidation state. These include the dioxide(2−) ion, O<sub>2</sub><sup>2−</sup>; the dioxide(1−) ion, O<sub>2</sub><sup>−</sup>; and the trioxide(1−) ion, O<sub>3</sub><sup>−</sup>. These exist only in solid-phase compounds, specifically those in which the metal cation has a charge density low enough to stabilize these large, low-charge anions.

Compounds in which the other element appears to have an abnormally high oxidation number usually contain the peroxide —O—O— linkage, in which each oxygen atom has the oxidation number of −1. Recalculating the oxidation numbers in such cases gives the other element a normal oxidation number. For example, in K<sub>2</sub>O<sub>2</sub>, the oxygen has the peroxide oxidation number of −1 rather than the oxide oxidation number of −2.

**TABLE 16.7** An approximate relationship between oxidation state and acid-base properties for nonmetal oxides

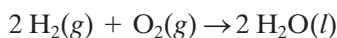
Oxidation state	Properties	Examples
+1, +2	Neutral	N <sub>2</sub> O, CO
+3, +4	Acidic	N <sub>2</sub> O <sub>3</sub> , NO <sub>2</sub> , CO <sub>2</sub> , SO <sub>2</sub>
+5, +6, +7	Strongly acidic	N <sub>2</sub> O <sub>5</sub> , SO <sub>3</sub> , Cl <sub>2</sub> O <sub>7</sub>



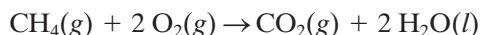
## 16.7 Hydrogen Oxides

### Water (Dihydrogen Oxide)

Water is formed when hydrogen gas and oxygen gas are mixed and a spark provided:



It is also one of the products when organic compounds, such as hydrocarbon fuels, are burned. For example, methane burns to give carbon dioxide and water:



Water is the ubiquitous liquid on Earth. In most ways it controls the chemistry of our planet. Liquid water has formed and re-formed Earth's surface over geological time. It has been able to do this because it can dissolve ionic substances, particularly the alkali and alkaline earth metals and the common anions such as chloride and sulfate. Thus, the composition of seawater reflects the leaching of ions from minerals since the time that Earth cooled enough to form liquid water. The current composition of the oceans, which make up 97 percent of the water on Earth, is shown in Table 16.8.

Many of the Earth's mineral deposits were formed by aqueous processes. The massive deposits of the alkali and alkaline earth minerals were formed by deposition from ancient seas and lakes. Less obvious is the mechanism of formation of heavy metal sulfide deposits, such as lead(II) sulfide. In fact, they are also the result of aqueous solution processes. Even though these minerals are extremely insoluble at common temperatures and pressures, this is not the case under the extremely high pressures and very high temperatures that exist deep under the Earth's surface. Under those conditions, many ions dissolve and are transported near to the surface, where reductions in temperature and pressure cause precipitation to occur.

In addition to ionic minerals, water can dissolve many polar covalent compounds. The ability of water to function as such a wide-ranging solvent results mostly from the high polarity of the O—H bond, as we discussed in Chapter 7, Section 7.1, and Chapter 10, Section 10.4.

Although most people are concerned about dehydration, an increasing number of athletes (marathon runners, triathletes, and even hikers) are severely diluting their blood by drinking too much water or too many sports drinks. In

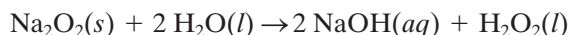
**TABLE 16.8** Ion proportions of the principal ionic constituents in seawater

Cation	Conc. (mol·L <sup>-1</sup> )	Anion	Conc. (mol·L <sup>-1</sup> )
Na <sup>+</sup>	0.469	Cl <sup>-</sup>	0.546
Mg <sup>2+</sup>	0.053	SO <sub>4</sub> <sup>2-</sup>	0.028
Ca <sup>2+</sup>	0.010	HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup>	0.002
K <sup>+</sup>	0.010	Br <sup>-</sup>	0.001

the 2002 Boston Marathon, 13 percent of the runners developed hyponatremia, abnormally low blood sodium levels, as a result of excessive water consumption. Typical symptoms are nausea, grogginess, and a lack of coherence. Death can ensue and has happened in several cases. Sports drinks labeled “isotonic” aim to prevent such symptoms by providing similar levels of salt and sugar as normally found in the body.

### Hydrogen Peroxide (Dihydrogen Dioxide)

There is a second combination of hydrogen and oxygen: hydrogen peroxide. Pure hydrogen peroxide is an almost colorless (slightly bluish), viscous liquid; its high viscosity is a result of strong hydrogen bonding between neighboring molecules. It is an extremely corrosive substance that should always be handled with great care. A solution of hydrogen peroxide can be prepared in the laboratory by the reaction of sodium peroxide with water:



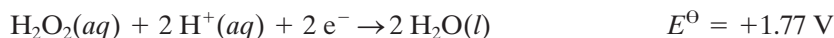
The shape of the molecule is unexpected; the H—O—O bond angle in the gas phase is only  $94.5^\circ$  (about  $10^\circ$  less than the H—O—H bond angle in water), and the two H—O units form a dihedral angle of  $111^\circ$  with each other (Figure 16.10).

Hydrogen peroxide is thermodynamically very unstable with respect to disproportionation:

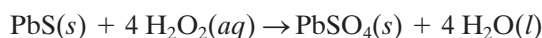


However, when pure, it is slow to decompose because of kinetic factors; that is, the reaction pathway must have a high-activation energy. Almost anything—transition metal ions, metals, blood, dust—will catalyze the decomposition.

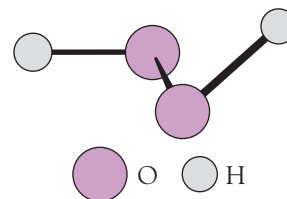
It is advisable to handle even dilute solutions of hydrogen peroxide with gloves and eye protection because it attacks the skin. Hydrogen peroxide can act as an oxidizing or reducing agent in both acidic and basic solutions. Oxidations are usually performed in acidic solution; reductions, in basic solution:



Hydrogen peroxide will oxidize iodide ion to iodine and reduce permanganate ion in acid solution to manganese(II) ion. A solution of hydrogen peroxide has an important application to the restoration of antique paintings. One of the favored white pigments was white lead, a mixed carbonate-hydroxide,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ . Traces of hydrogen sulfide cause the conversion of this white compound to black lead(II) sulfide, which discolors the picture. Application of hydrogen peroxide oxidizes the lead(II) sulfide to white lead(II) sulfate, thereby restoring the correct color of the painting:



Hydrogen peroxide is a major industrial chemical; about  $10^6$  tonnes are produced worldwide every year. Its uses are highly varied, from paper bleaching to household products, particularly hair bleaches. Hydrogen peroxide is



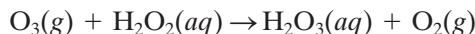
**FIGURE 16.10** The hydrogen peroxide molecule.



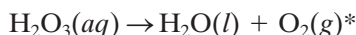
also used as an industrial reagent; for example, in the synthesis of sodium peroxoborate (see Chapter 13, Section 13.2).

### Dihydrogen Trioxide

Commonly called *trioxidane*, dihydrogen trioxide is formed from the reaction of ozone with hydrogen peroxide. This mixture is commonly used to decompose organic contaminants in groundwater, a method known as the *peroxone process*.



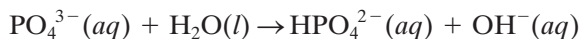
In organic solvents at room temperature, the molecule has a half-life of about 16 minutes, but in water, it lasts only milliseconds as a result of the reaction below, in which the highly reactive singlet oxygen molecule is produced.



## 16.8 Hydroxides

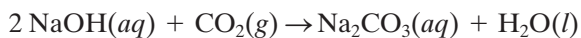
Almost every metallic element forms a hydroxide. The colorless hydroxide ion is the strongest base in aqueous solution. It is very hazardous because it reacts with the proteins of the skin, producing a white opaque layer. For this reason, it is especially hazardous to the eyes. Despite its dangerous nature, many household products, particularly oven and drain cleaners, utilize solid or concentrated solutions of sodium hydroxide. Sodium hydroxide is prepared by electrolysis of aqueous brine (see Chapter 11, Section 11.8).

It is also important to realize that, through hydrolysis, very high levels of hydroxide ion are present in products that do not appear to contain them. For example, the phosphate ion, used in sodium phosphate-containing cleansers, reacts with water to give hydroxide ion and the hydrogen phosphate ion:



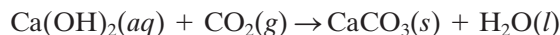
### Reaction with Carbon Dioxide

Solutions of the soluble hydroxides (the alkali metals, barium, and ammonium) react with the acidic oxide carbon dioxide present in the air to give the metal carbonate. For example, sodium hydroxide reacts with carbon dioxide to give sodium carbonate solution:



For this reason, solutions of hydroxides should be kept sealed except while being used. It is also one of the reasons why sodium hydroxide contained in glass bottles should be sealed with a rubber stopper rather than with a glass stopper. Some of the solution in the neck of the bottle will react to form crystals of sodium carbonate—enough to effectively “glue” the glass stopper into the neck of the bottle.

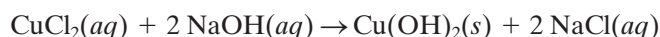
Alkali and alkaline earth metal hydroxides react with carbon dioxide, even when they are in the solid phase. For example, calcium hydroxide reacts with carbon dioxide to give calcium carbonate:



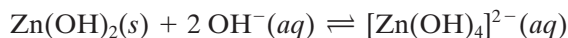
Calcium hydroxide is only partially water soluble—but soluble enough to give a significantly basic solution. A mixture of the saturated solution with a suspension of excess solid calcium hydroxide was referred to as “whitewash,” and it was used as a low-cost white coating for household painting. In fact, “whitewashing” first involves the penetration of the hydroxide ion into the wood or plaster surface, killing insects and mold spores. Then, over the following hours and days, it reacts with the carbon dioxide in the air to give microcrystalline, very insoluble, intensely white calcium carbonate. This process, performed by many of our ancestors, involved some very practical chemistry!

### Reaction with Metal Ions

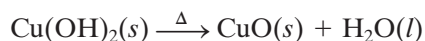
Many metal hydroxides can be prepared by adding a metal ion solution to a hydroxide ion solution. Thus, green-blue copper(II) hydroxide can be prepared by mixing solutions of copper(II) chloride with sodium hydroxide:



Most of the insoluble hydroxides precipitate out of solution as *gelatinous* (jellylike) solids, making them difficult to filter. The amphoteric hydroxides redissolve on addition of excess hydroxide ion. For example, zinc hydroxide redissolves to form the tetrahydroxozincate ion,  $[\text{Zn}(\text{OH})_4]^{2-}$ :



A few metal hydroxides are unstable; they lose water to form the oxide, which, with its higher charge, forms a more stable lattice. For example, even gentle warming of the green-blue copper(II) hydroxide gel produces the black solid copper(II) oxide:

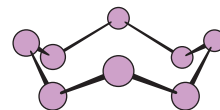


## 16.9 Allotropes of Sulfur

### cyclo-Octasulfur

The most common naturally occurring allotrope,  $\text{S}_8$ , *cyclo*-octasulfur, has a zigzag arrangement of the atoms around the ring (Figure 16.11). This allotrope forms needle-like crystals above  $95^\circ\text{C}$ , but below that temperature, “chunky” crystals are formed. The crystals, which are referred to as monoclinic and rhombic forms, differ simply in the way in which the molecules pack. These two forms are *polymorphs* of each other, not allotropes. Polymorphs are defined as different crystal forms in which identical units of the same compound are packed differently.

At its melting point of  $119^\circ\text{C}$ , *cyclo*-octasulfur forms a low-viscosity, straw-colored liquid. But when the liquid is heated, there is an abrupt change

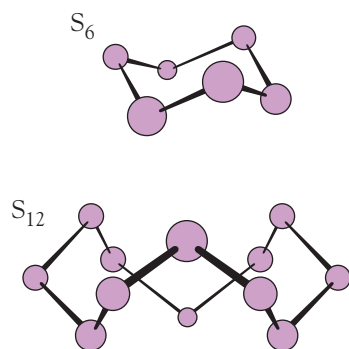


**FIGURE 16.11** The *cyclo*-octasulfur molecule.

in properties at 159°C. The most dramatic transformation is a 10 000-times increase in viscosity. The liquid also darkens considerably. These changes result from a rupture of the rings followed by a linking of the octasulfur chains to form polymers containing as many as 20 000 sulfur atoms. These intertwined chains have strong dispersion-force interactions between neighboring molecules.

As the temperature increases toward the boiling point of sulfur (444°C), the viscosity slowly drops as the polymer units start to fragment as a result of the greater thermal motion. If this liquid is poured into cold water, a brown transparent rubbery solid, called *plastic sulfur*, is formed. This material slowly changes to microcrystals of rhombic sulfur.

Boiling sulfur produces a green gaseous phase, most of which consists of *cyclo*-octasulfur. Raising the temperature even more causes the rings to fragment, and by 700°C, a violet gas is observed. This gas contains disulfur molecules,  $S_2$ , analogous to dioxygen.

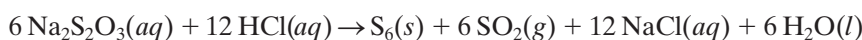


**FIGURE 16.12** The *cyclo*-hexasulfur and *cyclo*-dodecasulfur molecules.

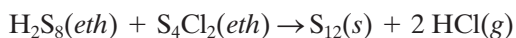
### *cyclo*-Hexasulfur and *cyclo*-Dodecasulfur

Over 100 years ago, a sulfur allotrope with a ring size other than 8 was first synthesized. This allotrope,  $S_6$ , *cyclo*-hexasulfur, was the second of many true allotropes of sulfur to be discovered. To distinguish allotropes and polymorphs, we can more correctly define *allotropes* as forms of the same element that contain different molecular units. Sulfur allotropes with ring sizes that range from 6 to 20 have been definitely synthesized, and there is evidence that allotropes with much larger rings exist. The most stable, apart from *cyclo*-octasulfur, is  $S_{12}$ , *cyclo*-dodecasulfur. The structures of *cyclo*-hexasulfur and *cyclo*-dodecasulfur are shown in Figure 16.12.

*Cyclo*-hexasulfur can be synthesized by mixing sodium thiosulfate,  $Na_2S_2O_3$ , and concentrated hydrochloric acid:



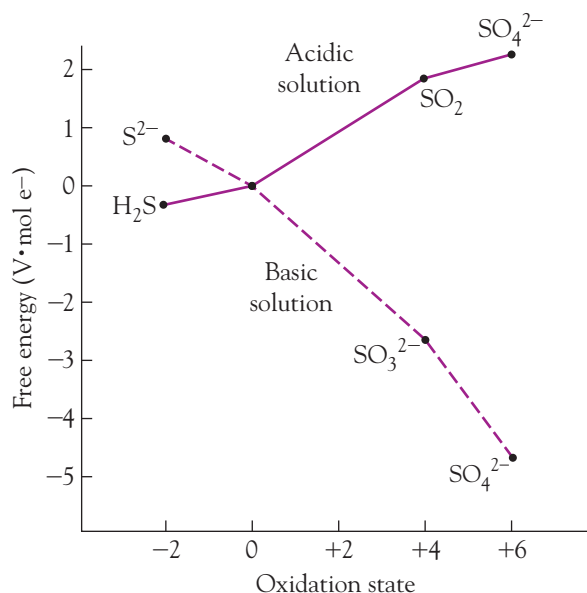
However, there is now a fairly logical synthesis of the even-numbered rings (which are more stable than the odd-numbered rings). The method involves the reaction of the appropriate hydrogen polysulfide,  $H_2S_x$ , with the appropriate polysulfur dichloride,  $S_yCl_2$ , such that  $(x + y)$  equals the desired ring size. Thus, *cyclo*-dodecasulfur can be prepared by mixing dihydrogen octasulfide,  $H_2S_8$ , and tetrasulfur dichloride,  $S_4Cl_2$ , in ethoxyethane,  $(C_2H_5)_2O$ , a solvent:



## 16.10 Overview of Sulfur Chemistry

### Stability of Oxidation States

Sulfur has a range of even oxidation states from +6 through +4 and +2 to −2. The oxidation-state diagram for sulfur in acidic and basic solutions is shown in Figure 16.13. The comparatively low free energy of the sulfate ion in acidic



**FIGURE 16.13** Frost diagram for sulfur in acidic and basic solutions.

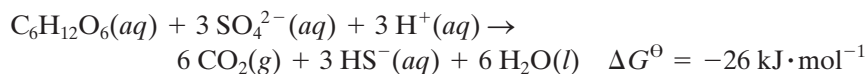
solution indicates that the ion is only weakly oxidizing. In basic solution, the sulfate ion is completely nonoxidizing, and it is the most thermodynamically stable sulfur species, although on a convex curve, the +4 oxidation state is actually quite kinetically stable. The Frost diagram does show that in acidic solution, the +4 state tends to be reduced, whereas in basic solution, it tends to be oxidized. The element itself is usually reduced in acidic environments but oxidized in base. Figure 16.13 also shows that the sulfide ion (basic solution) is a fairly strong reducing agent but that hydrogen sulfide is a thermodynamically stable species.

After carbon, sulfur is the element most prone to catenate. However, there are only two available bonds. Thus, the structures are typically chains of sulfur atoms with some other element or group of elements at each end. As examples, dihydrogen polysulfides have the formula HS—S<sub>n</sub>—SH and polysulfur dichlorides, ClS—S<sub>n</sub>—SCl, where *n* can have any value between 0 and 20.

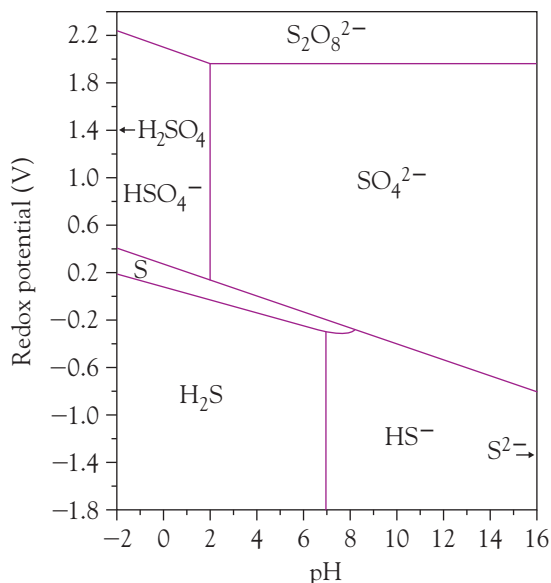
### pH Dependence of Oxidation States

As indicated by the Pourbaix diagram (Figure 16.14), under the normal range of potential and pH, sulfate is the thermodynamically favored species.

If sulfur(+6) is thermodynamically preferred, an obvious question is how sulfur(−2) is such a common oxidation state in nature. Organisms accomplish the reduction by coupling it with a strongly thermodynamically favored oxidation to give a net negative free energy change. A typical example is the oxidation of a carbohydrate to carbon dioxide:



**FIGURE 16.14** The Pourbaix diagram for sulfur. [From W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life* (Chichester, U.K.: John Wiley, 1994), p. 324.]

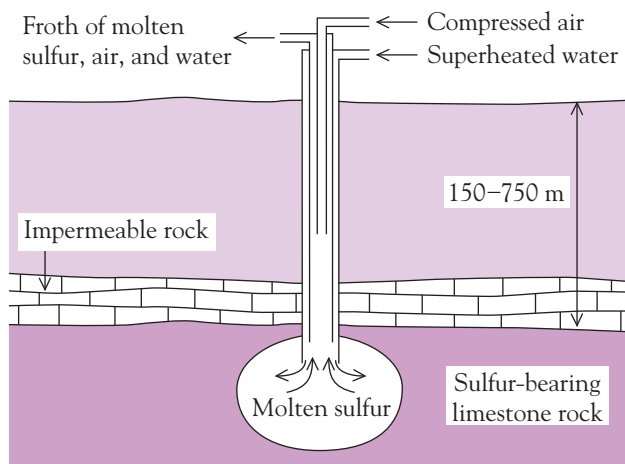


### The Industrial Extraction of Sulfur

Elemental sulfur is found in large underground deposits in both the United States and Poland. It is believed that these deposits were formed by the action of anaerobic bacteria on lake-bottom deposits of sulfate minerals.

The method of extraction, the *Frasch process*, was devised by the Canadian scientist Herman Frasch (Figure 16.15). The sulfur deposits are between 150 and 750 m underground and are typically about 30 m thick. A pipe, 20 cm in diameter, is sunk almost to the bottom of the deposit. Then a 10-cm pipe is inserted inside the larger one; this pipe is a little shorter than the outer pipe. Finally, a 2.5-cm pipe is inserted into the middle pipe but ends about halfway down the length of the outer pipes.

**FIGURE 16.15** The Frasch method of extraction of sulfur.



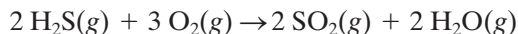
Water at 165°C is initially pumped down both outer pipes; this water melts the surrounding sulfur. The flow of superheated water down the 10-cm pipe is discontinued, and liquid pressure starts to force the dense liquid sulfur up that pipe. Compressed air is pumped down the 2.5-cm pipe, producing a low-density froth that flows freely up the 10-cm pipe to the surface. At the surface, the sulfur-water-air mixture is pumped into gigantic tanks, where it cools and the violet sulfur liquid crystallizes to a solid yellow block. The retaining walls of the tank are then removed, and dynamite is used to break up the blocks to a size that can be transported by railcar.

As we mentioned previously, the United States and Poland are the only countries fortunate enough to have large underground deposits of elemental sulfur. For their sulfur needs, other nations must resort to natural gas deposits, many of which contain high levels of hydrogen sulfide. Deposits that are low in hydrogen sulfide are known as “sweet gas,” and those containing high levels, between 15 and 20 percent typically, are known as “sour gas.” Gas producers are obviously only too pleased to find a market for this contaminant of the hydrocarbon mixtures.

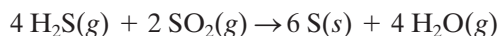
The production of elemental sulfur from the hydrogen sulfide in natural gas is accomplished by using the *Claus process*. The hydrogen sulfide is first extracted from the sour natural gas by bubbling the gas through ethanolamine,  $\text{HOCH}_2\text{CH}_2\text{NH}_2$ , a basic organic solvent, with the hydrogen sulfide acting as a Brønsted-Lowry acid:



The solution is removed and warmed, causing the hydrogen sulfide gas to be released. The hydrogen sulfide is then mixed with dioxygen in a 2:1 mole ratio rather than the 2:3 mole ratio that would be needed to oxidize all the hydrogen sulfide to water and sulfur dioxide. One-third of the hydrogen sulfide burns to give sulfur dioxide gas:



The sulfur dioxide produced then reacts with the remaining two-thirds of the hydrogen sulfide to give elemental sulfur:



To meet current emissions standards, the process has been improved; in modern plants, 99 percent conversion occurs, an extraction much better than the 95 percent conversion achieved in older plants.

Most of the world's sulfur production is needed for the synthesis of sulfuric acid, a process discussed in Section 16.17. The remainder is used to synthesize sulfur chemicals such as carbon disulfide for the vulcanization (hardening) of rubber and for the synthesis of sulfur-containing organic dyes. Some of the elemental sulfur is added to asphalt mixes to make more frost-resistant highway surfaces.



### Cosmochemistry: Io, the Sulfur-Rich Moon

Io, a moon of Jupiter, has a unique chemistry. The moon is about the same size as our own Moon, but Io's surface, unlike the Moon's dull gray surface, is ablaze with color—yellows, reds, and blues. The colors are believed to be largely the result of allotropes of sulfur and of sulfur compounds. Sulfur volcanoes dot the surface of Io, and the fountain-like plumes of the erupting sulfur volcanoes are among the most impressive and beautiful sights in the solar system. In fact, the eruptions resemble giant sulfur geysers, like fantastic yellow “Old Faithful” jets, spewing molten sulfur and sulfur compounds over 20 km into space before Io's weak gravity causes the sulfur “snow” to settle slowly back to the surface.

The chemistry of the tenuous atmosphere is also unusual, consisting mostly of sulfur dioxide together with more exotic species such as sulfur monoxide. Why is Io's chemistry unique? Sulfur is a common element throughout the solar system, but on planets such as Earth, sulfur is found as metal sulfides, particularly iron(II) sulfide. The heat that keeps Io's volcanoes active derives from the enormous gravitational attraction of Jupiter (and, to a lesser extent, that of Europa, another of Jupiter's moons). We have very little idea what chemical processes occur on this unique body, and many sulfur compounds on Io must be unknown to us on Earth. A visit to Io would certainly be top priority for any cosmochemist!

## 16.11 Hydrogen Sulfide

Most people have heard of the gas that smells like “rotten eggs,” although not as many could identify which gas it is. In fact, the obnoxious odor of hydrogen sulfide is almost unique. More important, this colorless gas is extremely toxic—more toxic than hydrogen cyanide. Because it is much more common, hydrogen sulfide presents a much greater hazard. As mentioned earlier, it sometimes is a component of the natural gas that issues from the ground; thus, gas leaks from natural gas wellheads can be dangerous. The odor can be detected at levels as low as 0.02 ppm; headaches and nausea occur at about 10 ppm, and death, at 100 ppm. Using smell to detect the gas is not completely effective because it kills by affecting the central nervous system, including the sense of smell.

### Bonding in Hydrogen Sulfide

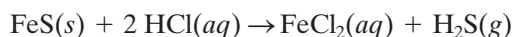
The hydrogen sulfide molecule has a V-shaped structure, as would be expected for an analog of the water molecule. However, as we descend the group, the bond angles in their hydrides decrease (Table 16.9). The variation of bond angle can be explained in terms of a decreasing use of hybrid orbitals by elements beyond Period 2. Hence, it can be argued that the bonding in hydrogen selenide involves p orbitals only. This reasoning is the most commonly accepted explanation because it is consistent with observed bond angles in other sets of compounds.

**TABLE 16.9** Bond angles of three Group 16 hydrides

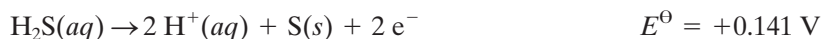
Hydride	Bond angle
H <sub>2</sub> O	104.5°
H <sub>2</sub> S	92.5°
H <sub>2</sub> Se	90°

### Properties of Hydrogen Sulfide

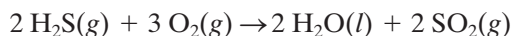
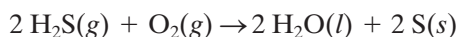
Hydrogen sulfide is produced naturally by anaerobic bacteria. In fact, this process, which occurs in rotting vegetation and bogs and elsewhere, is the source of most of the natural-origin sulfur in the atmosphere. The gas can be prepared in the laboratory by reacting a metal sulfide with a dilute acid, such as iron(II) sulfide with dilute hydrochloric acid:



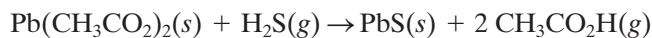
In solution, it is oxidized to sulfur by almost any oxidizing agent:



Hydrogen sulfide burns in air to give sulfur or sulfur dioxide, depending on the gas-to-air ratio:



The common test for the presence of significant concentrations of hydrogen sulfide utilizes lead(II) acetate paper (or a filter paper soaked in any soluble lead(II) salt, such as the nitrate). In the presence of hydrogen sulfide, the colorless lead(II) acetate is converted to black lead(II) sulfide:



In an analogous reaction, the blackening of silver tableware is usually attributed to the formation of black silver(I) sulfide.

### WORKED EXAMPLE 16.2

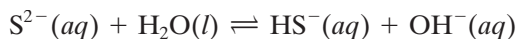
For the chalcogens, the boiling point increases from H<sub>2</sub>S to H<sub>2</sub>Te. Why, then, does H<sub>2</sub>O have an anomalously high boiling point?

#### Answer

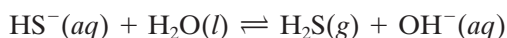
From H<sub>2</sub>S to H<sub>2</sub>Te, London (dispersion) forces predominate between molecules. These forces are dependent upon the number of electrons and hence increase down the Group. The high electronegativity difference between hydrogen and oxygen results in such a polar bond that strong hydrogen-bonding results in a high boiling point. ■

## 16.12 Sulfides

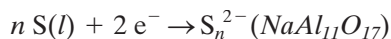
Only the Groups 1 and 2 metal ions, the ammonium ion, and the aluminum ion form soluble sulfides. These readily hydrolyze in water, and, as a result, solutions of sulfides are very basic:



There is enough hydrolysis of the hydrogen sulfide ion, in turn, to give the solution a strong odor of hydrogen sulfide:



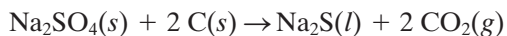
The sodium-sulfur system provides the basis for a high-performance battery. In most batteries, the electrodes are solids and the electrolyte a liquid. In this battery, however, the two electrodes, sodium and sulfur, are liquids and the electrolyte,  $\text{NaAl}_{11}\text{O}_{17}$ , is a solid. The electrode processes are:



The battery is extremely powerful, and it can be recharged readily. It shows great promise for industrial use, particularly for commercial electricity-driven delivery vehicles. However, adoption of this battery for household purposes is unlikely because it operates at about 300°C. Of course, it has to remain sealed to prevent reaction of the sodium and sulfur with the oxygen or water vapor in the air.

### Sodium Sulfide

Today, sodium sulfide is the sulfide in highest demand. Between  $10^5$  and  $10^6$  tonnes are produced every year by the high-temperature reduction of sodium sulfate with coke:



Sodium sulfide is used to remove hair from hides in the tanning of leather. It is also used in ore separation by flotation, for the manufacture of sulfur-containing dyes, and in the chemical industry, such as the precipitation of toxic metal ions, particularly lead.

### Insoluble Sulfides

All other metal sulfides are very insoluble. Many minerals are sulfide ores; the most common of these are listed in Table 16.10. Sulfides tend to be used for specialized purposes. The intense black diantimony trisulfide was one of the first cosmetics, used as eye shadow from earliest recorded times.

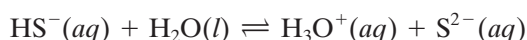
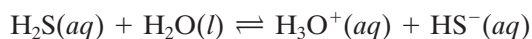
Other sulfides in commercial use are selenium disulfide,  $\text{SeS}_2$ , a common additive to antidandruff hair shampoos, and molybdenum(IV) sulfide,  $\text{MoS}_2$ , an excellent lubricant for metal surfaces, either on its own or suspended in oil. Metal sulfides tend to be dense, opaque solids, and it is this property

**TABLE 16.10** Common sulfide minerals

Common name	Formula	Systematic name
Cinnabar	HgS	Mercury(II) sulfide
Galena	PbS	Lead(II) sulfide
Pyrite	FeS <sub>2</sub>	Iron(II) disulfide
Sphalerite	ZnS	Zinc sulfide
Orpiment	As <sub>2</sub> S <sub>3</sub>	Diarsenic trisulfide
Stibnite	Sb <sub>2</sub> S <sub>3</sub>	Diantimony trisulfide
Chalcopyrite	CuFeS <sub>2</sub>	Copper(II) iron(II) sulfide

that makes the bright yellow cadmium sulfide, CdS, a popular pigment for oil painting.

The formation of insoluble metal sulfides used to be common in inorganic qualitative analysis. Hydrogen sulfide is bubbled through an acid solution containing unknown metal ions. The presence of the high hydrogen ion concentration reduces the sulfide ion concentration to extremely low levels:



This very low level of sulfide ion is still enough to precipitate the most insoluble metal sulfides, those with a solubility product,  $K_{\text{sp}}$ , smaller than  $10^{-30}$ . These metal sulfides are separated by filtration or centrifugation, and the pH of the filtrate is increased by adding base. This increase shifts the sulfide equilibrium to the right, thereby raising the concentration of sulfide ions to the point where those metal sulfides with a solubility product between  $10^{-20}$  and  $10^{-30}$  (mainly the transition metals of Period 4) precipitate. Specific tests can then be used to identify which metal ions are present. Alternatively, thioacetamide, a reagent that hydrolyzes to hydrogen sulfide, has been used for such tests.

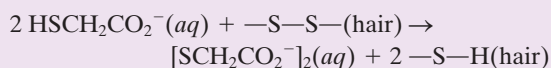


## Disulfides

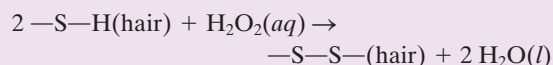
Unfortunately, chemists use the term *disulfide* for several different species. For example, carbon disulfide refers to the double-bonded covalent molecule,  $\text{S}=\text{C}=\text{S}$ . Also, molybdenum(IV) sulfide,  $\text{MoS}_2$  (see Chapter 21, Section 21.6), is commonly and incorrectly called *molybdenum disulfide*. Here we are referring to solid compounds containing the disulfide(2−),  $\text{S}_2^{2-}$ , ions analogous to, and more common than, the dioxide(2−),  $\text{O}_2^{2-}$ , ion. Thus,  $\text{FeS}_2$  does not contain iron in a high oxidation state but the disulfide(2−) ion and the iron(II) ion. These solid-state structures are found for manganese, iron, cobalt, nickel, ruthenium, and osmium. The crystal packing in each case can be described as a distorted NaCl-type lattice with the rod-shaped  $\text{S}_2$  units occupying the chloride sites and the metal ions, the sodium sites.

## Disulfide Bonds and Hair

Hair consists of amino acid polymers (proteins) cross-linked by disulfide units. In about 1930, researchers at the Rockefeller Institute showed that these links can be broken by sulfides or molecules containing —SH groups in slightly basic solution. This discovery proved to be the key to the present-day method for “permanently” changing the shape of hair, from curly to straight or vice versa. In the process, a solution of the thioglycollate ion,  $\text{HSCH}_2\text{CO}_2^-$ , is poured on the hair, reducing the —S—S— cross-links to —SH groups:



By using curlers or straighteners, the protein chains can then be mechanically shifted with respect to their neighbors. Application of a solution of hydrogen peroxide then reoxidizes the —SH groups to re-form new cross-links of —S—S—, thus holding the hair in the new orientation:



This is also the chemistry that is involved in chemical depilation but instead of remaking the S—S bonds, the weakened hair is scraped or washed away.

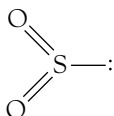
The disulfide ion also forms compounds with the alkali and alkaline earth metals. These particular disulfides are part of the polysulfide family, containing the  $\text{S}_n^{2-}$  ion, where  $n$  has values between 2 and 6. Unlike the heavy metal disulfides, these are water soluble.

## 16.13 Sulfur Oxides

There are two sulfur oxides of importance: the common pollutant sulfur dioxide and the less common, but equally important, sulfur trioxide. The activation energy for the oxidation of sulfur dioxide to sulfur trioxide is exceedingly high. This is very fortunate—it means we are faced with the weakly acidic dioxide as an atmospheric pollutant rather than the strongly acidic sulfur trioxide.

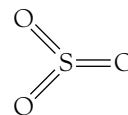
### Bonding in the Sulfur Oxides

The two oxides have related structures, so they will be discussed together. The sulfur dioxide molecule is V-shaped, with an S—O bond length of 143 pm and an O—S—O bond angle of  $119^\circ$ . The bond length is much shorter than that of a sulfur-oxygen single bond (163 pm) and very close to that of a typical sulfur-oxygen double bond (140 pm). The bonding and shape are shown in Figure 16.16. The similarity of the sulfur dioxide bond angle to the trigonal angle of  $120^\circ$  ( $\text{sp}^2$  hybridization) can be explained in terms of a  $\sigma$  bond between each sulfur-oxygen pair and a lone pair of electrons on the sulfur atom. We might expect the  $\pi$ -bond system to resemble that of the nitrite ion, but in addition, we could invoke some contribution to multiple bonding by interaction between the empty 3d orbitals of sulfur and full p orbitals of the oxygen atoms.



**FIGURE 16.16** A possible representation of the bonding in sulfur dioxide.

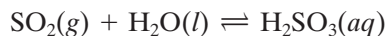
Gaseous sulfur trioxide is planar. Like sulfur dioxide, all the sulfur-oxygen bond lengths are equally short (142 pm) and very close to the typical double bond value. So in this case, the double bond  $\pi$  system is spread over all four atoms (Figure 16.17).



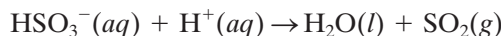
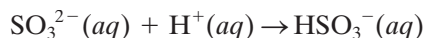
**FIGURE 16.17** A possible representation of the bonding in sulfur trioxide.

## Sulfur Dioxide

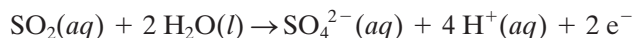
The common oxide of sulfur, sulfur dioxide, is a colorless, dense, toxic gas with an acid “taste.” The maximum tolerable levels for humans is about 5 ppm, but plants begin to suffer in concentrations as low as 1 ppm. The taste is a result of the reaction of sulfur dioxide with water on the tongue to give the weak acid sulfurous acid:



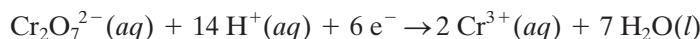
Sulfur dioxide is very water soluble, but like ammonia and carbon dioxide, almost all the dissolved gas is present as the sulfur dioxide molecule; only a very small proportion forms sulfurous acid. To prepare the gas in the laboratory, a dilute acid is added to a solution of a sulfite or a hydrogen sulfite:



Sulfur dioxide is a reducing agent, itself being easily oxidized to the sulfate ion:



To test for reducing gases, such as sulfur dioxide, we can use an oxidizing agent that undergoes a color change, the most convenient one being the dichromate ion. A filter paper soaked in acidified orange dichromate ion will turn green as a result of the formation of the chromium(III) ion:

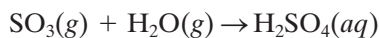
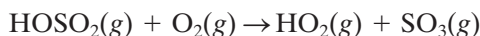
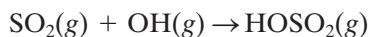


## Sulfur Dioxide as a Pollutant

Since Earth first solidified, sulfur dioxide has been released by volcanoes in large quantities. However, we are now adding additional, enormous quantities of this gas to the atmosphere. Combustion of coal is the worst offender because most coals contain significant levels of sulfur compounds. In London, the yellow smog of the 1950s caused by home coal fires led to thousands of premature deaths. Currently, coal-fired electric power stations are the major sources of unnatural sulfur dioxide in the atmosphere. Oil, too, contributes to the atmospheric burden of sulfur dioxide, for the lowest-cost heating oil is sulfur-rich. Finally, many metals are extracted from sulfide ores, and the traditional smelting process involves the oxidation of sulfide to sulfur dioxide, thereby providing an additional source of the gas. Copper is one such metal that is extracted from sulfide ores (see Chapter 20, Section 20.9).

In the past, the easiest solution to industrial air pollution problems was to provide ever-taller smokestacks so that the sulfur dioxide would travel

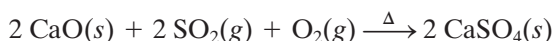
appreciable distances from the source. But during its time in the upper atmosphere, the sulfur dioxide is oxidized by the hydroxyl radical and hydrated to give droplets of sulfuric acid, a much stronger acid than sulfurous acid:



This product precipitates as acid rain, many hundreds or thousands of kilometers away, making the problem “someone else’s.” Currently, researchers are studying methods to minimize sulfur dioxide emissions. One of these involves the conversion of sulfur dioxide to solid calcium sulfate. In a modern coal-burning power plant, powdered limestone (calcium carbonate) is mixed with the powdered coal. The coal burns, producing a flame at about 1000°C, a temperature high enough to decompose the calcium carbonate:



Then the calcium oxide reacts with sulfur dioxide and oxygen gas to give calcium sulfate:



Because the second step is about as exothermic as the first step is endothermic, no heat is lost in the overall process. The fine dust of calcium sulfate is captured by electrostatic precipitators.

The solid calcium sulfate can be used for fireproof insulation and roadbed cement. However, as this process becomes more and more widely used, the supply of calcium sulfate will outstrip demand and using it for landfill will become more and more common. Thus, we have replaced a gaseous waste by a less harmful solid waste, but we have not eliminated the waste problem completely.

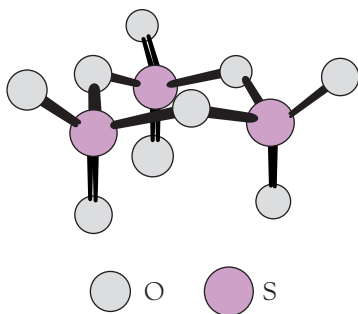
Sulfur dioxide does have some positive uses. It is used as a bleach and as a preservative, particularly for fruits. In this latter role, it is very effective at killing molds and other fruit-destroying organisms. Unfortunately, some people are sensitive to traces of the substance.

### Sulfur Trioxide

Most people have heard of sulfur dioxide, but few have heard of the other important oxide, sulfur trioxide, a colorless liquid at room temperature. The liquid and gas phases contain a mixture of sulfur trioxide,  $\text{SO}_3$ , and the trimer, trisulfur nonaoxide,  $\text{S}_3\text{O}_9$  (Figure 16.18). The liquid freezes at 16°C to give crystals of trisulfur nonaoxide. The trimer is isoelectronic and isostructural with the polyphosphate ion,  $(\text{P}_3\text{O}_9)^{3-}$ , and the polysilicate ion,  $(\text{Si}_3\text{O}_9)^{6-}$ . Sulfur trioxide is a very acidic, deliquescent oxide, reacting with water to form sulfuric acid:

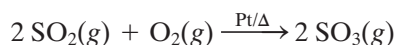


This oxide is so little known because oxidation of sulfur almost always gives sulfur dioxide, not sulfur trioxide. Even though the formation of sulfur trioxide



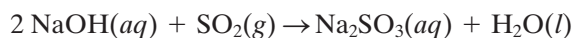
**FIGURE 16.18** The shape of the trisulfur nonaoxide.

is even more thermodynamically favored than that of sulfur dioxide ( $-370 \text{ kJ}\cdot\text{mol}^{-1}$  for sulfur trioxide,  $-300 \text{ kJ}\cdot\text{mol}^{-1}$  for sulfur dioxide), the oxidation has a high activation energy. Thus, the pathway from sulfur dioxide to sulfur trioxide is kinetically controlled:



## 16.14 Sulfites

Although sulfurous acid is mostly an aqueous solution of sulfur dioxide, the sulfite and hydrogen sulfite ions are real entities. In fact, sodium sulfite is a major industrial chemical with annual production of about  $10^6$  tonnes. It is most commonly prepared by bubbling sulfur dioxide into sodium hydroxide solution:



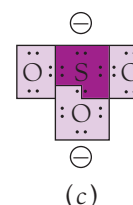
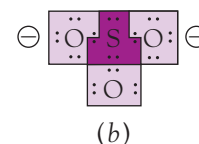
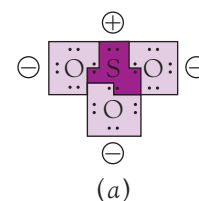
In the laboratory and in industry, sodium sulfite is used as a reducing agent, itself being oxidized to sodium sulfate:



The main use of sodium sulfite is as a bleach in the *Kraft process* for the production of paper. In this process, the sulfite ion attacks the polymeric material (lignin) that binds the cellulose fibers together (the loose cellulose fibers make up the paper structure). A secondary use, as we will see shortly, is in the manufacture of sodium thiosulfate. Like sulfur dioxide, sodium sulfite can be added to fruit as a preservative.

The sulfur-oxygen bond lengths in the sulfite ion are 151 pm, slightly longer than the 140 pm  $\text{S}=\text{O}$  bond. Although it is possible to draw electron-dot structures with all single bonds, we can use formal charge representations to see why multiple bonds are preferred (Figure 16.19).

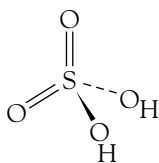
In Figure 16.19a, the single bond representation has formal charges on each atom, which makes this bonding arrangement unlikely. Figure 16.19c shows two double bonds and negative charges on neighboring atoms, again an unlikely scenario. It is the structure in Figure 16.19b, with one double bond, that has the minimum formal charge arrangement. However, it should be kept in mind that formal charge is a very simplistic method of approaching bonding and



**FIGURE 16.19** Three formal charge representations for the sulfite ion.



that a molecular orbital study provides a much more valid picture. If we take Figure 16.19b to represent one of three possible resonance structures, then each sulfur-oxygen bond can be assigned an average bond order of  $1/3$ .



**FIGURE 16.20** A possible representation of the bonding in sulfuric acid.

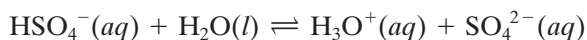
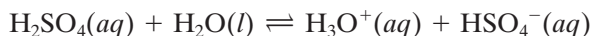
## 16.15 Sulfuric Acid

Hydrogen sulfate is an oily, dense liquid that freezes at  $10^{\circ}\text{C}$ . Concentrated sulfuric acid is a water mixture with an acid concentration of  $18\text{ mol}\cdot\text{L}^{-1}$ . Hydrogen sulfate mixes with water very exothermically. For this reason, it should be slowly added to water, not the reverse process, and the mixture should be stirred continuously. The molecule contains a tetrahedral arrangement of oxygen atoms around the central sulfur atom (Figure 16.20). The short bond lengths and the high bond energies suggest that there must be double bond character in the sulfur bonds to each terminal oxygen atom.

### Reactions of Sulfuric Acid

We usually think of sulfuric acid as just an acid, but in fact it can react in five different ways:

1. Dilute sulfuric acid is used most often as an acid. It is a strong, diprotic acid, forming two ions, the hydrogen sulfate ion and the sulfate ion:



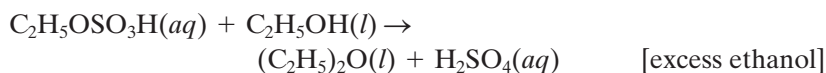
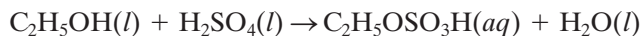
The first equilibrium lies far to the right, but the second one, less so. Thus, the predominant species in a solution of sulfuric acid are the hydronium ion and the hydrogen sulfate ion.



2. Sulfuric acid can also act as a dehydrating agent. The concentrated acid will remove the elements of water from a number of compounds. For example, sugar is converted to carbon and water. This exothermic reaction is spectacular:

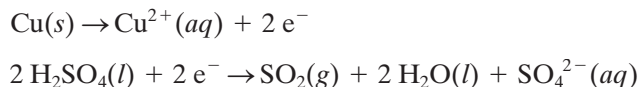


The acid serves this function in a number of important organic reactions. For example, addition of concentrated sulfuric acid to ethanol produces ethene,  $\text{C}_2\text{H}_4$ , or ethoxyethane,  $(\text{C}_2\text{H}_5)_2\text{O}$ , depending on the reaction conditions:

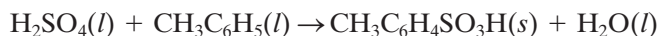


3. Although sulfuric acid is not as strongly oxidizing as nitric acid, if it is hot and concentrated, it will function as an oxidizing agent. For example,

hot concentrated sulfuric acid reacts with copper metal to give the copper(II) ion, and the sulfuric acid itself is reduced to sulfur dioxide and water:



4. Sulfuric acid can act as a sulfonating agent. The concentrated acid is used in organic chemistry to replace a hydrogen atom by the sulfonic acid group ( $-\text{SO}_3\text{H}$ ):

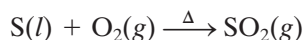


5. In special circumstances, sulfuric acid can behave as a base. A Brønsted-Lowry acid can only act as a base if it is added to a stronger proton donor. Sulfuric acid is a very strong acid; hence, only extremely strong acids such as fluorosulfonic acid (see the feature “Superacids” in Chapter 7) can cause it to behave as a base:



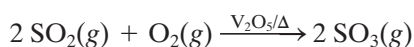
## The Industrial Synthesis of Sulfuric Acid

Sulfuric acid is synthesized in larger quantities than any other chemical. In the United States alone, production is about 165 kg per person per year! All synthetic routes use sulfur dioxide, and in some plants, this reactant is obtained directly from the flue gases of smelting processes. However, in North America, most of the sulfur dioxide is produced by burning molten sulfur in dry air:

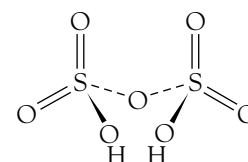
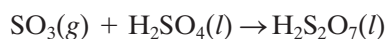


It is more difficult to oxidize sulfur further. As we mentioned in Section 16.15, there is a kinetic barrier to the formation of sulfur trioxide. Thus, an effective catalyst must be used to obtain commercially useful rates of reaction. We also need to ensure that the position of equilibrium is to the right side of the equation. To accomplish this, we invoke the Le Châtelier principle, which predicts that an increase in pressure will favor the side of the equation with the fewer moles of gas—in this case, the product side. This reaction is also exothermic; thus, the choice of temperature must be high enough to produce a reasonable rate of reaction, even though these conditions will result in a decreased yield.

In the *contact process*, pure, dry sulfur dioxide and dry air are passed through a catalyst of vanadium(V) oxide on an inert support. The gas mixture is heated to between 400 and 500°C, which is the optimum temperature for conversion to sulfur trioxide with a reasonable yield at an acceptable rate:



Sulfur trioxide reacts violently with water. However, it does react more controllably with concentrated sulfuric acid itself to give pyrosulfuric acid,  $\text{H}_2\text{S}_2\text{O}_7$  (Figure 16.21):



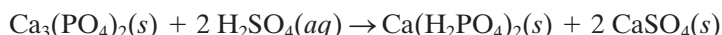
**FIGURE 16.21** A possible representation of the bonding in the pyrosulfuric acid molecule.

The pyrosulfuric acid is then diluted with water to produce an additional mole of sulfuric acid:

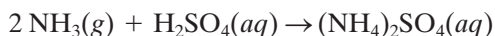


All steps in the process are exothermic. In fact, the entire process of converting elemental sulfur to sulfuric acid produces  $535 \text{ kJ} \cdot \text{mol}^{-1}$  of heat. An essential feature of any sulfuric acid plant is effective utilization of this waste heat, either as direct heating for some other industrial synthesis or in the production of electricity.

Use of the sulfuric acid varies from country-to-country. In the United States, the vast majority of acid is employed in the manufacture of fertilizers, such as the conversion of the insoluble calcium phosphate to the more soluble calcium dihydrogen phosphate:

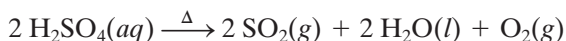


or the production of ammonium sulfate fertilizer:



In Europe, a higher proportion of the acid is used for manufacturing other products such as paints, pigments, and sulfonate detergents.

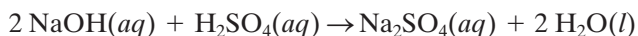
There is an increasing interest in trying to reclaim waste sulfuric acid. At present, the cost of removing contaminants and concentrating the dilute acid is greater than the cost of preparing the acid from sulfur. However, recovery is now preferred over dumping. If the acid is pure but too dilute, then pyrosulfuric acid is added to increase the concentration of acid to usable levels. For contaminated acid, high-temperature decomposition produces gaseous sulfur dioxide, which can be removed and used to synthesize fresh acid:



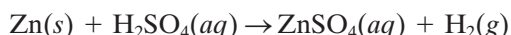
## 16.16 Sulfates and Hydrogen Sulfates

### Sulfates

Sulfates can be prepared by the reaction between a base, such as sodium hydroxide, and the stoichiometric quantity of dilute sulfuric acid:



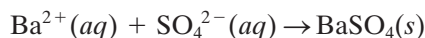
or by the reaction between an electropositive metal, such as zinc, and dilute sulfuric acid:



or by the reaction between a metal carbonate, such as copper(II) carbonate, and dilute sulfuric acid:



The common test for the presence of sulfate ion is the addition of barium ion, which reacts with the anion to give a dense white precipitate, barium sulfate:



Like the sulfite ion, the sulfate ion has a short sulfur-oxygen bond, a characteristic indicating considerable multiple bond character. In fact, at 149 pm, its length is about the same as that in the sulfite ion, within experimental error.

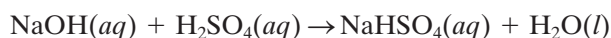
### The Sulfate Ion as a Counter-Ion

Sulfates and nitrates are the most commonly encountered metal salts. There are several reasons for the use of sulfates instead of nitrates:

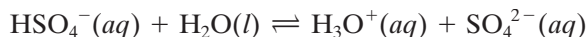
1. Most sulfates, but not all, are water soluble, making them a useful source of the metal cation. Two important exceptions are lead(II) sulfate, which plays an important role in the lead-acid battery, and barium sulfate, used in X-rays of soft tissues such as the stomach.
2. The sulfate ion is not oxidizing or reducing. Hence, the sulfate ion can form salts with metals in both their higher and their lower common oxidation states; for example, iron(II) sulfate and iron(III) sulfate. Furthermore, when dissolved in water, the sulfate ion will not initiate a redox reaction with any other ion present.
3. The sulfate ion is the conjugate base of a moderately strong acid (the hydrogen sulfate ion), so the anion will not significantly alter the pH of a solution.
4. The sulfates tend to be thermally stable, at least more stable than the equivalent nitrate salts.

### Hydrogen Sulfates

Hydrogen sulfates can be prepared by mixing the stoichiometric quantities of sodium hydroxide and sulfuric acid and evaporating the solution:



Like the hydrogen carbonates, only large, low-charge cations (such as the larger alkali metal ions), have charge densities low enough to stabilize these large, low-charge anions in the solid phase. The value of the second ionization of sulfuric acid is quite large, so the hydrogen sulfates give an acidic solution:



It is the high acidity of the solid sodium hydrogen sulfate that makes it useful as a household cleaning agent, such as Sani-Flush.

## 16.17 Other Oxosulfur Anions

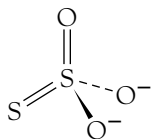
In addition to sulfate and sulfite, there are several other oxosulfur anions. For example, heating solid sodium hydrogen sulfate results in the formation of sodium pyrosulfate:



The pyrosulfate ion has the oxygen-bridged structure  $[\text{O}_3\text{S}-\text{O}-\text{SO}_3]^{2-}$ . This ion is not of great significance, but two others are, the thiosulfate ion,  $\text{S}_2\text{O}_3^{2-}$ , and the peroxodisulfate ion,  $\text{S}_2\text{O}_8^{2-}$ .

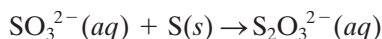
### Thiosulfates

The thiosulfate ion resembles the sulfate ion, except that one oxygen atom has been replaced by a sulfur atom (*thio-* is a prefix meaning “sulfur”). These two sulfur atoms are in completely different environments; the additional sulfur behaves more like a sulfide ion. In fact, a formal assignment of oxidation numbers gives the central sulfur a value of +5 and the other one, a value of −1, as discussed in Chapter 8, Section 8.3. The shape of the thiosulfate ion is shown in Figure 16.22. Although the ion is depicted as having two double bonds and two single bonds, the multiple bond character is actually spread more evenly over all the bonds.

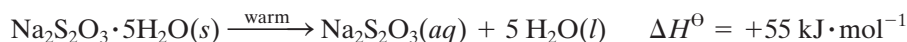


**FIGURE 16.22** A possible representation of the bonding in the thiosulfate ion.

Sodium thiosulfate pentahydrate, commonly called “hypo,” can easily be prepared by boiling sulfur in a solution of sodium sulfite:



Gentle warming causes the sodium thiosulfate pentahydrate to lose the water of crystallization in a reversible endothermic process:

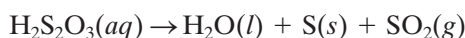
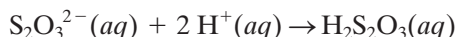


The equilibrium has generated considerable interest as a heat storage system. In this process, heat from the Sun is absorbed by solar panels and transferred to an underground tank of the hydrated compound. This input of heat causes the hydrate to decompose and dissolve in the water produced. Then, in the cool of the night, heat released as the compound crystallizes can be used to heat the dwelling.

Heating sodium thiosulfate strongly causes disproportionation into three different oxidation states of sulfur: sodium sulfate, sodium sulfide, and sulfur:

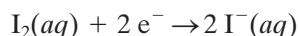


When handling solutions of the thiosulfate ion, it is important to avoid the presence of acid. The hydrogen (hydronium) ion first reacts to form thiosulfuric acid, which decomposes rapidly to give a white suspension of sulfur and the characteristic odor-taste of sulfur dioxide. This particular disproportionation is further evidence that the two sulfur atoms are in different oxidation states. Presumably, it is the central sulfur that provides the higher-oxidation-state sulfur in sulfur dioxide:



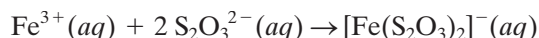
Sodium thiosulfate is also used in redox titrations. For example, it is used to determine the concentration of iodine in aqueous solutions. During the assay,

the iodine is reduced to iodide, and the thiosulfate ion of known concentration is oxidized to the tetrathionate ion,  $\text{S}_4\text{O}_6^{2-}$ :

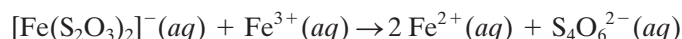


The tetrathionate ion contains bridging sulfur atoms (Figure 16.23).

Mixing cold solutions of thiosulfate ion and iron(III) ion gives a characteristic deep purple complex ion:

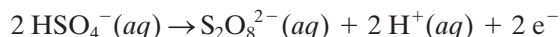


When warmed, this bis(thiosulfato)ferrate(III) ion,  $[\text{Fe}(\text{S}_2\text{O}_3)_2]^{-}$ , undergoes a redox reaction to give the iron(II) ion and the tetrathionate ion:



### Peroxodisulfates

Although the sulfate ion contains sulfur in its highest possible oxidation state of +6, it can be oxidized electrolytically to the peroxodisulfate ion by using smooth platinum electrodes, acidic solution, and high current densities. These conditions favor oxidations that do not produce gases such as the competing oxidation of water to dioxygen:



This ion contains a dioxo bridge (Figure 16.24) with an analogous structure to that of the tetrathionate ion (see Figure 16.23). Hence, the two sulfur atoms still have formal oxidation states of +6, but the bridging oxygen atoms have been oxidized from  $-2$  to  $-1$ . The terminal S—O bond lengths are all equivalent at 150 pm; once again, there must be considerable multiple bonding. The parent acid, peroxodisulfuric acid, is a white solid, but it is the two salts, potassium peroxodisulfate and ammonium peroxodisulfate, that are important as powerful, stable oxidizing agents:

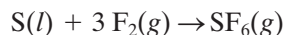


## 16.18 Sulfur Halides

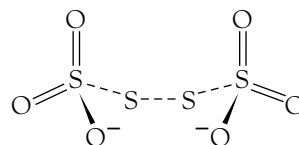
Whereas sulfur hexafluoride,  $\text{SF}_6$ , is a chemically inert gas, sulfur tetrafluoride,  $\text{SF}_4$ , is highly reactive. Surprisingly, the only stable chloride species are those in low oxidation states, sulfur dichloride,  $\text{SCl}_2$ , and disulfur dichloride,  $\text{S}_2\text{Cl}_2$ .

### Sulfur Hexafluoride

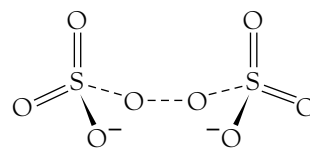
The most important compound of sulfur and fluorine is sulfur hexafluoride,  $\text{SF}_6$ . This compound is a colorless, odorless, unreactive gas. About 6500 tonnes are produced per year by simply burning molten sulfur in fluorine gas:



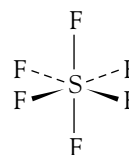
As would be expected from simple valence-shell electron-pair repulsion (VSEPR) theory, the molecule is octahedral (Figure 16.25).



**FIGURE 16.23** A possible representation of the bonding in the tetrathionate ion.



**FIGURE 16.24** A possible representation of the bonding in the peroxodisulfate ion.



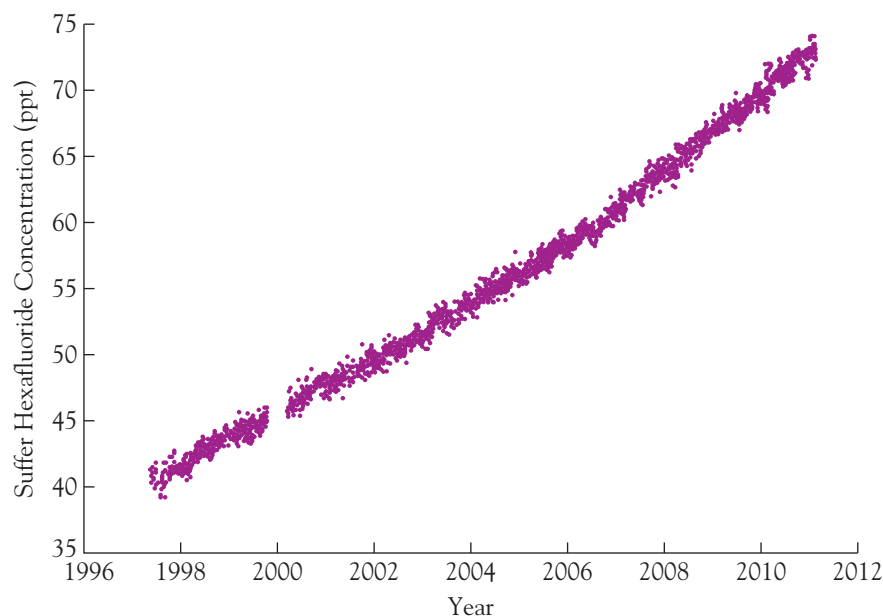
**FIGURE 16.25** The sulfur hexafluoride molecule.

As a result of its stability, low toxicity, and inertness, sulfur hexafluoride is used as an insulating gas in high-voltage electrical systems. At a pressure of about 250 kPa, it will prevent a discharge across a 1 MV potential difference that is separated by only 5 cm. Another major use is to blanket molten magnesium during the refining of the metal. There are many other uses, including filling noise-insulating double- and triple-glazed windows.

The very high molar mass of this gas makes it useful for several scientific applications. For example, air pollution can be tracked for thousands of kilometers by releasing a small amount of sulfur hexafluoride at the pollution source. The extremely high molar mass is so unique that the contaminated air mass can be identified days later by its tiny concentration of sulfur hexafluoride molecules. Similarly, deep ocean currents are being identified by bubbling sulfur hexafluoride into deep-water layers and then tracking the movement of the gas.

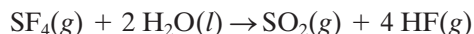
However, the very inertness of sulfur hexafluoride makes it a particular problem in the context of climatic impact. The gas absorbs radiation throughout much of the otherwise transparent part of the infrared region in the atmosphere. As a result, it is an extraordinarily effective greenhouse gas: 1 tonne of sulfur hexafluoride is equivalent to 23 900 tonnes of carbon dioxide in terms of infrared absorption. Further, there are no destruction pathways for sulfur hexafluoride, except above 60 km, where it is destroyed by the intense ultraviolet radiation. Thus, the atmospheric lifetime of the gas is estimated as at least 3000 years. Compared to total carbon dioxide emissions, sulfur hexafluoride represents less than 1 percent of contributions to increased energy absorption. However, with the increasing use of this gas, it is imperative that we take all possible steps to ensure that as little sulfur hexafluoride as possible escapes into the atmosphere. Figure 16.26 shows the rapid increase in atmospheric concentration of sulfur hexafluoride over recent years.

**FIGURE 16.26** The increase in the atmospheric concentration of sulfur hexafluoride in recent decades.

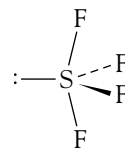


### Sulfur Tetrafluoride

It is interesting that the other common sulfur-fluorine compound, sulfur tetrafluoride, is extremely reactive. It decomposes in the presence of moisture to hydrogen fluoride and sulfur dioxide:



Its high reactivity might be due to the “exposed” lone pair site, where reaction can take place. The compound is a convenient reagent for the fluorination of organic compounds. For example, it converts ethanol to fluoroethane. As simple VSEPR theory predicts, it has a slightly distorted seesaw shape (Figure 16.27).



**FIGURE 16.27** The sulfur tetrafluoride molecule.

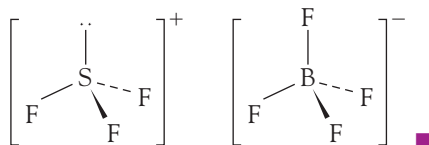
### WORKED EXAMPLE 16.3

$\text{SF}_4$  reacts with  $\text{BF}_3$  to form  $[\text{SF}_3]^+[\text{BF}_4]^-$ . Use VSEPR theory to predict the shapes of the cation and anion.

#### Answer

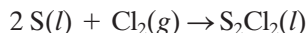
The cation is  $[\text{SF}_3]^+$ . There will be a total of 26 valence electrons; 6 from S plus 7 from each F and minus 1 to account for the charge. This results in 3 bonding pairs and 1 lone pair so the cation is a trigonal pyramid.

The anion is  $[\text{BF}_4]^-$ . There will be a total of 32 valence electrons; 3 from B plus 7 from each F plus 1 to account for the charge. This results in 4 bonding pairs so the anion is tetrahedral.



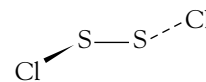
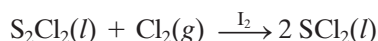
### Sulfur Chlorides

Whereas sulfur forms high-oxidation-state compounds with fluorine, it forms stable low-oxidation-state compounds with chlorine. Bubbling chlorine through molten sulfur produces disulfur dichloride,  $\text{S}_2\text{Cl}_2$ , a toxic, yellow liquid with a revolting odor:



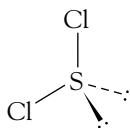
The compound is used in the *vulcanization* of rubber; that is, the formation of disulfur cross-links between the carbon chains that make the rubber stronger. The shape of the molecule resembles that of hydrogen peroxide (Figure 16.28).

No compound of sulfur and chlorine containing a higher sulfur oxidation state than +2 is stable at room temperature. If chlorine is bubbled through disulfur dichloride in the presence of catalytic diiodine, sulfur dichloride,  $\text{SCl}_2$ , is formed:



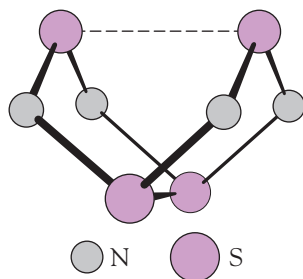
**FIGURE 16.28** The disulfur dichloride molecule.





**FIGURE 16.29** The sulfur dichloride molecule.

This foul-smelling red liquid is used in the manufacture of a number of sulfur-containing compounds, including the notorious mustard gas,  $\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2$ . Mustard gas was used in World War I and, more recently, by the former Iraqi regime against some of its citizens. Liquid droplets containing this gas cause severe blistering of the skin, followed by death. As predicted by VSEPR theory, the sulfur dichloride molecule is V-shaped (Figure 16.29).



**FIGURE 16.30** The tetrasulfur tetranitride molecule.

There are several sulfur-nitrogen compounds. Some of these are of interest because their shapes and bond lengths cannot be explained in terms of simple bonding theory. The classic example is tetrasulfur tetranitride,  $\text{S}_4\text{N}_4$ . Unlike the crown structure of octasulfur, tetrasulfur tetranitride has a closed, basket-like shape, with multiple bonding around the ring and weak bonds cross-linking the pairs of sulfur atoms (Figure 16.30).

Of much more interest, however, is the polymer  $(\text{SN})_x$ , commonly called *polythiazyl*. This bronze-colored, metallic-looking compound was first synthesized in 1910, yet it was not until 50 years later that an investigation of its properties showed it to be an excellent electrical conductor. In fact, at very low temperatures (0.26 K), it becomes a superconductor. There is an intense interest in making related nonmetallic compounds that have metallic properties, both because of their potential for use in our everyday lives and because they may help us develop the theory of metals and superconductivity.

## 16.20 Selenium

Until the 1960s, the only major use of selenium was as a glass additive. Addition of cadmium selenide,  $\text{CdSe}$ , to a glass mixture results in a pure ruby red color that is much valued by glass artisans. Cadmium selenide is a semiconductor compound used in photocells because its electrical conductivity varies as a function of the light intensity to which it is exposed.

It was the invention of xerography (from the Greek *xero*, “dry,” *graphy*, “writing”) as a means for duplicating documents that turned an element of little interest into one that affects everyone’s life. Xerography is made feasible by the unique photoconducting properties of selenium. The heart of a photocopier (and a laser printer) is a drum coated with selenium. The surface is charged in an electric field of about  $10^5 \text{ V}\cdot\text{cm}^{-1}$ . The areas exposed to a high light intensity (the white areas of the image) lose their charge as a result of photoconductivity. Toner powder then adheres to the charged areas of the drum (corresponding to the black parts of the image). In the next step, the toner is transferred to the paper, where a heat source melts the particles, bonding them to the paper fibers and producing the photocopy. Tellurium is used in color photocopiers to alter the color sensitivity of the drum.

## 16.21 Biological Aspects

### Oxygen: The Most Essential Element

We can live without food for days, without water for hours or days (depending on the temperature), but without dioxygen, life ceases in a very short time. We inhale about 10 000 L of air per day, from which we absorb about 500 L of oxygen gas. The dioxygen molecule bonds at the lung surface to a hemoglobin molecule; in fact, an oxygen molecule covalently bonds to each of the four iron atoms in a hemoglobin molecule. The process of uptake is amazing in that once the first dioxygen molecule is bonded to an iron atom, the ease of bonding of the second dioxygen is increased, as is that of the third and fourth in turn. This *cooperative effect* contrasts strikingly with the normal chemical equilibria, in which successive steps are usually less favored.

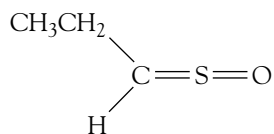
The hemoglobin transports the dioxygen to the muscles and other energy-utilizing tissues, where it is transferred to myoglobin molecules. The myoglobin molecule (similar to one of the units in hemoglobin) contains one iron ion, and it bonds with the dioxygen molecule even more strongly than the hemoglobin molecule does. Once the first dioxygen molecule is removed from the hemoglobin, the cooperative effect operates again, this time making it easier and easier to remove the remaining dioxygen molecules. The myoglobin molecules store the dioxygen until it is needed in the energy-producing redox reaction with sugars that provides the energy our bodies require to survive and function.

### Sulfur: The Importance of Oxidation State

Sulfur resembles nitrogen in that its biologically important oxidation state is the negative one. Just as amino acids incorporate  $\text{—NH}_2$  (ox. no. N =  $-3$ ), so they incorporate  $\text{—SH}$  (ox. no. S =  $-2$ ), the thiol unit in the important amino acid cysteine,  $\text{HSCH}_2(\text{NH}_3^+)\text{COO}^-$ . The presence of sulfur enables this specific amino acid in a protein chain to cross-link to another, as we mentioned earlier in this chapter in the feature “Disulfide Bonds and Hair.” Sulfur is also one of the most crucial coordination sites in proteins for metal ions. It bonds to the widest range of metal ions of any amino acid functional group. The metal ions might be expected to be those favoring a soft base, but in fact, the sulfur is a strong bonding site for some metals one might think prefer hard bases. The metal ions are zinc(II), copper(I), copper(II), iron(II), iron(III), molybdenum(IV)–(VI), and nickel(I)–(III).

Other sulfur-containing biological molecules include vitamin B<sub>1</sub> (thiamine) and the coenzyme biotin (which, in spite of its name, does not contain tin). Furthermore, many of our antibiotics, such as penicillin, cephalosporin, and sulfanilamide, are sulfur-containing substances. In the  $-2$  oxidation state, the majority of the simple sulfur-containing compounds have obnoxious odors. For example, the odorous molecules from onion, garlic, and skunk all contain sulfur in this oxidation state. Many of the naturally occurring sulfur-containing molecules involve rather bizarre chemical structures. For example, the lachrymatory

Ethanethiol,  $\text{CH}_3\text{CH}_2\text{SH}$ , listed in the *Guinness Book of World Records* as the world's most evil-smelling substance, is added to odorless natural gas supplies so that we can detect leaks. Concentrations as low as 50 ppb are detectable by the human nose.



**FIGURE 16.31** The molecule responsible for the eye irritation that accompanies the task of peeling onions.

(tear-inducing) factor in onions is the molecule depicted in Figure 16.31, containing the unusual C—S—O group.

### Selenium: A Little Does You Good

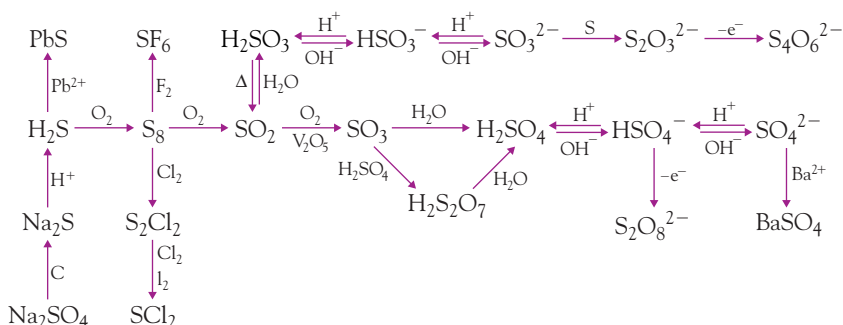
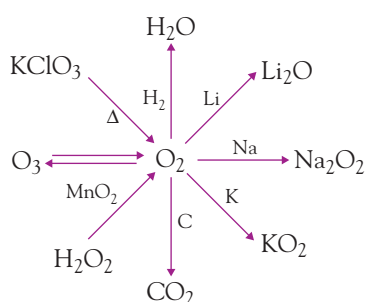
Selenium is essential to health as we described in the Context section of Chapter 2. Selenium deficiency is much more prevalent than excess. In the United States, the Pacific Northwest, the Northeast, and Florida have soils that are very low in selenium. Animals whose diet is low in selenium suffer from muscular degeneration, known as “white muscle disease.” For humans, the continent-wide movement of foodstuffs normally provides an adequate level of selenium in a balanced diet. To ensure adequate selenium intake (about 100 mg per year), one should ensure having a diet containing selenium-rich foods such as mushrooms, garlic, asparagus, fish, and animal liver or kidney. A correlation has been shown between higher levels of selenium in water supplies and decreased incidence of breast and colon cancer.

In parts of China, the soils are almost totally selenium-deficient and major human health problems exist. In addition to health problems directly attributable to selenium deficiency, the deficiency results in a lowered resistance to viral infection. Kashan disease, fatal and endemic across a broad band of rural China, results from inflammation of heart muscles by the family of Cocksackieviruses. These viruses are normally harmless but mutate into a virulent form in the weakened immune system of a selenium-deficient host. It has been suggested that the Asian origin of most new influenza viruses might have the same cause: that they similarly mutate in the selenium-deficient population of the region. Perhaps a massive international effort to eradicate selenium deficiency in China might have the side benefit to all humanity of reducing the incidence of new flu strains.

Although we talk about a deficiency in selenium, it is important to realize that, in reality, we are referring to compounds of selenium. In the typical biological range of *E* and pH, the most common species are those of selenium(IV), specifically the selenite ion,  $\text{SeO}_3^{2-}$ , and the hydrogen selenite ion,  $\text{HSeO}_3^-$ .

## 16.23 Element Reaction Flowcharts

Flowcharts are shown for both oxygen and sulfur, the two key elements in Group 16.



## KEY IDEAS

- Oxygen has properties that are quite different from those of other members of the group.
- Dioxygen has important electronically excited states.
- Trioxxygen, ozone, is a strongly oxidizing allotrope of oxygen.
- Oxides range from strongly basic to strongly acidic.
- Water is a crucial solvent for chemical reactions.
- Sulfur exists in several allotropes.
- Sulfides are very insoluble, and many minerals are metal sulfides.
- Sulfuric acid serves many roles in chemistry.
- Sulfate is a commonly used anion.

## EXERCISES

**16.1** Write balanced chemical equations for the following chemical reactions:

- finely divided iron with dioxygen
- solid barium sulfide with trioxxygen
- solid barium dioxide ( $2-$ ) and water
- potassium hydroxide solution with carbon dioxide
- sodium sulfide solution with dilute sulfuric acid
- sodium sulfite solution and sulfuric acid
- sodium sulfite solution with *cyclo*-octasulfur

**16.2** Write balanced chemical equations for the following chemical reactions:

- heating potassium chlorate
- solid iron(II) oxide with dilute hydrochloric acid
- iron(II) chloride solution with sodium hydroxide solution
- dihydrogen octasulfide with octasulfur dichloride in ethoxyethane
- heating sodium sulfate with carbon
- sulfur trioxide gas and liquid sulfuric acid
- peroxodisulfate ion with sulfide ion

**16.3** Why is polonium the only element in this group to be classified as a metal?

**16.4** Discuss the essential differences between oxygen and the other members of Group 16.

**16.5** Define the following terms: (a) pyrophoric; (b) polymorphs; (c) cooperative effect.

**16.6** Define the following terms: (a) mixed metal oxide; (b) vulcanization; (c) the Claus process.

**16.7** Why is Earth's atmosphere so chemically different from that of Venus?

**16.8** River and lake waters are commonly used by electrical generating plants for cooling purposes. Why is this a potential problem for wildlife?

**16.9** Predict the bond order in the trioxxygen cation,  $O_3^+$ . Explain your reasoning. Is the ion paramagnetic or diamagnetic?

**16.10** As we have seen, dioxygen forms two anions,  $O_2^-$  and  $O_2^{2-}$ , with bond lengths of 133 and 149 pm, respectively; the length of the bond in the dioxygen molecule itself is 121 pm. In addition, dioxygen can form a cation,  $O_2^+$ . The bond length in this ion is 112 pm. Use a molecular orbital diagram to deduce the bond order and the number of unpaired electrons in the dioxygen cation. Is the bond order what you would expect for the bond length?

**16.11** Dibromine oxide decomposes above  $240^\circ\text{C}$ . Would you expect the  $\text{Br}-\text{O}-\text{Br}$  bond angle to be larger or smaller than the  $\text{Cl}-\text{O}-\text{Cl}$  bond angle in dichlorine oxide? Explain your reasoning.

**16.12** Osmium forms osmium(VIII) oxide,  $\text{OsO}_4$ , but the fluoride with the highest oxidation number of osmium is osmium(VII) fluoride,  $\text{OsF}_7$ . Suggest an explanation.

**16.13** Suggest a structure for the  $\text{O}_2\text{F}_2$  molecule, explaining your reasoning. Determine the oxidation number of oxygen in this compound and comment on it.

**16.14** The mineral thortveitite,  $\text{Sc}_2\text{Si}_2\text{O}_7$ , contains the  $[\text{O}_3\text{Si}-\text{O}-\text{SiO}_3]^{6-}$  ion. The  $\text{Si}-\text{O}-\text{Si}$  bond angle in this ion has the unusual value of  $180^\circ$ . Use hybridization concepts to account for this.

**16.15** The compound  $\text{F}_3\text{C}-\text{O}-\text{O}-\text{O}-\text{CF}_3$  is unusual for oxygen chemistry. Explain why.

**16.16** Barium forms a sulfide of formula  $\text{BaS}_2$ . Use an oxidation number approach to account for the structure of this compound. Suggest why this compound exists, but not similar compounds with the other alkaline earth metals.

**16.17** Draw structures of the following molecules and ions: (a) sulfuric acid; (b) the  $\text{SF}_5^-$  ion; (c) sulfur tetrafluoride; (d) the  $\text{SOF}_4$  molecule. *Hint:* The oxygen is in the equatorial plane.

**16.18** Draw structures of the following molecules and ions: (a) thiosulfate ion; (b) pyrosulfuric acid; (c) peroxodisulfuric acid; (d) the  $\text{SO}_2\text{Cl}_2$  molecule.

**16.19** Suggest a structure for the  $S_4(NH)_4$  molecule. Explain your reasoning.

**16.20** Disulfur difluoride,  $S_2F_2$ , rapidly converts to thiothionyl fluoride,  $SSF_2$ . Construct electron-dot diagrams for these two molecules. Use oxidation numbers to explain why this rearrangement would occur.

**16.21** The unstable molecule  $SO_4$  contains a three-membered ring of the sulfur atom and two oxygen atoms. The other two oxygen atoms are doubly bonded to the sulfur atom. Draw an electron-dot formula for the compound. Then derive the oxidation states of each atom in this molecule and show that no abnormal oxidation states are involved.

**16.22** Describe the hazards of (a) trioxygen; (b) hydroxide ion; (c) hydrogen sulfide.

**16.23** Describe, using a chemical equation, why “whitewash” was such an effective and inexpensive painting material.

**16.24** Although sulfur catenates, it does not have the extensive chemistry that is found for carbon. Explain briefly.

**16.25** Describe the changes in *cyclo*-octasulfur as it is heated. Explain the observations in terms of changes in molecular structure.

**16.26** Describe the essential features of the Frasch and the Claus processes.

**16.27** The bond angle in hydrogen telluride,  $H_2Te$ , is  $89.5^\circ$ ; that in water is  $104.5^\circ$ . Suggest an explanation.

**16.28** Explain why an aqueous solution of sodium sulfide has an odor of hydrogen sulfide.

**16.29** Describe the five ways in which sulfuric acid can behave in chemical reactions.

**16.30** Why must the formation of sulfur trioxide from sulfur dioxide be an exothermic reaction?

**16.31** Which will have the stronger average sulfur-oxygen bond energy, sulfur trioxide or the sulfite ion? Use formal charges to justify your answer.

**16.32** Suggest two alternative explanations why telluric acid has the formula  $H_6TeO_6$  rather than  $H_2TeO_4$ , analogous to sulfuric and selenic acids.

**16.33** Construct formal charge representations for (a) sulfate ion; (b) sulfurous acid.

**16.34** Why is the sulfate anion commonly used in chemistry?

**16.35** What are the chemical tests used to identify (a) hydrogen sulfide; (b) sulfate ion?

**16.36** What are the major uses for (a) sulfur hexafluoride; (b) sodium thiosulfate?

**16.37** Why is sulfur dioxide rather than sulfur trioxide the most common sulfur compound in the oxygen-rich atmosphere?

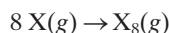
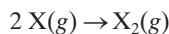
**16.38** What would happen on this planet if hydrogen bonding ceased to exist between water molecules?

**16.39** Whereas potassium ozonide,  $KO_3$ , is unstable and explosive, tetramethylammonium ozonide,  $[(CH_3)_4N]O_3$ , is stable up to  $75^\circ C$ . Suggest an explanation.

**16.40** Suggest an explanation why sulfur hexafluoride sublimates at  $-64^\circ C$  while sulfur tetrafluoride boils at  $-38^\circ C$ .

**16.41** Draw the structure of the  $NS_2^+$  ion. What neutral molecule is isoelectronic and isostructural with it?

**16.42** Given that the  $S=S$  bond energy is  $425 \text{ kJ}\cdot\text{mol}^{-1}$ , using data from Appendix 3, calculate the enthalpy of reaction for:



where  $X = \text{oxygen}$  and  $X = \text{sulfur}$ . Hence, show that the formation of the diatomic molecule is energetically preferable for oxygen, while it is the octamer that is favored for sulfur.

**16.43** “Selenium is beneficial and toxic to life.” Discuss this statement.

**16.44** Write balanced chemical equations corresponding to each transformation in the element reaction flowcharts for oxygen and sulfur (page 468).

## BEYOND THE BASICS

**16.45** Calculate the enthalpy of formation of (theoretical) gaseous sulfur hexachloride and compare it to the tabulated value for sulfur hexafluoride. Suggest why the values are so different.

**16.46**  $S_2F_{10}$  is an unusual fluoride of sulfur. It consists of two  $SF_5$  units joined by a sulfur-sulfur bond. Calculate

the oxidation number for the sulfur atoms. This molecule disproportionates. Suggest the products and write a balanced equation. Use oxidation numbers to explain why the products would be those that you have selected.

**16.47** Ammonium thioglycollate is used for hair straightening or curling, while calcium thioglycollate is used for

hair removal. The ammonium glycolate does not act so drastically on the hair because the solution is less basic than that of the calcium salt. Explain the reason for the difference in solution pH.

**16.48** Use an approximate molecular orbital diagram to determine the bond order in the hydroxyl radical.

**16.49** If the daytime hydroxyl radical concentration is  $5 \times 10^5 \text{ molecule} \cdot \text{cm}^{-3}$ , what concentration does that represent in parts per million (ppm) or parts per billion (ppb) at SATP (25°C and 100 kPa)? The gas constant,  $R$ , is  $8.31 \text{ kPa} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .

**16.50** (a) Sulfur tetrafluoride reacts with cesium fluoride to give an electrically conducting solution of a monatomic cation and a polyatomic anion containing the sulfur atom. Write a chemical equation for the reaction.

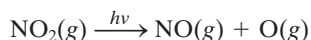
(b) Sulfur tetrafluoride reacts with boron trifluoride to give an electrically conducting solution in which the polyatomic cation contains the sulfur. Write a chemical equation for the reaction.

(c) Suggest an explanation why sulfur tetrafluoride behaved differently in the two reactions.

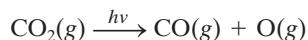
**16.51** Calculate the length of side of the unit cell of the perovskite calcium titanate, assuming

- the titanium and oxide ions are in contact or
- the calcium and oxide ions are in contact. The radius of the  $\text{Ti}^{4+}$  ion is 74 pm.

**16.52** The crucial reaction in polluted tropospheric air is:



It is this energy input and the formation of reactive oxygen atoms that initiate most of the pollution chemistry cycles. Calculate the minimum energy needed for this process and hence the longest wavelength of light that could initiate this process. Also, show that the parallel reaction



is not feasible in terms of the wavelength of light required.

**16.53** Construct two possible electron-dot diagrams for the  $\text{SOCl}_2$  molecule. Use formal charge principles to deduce which is the more likely. Then draw the structural formula and mark the approximate bond angles.

**16.54** The bacteria in hydrothermal vents derive their metabolic energy from the oxidation of the hydrogen sulfide ion to the sulfate ion. Calculate the free energy change for this process at 298 K from standard reduction potentials from online Appendix 9.

**16.55** Sulfur dioxide is the most important contributor to acid rain. It can be removed from coal-burning power

plants using calcium carbonate. Write a balanced equation for the reaction. If a coal contained 3.0 percent sulfur, what mass of calcium carbonate would be needed to react with the sulfur dioxide produced from 1000 tonnes of coal?

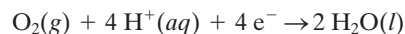
**16.56** When hydrogen peroxide is added to a basic solution of potassium chromate, a compound of formula  $\text{K}_3\text{CrO}_8$  is formed. Deduce the oxidation state of chromium in this compound, explaining your reasoning.

**16.57** Another oxyacid of sulfur is  $\text{H}_2\text{SO}_5$ . Calculate the apparent oxidation number of sulfur in this compound. Is this oxidation number feasible? Suggest a structure of the compound that would give a common oxidation number for the sulfur atom. *Hint:* This acid reacts with water to form sulfuric acid and another product.

**16.58** Which, dinitrogen trioxide or dinitrogen pentoxide, is likely to be the more acidic oxide? Give your reasoning.

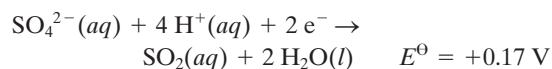
**16.59** Write a balanced equation for the reaction of aqueous sulfite ion with aqueous peroxodisulfate ion.

**16.60** The half-reaction for the reduction of dioxygen to water is:



The standard potential provided in online Appendix 9 is not relevant to normal atmospheric conditions of  $p\text{O}_2$  of 20 kPa and a pH of about 7. Calculate the reduction potential under these more realistic conditions.

**16.61** The standard electrode potential for the reduction of sulfate under acid conditions is given by



Calculate the potential under basic conditions.

**16.62** Identify each of the following reactants, writing balanced chemical equations for each reaction.

(a) A metal (A) reacts with water to give a colorless solution of compound (B) and a colorless gas (C). Common dilute diprotic acid (D) is added to (B), forming a dense white precipitate (E).

(b) A solution of (F) slowly decomposes to give a liquid (G) and a colorless gas (H). Gas (H) reacts with colorless gas (C) to give liquid (G).

(c) Under certain conditions, colorless acidic gas (I) will react with gas (H) to give a white solid (J). Addition of (G) to (J) gives a solution of acid (D).

(d) (A) burns in excess gas (H) to give compound (K). Compound (K) dissolves in water to produce a solution of (B) and (F).



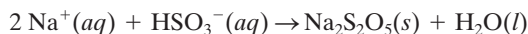
**16.63** A gas (A) was bubbled into a solution of a common monovalent hydroxide (B) to give a solution of the salt (C). The cation of (B) gives a precipitate with the tetraphenylborate ion. Heating yellow solid (D) with a solution of (C) and evaporating the water gives crystals containing anion (E). Addition of iodine to a solution of anion (E) gives iodide ion and a solution of anion (F). Addition of hydrogen ion to a solution of anion (E) initially produces acid (G), which decomposes to form solid (D) and gas (A). Identify (A) through (G), writing balanced equations for each step.

**16.64** Write a balanced equation for the reaction of pure liquid sulfuric acid with pure liquid perchloric acid (a stronger acid).

**16.65** Construct an electron-dot structure for the  $\text{NSF}_3$  molecule in which the nitrogen-sulfur bond is: (a) double; (b) triple. Decide which structure is most likely the major contributor to the bonding on the basis of formal charge.

**16.66**  $\text{S}_4\text{N}_4$  can be fluorinated to give  $\text{S}_4\text{N}_4\text{F}_4$ . Are the fluorine atoms bonded to the sulfur or nitrogen atoms of the ring? Suggest an answer and explain your reasoning.

**16.67** If you have a solution of sodium hydrogen sulfite and allow it to crystallize, you do not obtain that compound but sodium metabisulfite instead:



Suggest why this reaction occurs and suggest a cation that would probably enable a solid hydrogen sulfite to be crystallized.

**16.68** Sulfur forms two unusual compounds with fluorine that have identical empirical formulas (structural isomers),  $\text{FSSF}$  and  $\text{SSF}_2$ . Draw electron-dot structures for these molecules and deduce the oxidation state of sulfur in each compound.

**16.69** Sulfur forms two other unusual compounds with fluorine that have identical empirical formulas (structural isomers),  $\text{SF}_2$  and  $\text{F}_3\text{SSF}$ . Draw electron-dot structures for these molecules and deduce the oxidation state of sulfur in each compound.

**16.70** It has been proposed that a third allotrope of oxygen,  $\text{O}_4$ , could be synthesized. If it has a ring structure, is it possible it could be formed by collision of two dioxygen molecules? Explain your reasoning using thermodynamic principles (including bond energies).

**16.71** There is an alternative structure for the hypothetical  $\text{O}_4$  molecule. Suggest how this might be formed from ozone. Identify two species that would be isostructural with this form of  $\text{O}_4$ .

## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

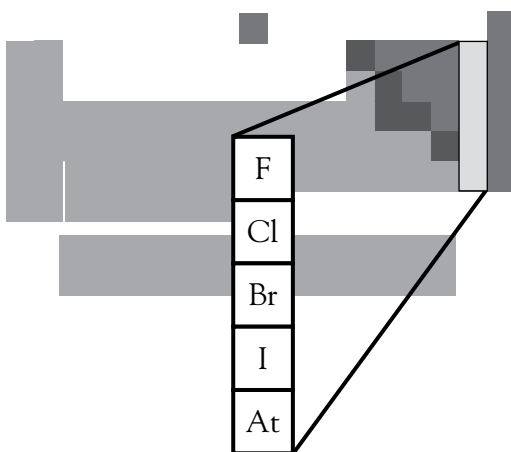


For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# THE GROUP 17 ELEMENTS:

## The Halogens

## CHAPTER 17



F
Cl
Br
I
At

We started with the group containing the most reactive metals, and now we have reached the group containing the most reactive nonmetals. Whereas the reactivity of the alkali metals increases down the group, the most reactive halogen, fluorine, is at the top.

### Context: Experimenting with the Atmosphere—The Antarctic Ozone Hole

We have been performing uncontrolled chemistry experiments on the atmosphere for decades. The most extreme experiment is that over the Antarctic continent, where we have caused major changes over a very short period of time. From the 1980s to the present time, the concentration of ozone, shielding the surface from the Sun's ultraviolet rays, has decreased dramatically, as can be seen in the following figure.

The Antarctic atmosphere is unique in that, for much of the year, it is isolated from the rest of the Earth's atmosphere, resulting in unusual chemical reactions. For the Antarctic winter, for three months, there is no solar radiation. A polar vortex forms around the land mass, trapping the cold air, resulting in temperatures of about  $-80^{\circ}\text{C}$  (see later). Some polar stratospheric clouds are not of ordinary ice, but of solidified hydrogen nitrate trihydrate,  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ , and surface reactions on these clouds produce a wide variety of exotic free-radical species. What has disturbed the chemistry has been our use of chlorofluorocarbons (CFCs), resulting in highly reactive chlorine atoms migrating into the

25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

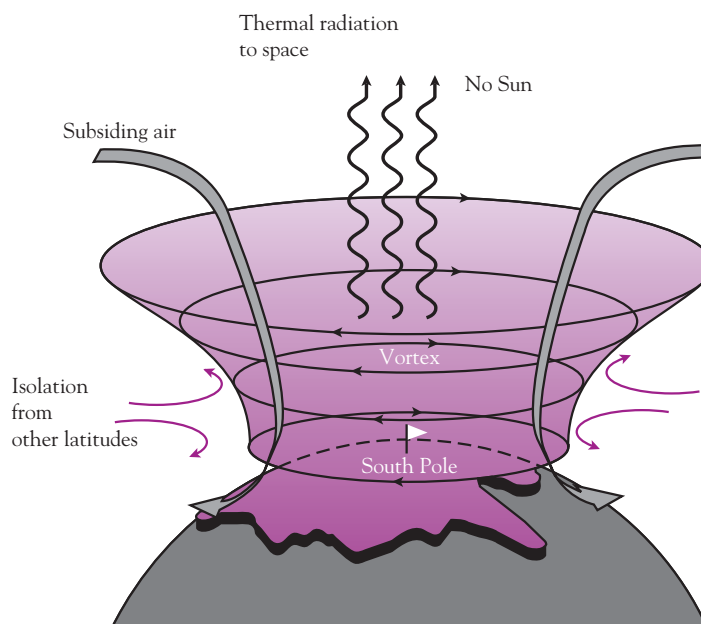
- 17.1 Group Trends
- 17.2 Contrasts in the Chemistry of Fluorine and the Other Halogens
- 17.3 Halides
- 17.4 Fluorine
- 17.5 Hydrogen Fluoride and Hydrofluoric Acid
- 17.6 Overview of Chlorine Chemistry
- 17.7 Chlorine
- 17.8 Hydrochloric Acid
- 17.9 Chlorine Oxides
- 17.10 Chlorine Oxoacids and Oxoanions
- 17.11 Interhalogen Compounds and Polyhalide Ions
- 17.12 Cyanide Ion as a Pseudo-halide Ion
- 17.13 Biological Aspects
- 17.14 Element Reaction Flowcharts





The minimum Antarctic ozone concentrations over recent time.

Antarctic atmosphere. As we will see in Section 17.9, the resulting chemical reactions between chlorine atoms and ozone molecules has led to a catastrophic decrease in the protective ozone layer. Although the reduction in the use of CFCs is resulting in an increase in ozone concentrations, it is a sobering warning that our atmosphere is thin and very susceptible to what we pump into it.



A schematic of the Antarctic vortex.

## 17.1 Group Trends

The properties of the elements are summarized in Table 17.1. Bromine is the only nonmetallic element that is liquid at room temperature. The vapor pressures of bromine and iodine are quite high. Thus, toxic red-brown bromine vapor is apparent when a container of bromine is opened, and toxic violet vapors are produced when iodine crystals are gently heated. Although iodine looks metallic, it behaves like a typical nonmetal in most of its chemistry.

As for previous groups, we will ignore the chemistry of the radioactive member of the group, in this case astatine. Astatine is formed as part of the decay sequence of isotopes of uranium. All of astatine's isotopes have very short half-lives, and hence are highly radioactive. The fleeting existence makes it very difficult to study the chemistry of astatine. The chemistry which has been feasible indicates that the properties of astatine follow the trends seen in the other members of this group.

Table 17.2 shows the smooth increase in the melting and boiling points of these nonmetallic elements. Because the diatomic halogens possess only dispersion forces between molecules, their melting and boiling points depend on the polarizability of the molecules, a property that, in turn, is dependent on the total number of electrons.

The formulas of the oxoacids in which the halogen atom is in its highest oxidation state parallel those of the Group 16 acids. Thus, the structure of perchloric acid can be represented as  $(\text{HO})\text{ClO}_3$ , and perbromic acid as  $(\text{HO})\text{BrO}_3$ . Periodic acid, however, has the structure of  $(\text{HO})_5\text{IO}$  (or  $\text{H}_5\text{IO}_6$ ), similar to that of isoelectronic telluric acid,  $\text{H}_6\text{TeO}_6$ , of Group 16.

**TABLE 17.1** Properties of the stable Group 17 elements

Element	Appearance at SATP	Acid-base properties of oxides
Fluorine	Pale yellow gas	Neutral
Chlorine	Pale green gas	Acidic
Bromine	Oily red-brown liquid	Acidic
Iodine	Lustrous violet-black solid	Acidic

**TABLE 17.2** Melting and boiling points of the Group 17 elements

Element	Melting point (°C)	Boiling point (°C)	Number of electrons
$\text{F}_2$	-219	-188	18
$\text{Cl}_2$	-101	-34	34
$\text{Br}_2$	-7	+60	70
$\text{I}_2$	+114	+185	106

## 17.2 Contrasts in the Chemistry of Fluorine and the Other Halogens

As previously noted for nitrogen and oxygen, the Period 2 members owe much of their distinctiveness to their bonding limitations. However, the contrast of fluorine and chlorine chemistry is particularly striking, and much of the difference can be ascribed to the weakness of the fluorine-fluorine covalent bond.

The bond energies of the halogens from chlorine to iodine show a systematic decrease, but the bond energy of fluorine does not fit the pattern (Table 17.3). To fit the trend, we would expect a F—F bond energy of about  $300 \text{ kJ}\cdot\text{mol}^{-1}$  rather than the actual value of  $155 \text{ kJ}\cdot\text{mol}^{-1}$ . Although a number of reasons have been suggested, most chemists believe that the weak F—F bond is a result of repulsions between the nonbonded electrons of the two atoms of the molecule. It accounts in part for the high reactivity of fluorine gas.

**TABLE 17.3** Bond energies of the Group 17 elements

Element	Bond energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )
F—F	155
Cl—Cl	240
Br—Br	190
I—I	149

### Ionic Bonding

For the formation of ionic fluorides, there are two key factors in the Born-Haber cycle. The first crucial enthalpy factor is the weak fluorine-fluorine bond that is broken; thus, less energy input is required compared with chloride and the other halogens. More energy is released with fluorides than with the other halides since fluorides have a high lattice energy of formation due to the small, high-charge-density fluoride ion. The significant effect of the fluoride ion on lattice energies can be seen in a comparison of lattice energies for the sodium halides (Table 17.4), all of which adopt the NaCl structure.

Because the fluoride ion is much smaller than the chloride ion, the solubilities of metal fluorides differ from those of the corresponding chlorides. For

**TABLE 17.4** The lattice energies of sodium halides

Halide	Lattice energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )
NaF	928
NaCl	788
NaBr	751
NaI	700

**TABLE 17.5** A comparison of formulas of the highest-oxidation-state fluorides and chlorides of the 3d transition metal series

<b>Fluoride</b>	TiF <sub>4</sub>	VF <sub>5</sub>	CrF <sub>6</sub>	MnF <sub>4</sub>	FeF <sub>3</sub>	CoF <sub>4</sub>	NiF <sub>2</sub>	CuF <sub>2</sub>
<b>Chloride</b>	TiCl <sub>4</sub>	VCl <sub>4</sub>	CrCl <sub>4</sub>	MnCl <sub>2</sub>	FeCl <sub>3</sub>	CoCl <sub>2</sub>	NiCl <sub>2</sub>	CuCl <sub>2</sub>

example, silver fluoride is soluble, whereas silver chloride is not. Conversely, calcium fluoride is insoluble, whereas calcium chloride is soluble. This pattern is a result of the differences in lattice energy between the metal fluorides and metal chlorides. Thus, the large silver ion has a relatively low lattice energy with the small fluoride ion. Conversely, the lattice energy is maximized when the small, high-charge-density calcium ion is matched with the small fluoride ion.

Fluorine, being a very strong oxidizing agent, often “brings out” a higher oxidation state in a metal than chlorine. Table 17.5 shows a comparison of formulas of the highest-oxidation-state fluorides and chlorides for the 3d transition metal series. For four of the eight 3d metals, there is a fluoride in a higher oxidation state than the highest-oxidation-state chloride. As we show in Chapter 21, Section 21.1, oxidation states in general are higher for the 4d and 5d transition metal series than the 3d metals. In addition, there is still the trend that fluorides are found in higher oxidation states than chlorides.

### Covalent Bonding

Just as fluorine compounds of metals are known with higher oxidation states than the corresponding chlorine compound, so a similar situation pertains to the compounds with nonmetals. For example, whereas sulfur readily forms sulfur hexafluoride, SF<sub>6</sub>, the highest chloride is the dichloride, SCl<sub>2</sub>.

Fluorine compounds tend to be more thermodynamically stable and chemically unreactive than the parallel chlorine compound. Likewise, the fluorides tend to have much lower melting and boiling points than the corresponding chloride. For example, nitrogen trifluoride is a very unreactive gas, whereas nitrogen trichloride is a dense, volatile, highly explosive liquid. The negative enthalpy of formation of covalent fluorides is partially due to the weak fluorine-fluorine bond, which is readily broken, and partially to the extremely strong element-fluoride bond that is formed. To illustrate, in Table 17.6, the bond energies of

**TABLE 17.6** A comparison of approximate fluorine and chlorine bond energies with other elements

<b>Fluorine bonds</b>	<b>Bond energy (kJ·mol<sup>-1</sup>)</b>	<b>Chlorine bonds</b>	<b>Bond energy (kJ·mol<sup>-1</sup>)</b>
F—F	155	Cl—Cl	240
C—F	485	C—Cl	327
H—F	565	H—Cl	428

**TABLE 17.7** A comparison of the pH dependency of the aqueous species of the hydrohalic acids

	Very Acidic	Acidic	Basic	Very Basic		
Fluoride	HF(aq)	F <sup>-</sup> (aq)				
Chloride						
Bromide						
Iodide						

fluorine and chlorine are compared for bonds with themselves and with carbon and with hydrogen.

### Strengths of the Hydrohalic Acids

Hydrofluoric acid is a weakish acid with a  $pK_a$  of 3.2, unlike the other hydrohalic acids, which are very strong, all having negative  $pK_a$  values (see Table 17.7). As discussed in Chapter 7, Section 7.2, the relative weakness of hydrofluoric acid can be ascribed to the fact that the hydrogen-fluorine bond is much stronger than the other hydrogen-halide bonds. Thus, the dissociation into ions is less energetically favorable.

#### WORKED EXAMPLE 17.1

Tellurium reacts with excess fluorine to form a fluoride in its highest oxidation state, the equivalent reaction with chlorine results in a lower oxidation state. Write the formulas of the two compounds.

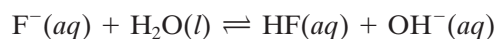
#### Answer

Tellurium is in Group 16, thus its highest oxidation state is +6, so the formula of the fluoride is TeF<sub>6</sub>. The next highest oxidation state will be +4, so the chloride will have a formula of TeCl<sub>4</sub>. ■

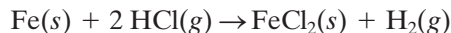
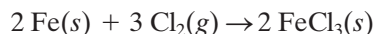
## 17.3 Halides

### Ionic Halides

Most ionic chlorides, bromides, and iodides are soluble in water, dissolving to give the metal ion and the halide ion. However, many metal fluorides are insoluble. For example, as mentioned earlier, calcium chloride is very water soluble, whereas calcium fluoride is insoluble. We explain these observations in terms of the greater lattice energy in crystals containing the small, high-charge-density anion and the high-charge-density cation. Solutions of soluble fluorides are basic because the fluoride ion is the conjugate base of the weak acid hydrofluoric acid:



There are two possible ways to form metal halides: combining metal and halogen to give a metal ion with the higher oxidation state and combining metal and hydrogen halide to give a metal ion with the lower oxidation state. The preparations of iron(III) chloride and iron(II) chloride illustrate this point:



In the first case, dichlorine is acting as a strong oxidizing agent, whereas in the second case hydrogen chloride is a weak oxidizing agent.

### Preparation of Ionic Halides

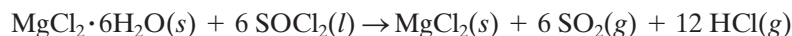
Hydrated metal halides can be prepared from the metal oxide, carbonate, or hydroxide and the appropriate hydrohalic acid. For example, magnesium chloride hexahydrate can be prepared from magnesium oxide and hydrochloric acid, followed by crystallization of the solution:



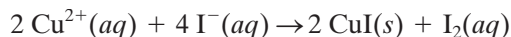
The anhydrous salt cannot be prepared by heating the hydrate because decomposition occurs instead. Thus, magnesium chloride hexahydrate gives magnesium hydroxide chloride,  $\text{Mg}(\text{OH})\text{Cl}$ , when heated:



To obtain anhydrous magnesium chloride from the hydrate, we have to chemically remove the water. This can be done (in a fume hood!) by using thionyl chloride,  $\text{SOCl}_2$ , with the reaction by-products being sulfur dioxide and hydrogen chloride gases:



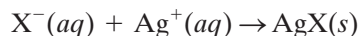
Not all metal iodides in which the metal ion takes its higher oxidation state can be prepared because the iodide ion itself is a reducing agent. For example, iodide ion will reduce copper(II) ion to copper(I):



As a result, copper(II) iodide does not exist.

### Test for Ionic Halide Ions

The common test for distinguishing chloride, bromide, and iodide ions involves the addition of silver nitrate solution to give a precipitate. Using  $\text{X}^{-}$  to represent the halide ion, we can write a general equation:



Silver chloride is white, silver bromide is cream-colored, and silver iodide is yellow. Like most silver compounds, they are light sensitive, and, over a period of hours, the solids change to shades of gray as metallic silver forms.

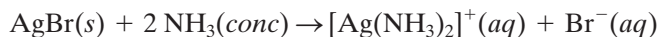


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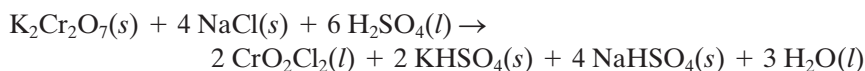
To confirm the identity of the halogen, dilute ammonia solution is added to the silver halide. A precipitate of silver chloride reacts with dilute ammonia to form the soluble diamminesilver(I) ion,  $[\text{Ag}(\text{NH}_3)_2]^+$ :



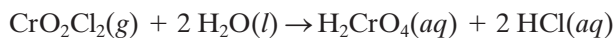
The other two silver halides do not react with low concentrations of ammonia solution. Silver bromide does react with concentrated ammonia, but silver iodide remains unreactive even under these conditions.



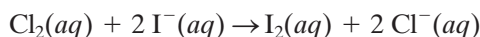
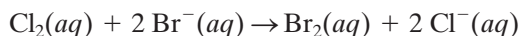
There also are specific tests for each halide ion. The chloride ion test is quite hazardous because it involves the reaction of the suspected chloride with a mixture of potassium dichromate and concentrated sulfuric acid. When warmed gently, the volatile, red, toxic compound chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , is produced:



The vapor can be bubbled into water, where it forms a yellow solution of chromic acid,  $\text{H}_2\text{CrO}_4$ :



To test for bromide ion and iodide ion, a solution of dichlorine in water (aqueous chlorine) is added to the halide ion solution. The appearance of a yellow to brown color suggests the presence of either of these ions:

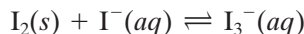


To distinguish dibromine and diiodine, we rely on the fact that the halogens themselves are nonpolar molecules. Thus, they will “prefer” to dissolve in nonpolar or low-polarity solvents, such as carbon tetrachloride. If the brownish aqueous solution is shaken with such a solvent, the halogen should transfer to the low-polarity, nonaqueous layer. If the unknown is dibromine, the color will be brown, whereas that of diiodine will be bright purple.

There is another, very sensitive test for iodine: it reacts with starch to give a blue color (blue-black when concentrated solutions are used). In this unusual interaction, the starch polymer molecules wrap themselves around the iodine molecules. There is no actual chemical bond involved. The equilibrium is employed qualitatively in starch-iodide paper. When the paper is exposed to an oxidizing agent, the iodide is oxidized to iodine. The starch in the paper forms the starch-iodine complex, and the blue-black color is readily observed. Quantitatively, starch is used as the indicator in redox titrations involving the iodide-iodine redox reaction.

Diiodine, as already mentioned, is a nonpolar molecule. Thus, its solubility in water is extremely low. It will, however, “dissolve” in a solution of iodide ion.

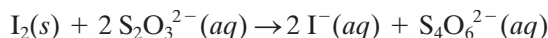
This is, in fact, a chemical reaction producing the triiodide ion,  $\text{I}_3^-$  (discussed in Section 17.10):



Iodide ion will also undergo a redox reaction with iodate ion,  $\text{IO}_3^-$ , in acid solution to give diiodine:



This reaction is often used in titrimetric analysis of iodide solutions. The diiodine can then be titrated with thiosulfate ion of known concentration:

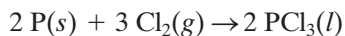
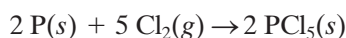


### Covalent Halides

As a result of weak intermolecular forces, most covalent halides are gases or liquids with low boiling points. The boiling points of these nonpolar molecules are directly related to the strength of the dispersion forces between the molecules. This intermolecular force, in turn, is dependent on the number of electrons in the molecule. A typical series is that of the boron halides (Table 17.8), which illustrates the relationship between boiling point and number of electrons.

### Preparation of Covalent Halides

Many covalent halides can be prepared by treating the element with the appropriate halogen. When more than one compound can be formed, the mole ratio can be altered to favor one product over the other. For example, in the presence of excess chlorine, phosphorus forms phosphorus pentachloride, whereas in the presence of excess phosphorus, phosphorus trichloride is formed:



If a nonmetallic element exists in a number of possible oxidation states, then the highest oxidation state is usually stabilized by fluorine and the lowest by iodine. This pattern reflects the decreasing oxidizing ability of elements in Group 17 as the group is descended. However, we must always be careful with

**TABLE 17.8** Boiling points of the boron halides

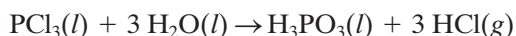
Compound	Boiling point (°C)	Number of electrons
$\text{BF}_3$	-100	32
$\text{BCl}_3$	+12	56
$\text{BBr}_3$	+91	110
$\text{BI}_3$	+210	164



our application of simplistic arguments. For example, the nonexistence of phosphorus pentaiodide,  $\text{PI}_5$ , is more likely to be due to the fact that the size of the iodine atom limits the number of iodine atoms that will fit around the phosphorus atom rather than to the spontaneous reduction of phosphorus from the +5 to the +3 oxidation state.

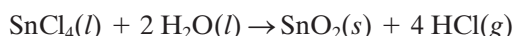
### Reactions of Covalent Halides

As we saw in Chapters 13, 14, and 15, most covalent halides react vigorously with water. For example, phosphorus trichloride reacts with water to give phosphonic acid and hydrogen chloride:



However, some covalent halides are kinetically inert, particularly the fluorides, such as carbon tetrafluoride and sulfur hexafluoride.

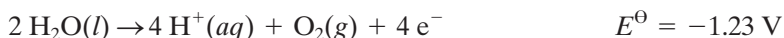
It is important to remember that metal halides can contain covalent bonds when the metal is in a high oxidation state. For example, tin(IV) chloride behaves like a typical covalent halide. It is a liquid at room temperature, and it reacts violently with water:



## 17.4 Fluorine

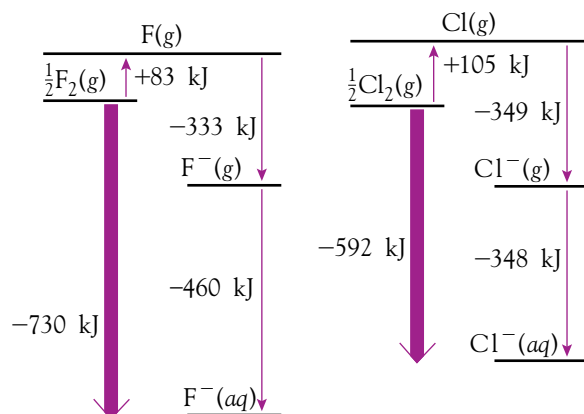
Difluorine is the most reactive element in the periodic table—in fact, it has been called the “Tyrannosaurus rex” of the elements. Fluorine gas is known to react with every other element in the periodic table except helium, neon, and argon. In the formation of fluorides, it is the enthalpy factor that is usually the predominant thermodynamic driving force.

Fluorine oxidizes water to oxygen gas while simultaneously being reduced to fluoride ion:



We can explain the reason for such a high fluorine reduction potential by comparing the free energy cycles for the formation of the hydrated fluoride and chloride ions from their respective gaseous elements (Figure 17.1).

The first step is (half of) the bond dissociation free energy, for which chlorine has the slightly higher value. In the next step, the energy required is the electron affinity, and the value for chlorine is again slightly higher, thus almost canceling out the fluorine advantage in the first step. It is the third step, the hydration of the respective ions, for which the free energy change of the fluoride ion is very much greater than that of the chloride ion. This large free energy change results from the strong interactions of the high-charge-density fluoride ion with surrounding water molecules to give a network of  $\text{F} \cdots \text{H}-\text{O}$  hydrogen bonds. Because  $\Delta G^\ominus = -nFE^\ominus$ , the large free energy of reduction

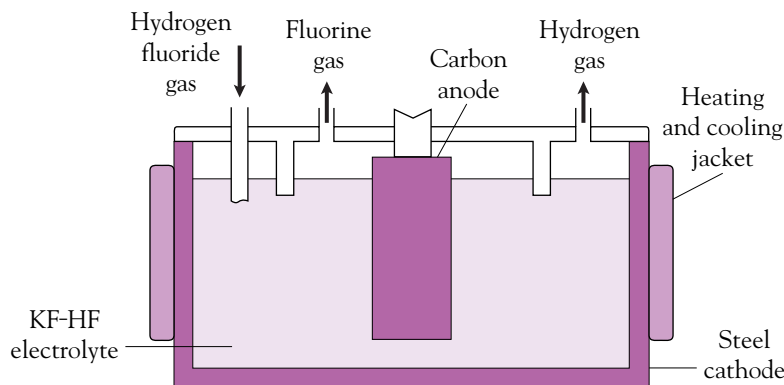
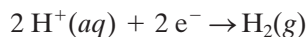
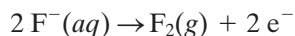


**FIGURE 17.1** The free energy terms in the reduction of difluorine and dichlorine to the aqueous fluoride and chloride ions, respectively.

directly translates to a very positive standard reduction potential, thus accounting for the great strength of difluorine as an oxidizing agent.

### The Industrial Extraction of Fluorine

Difluorine is still produced by the Moissan electrochemical method, a process devised 100 years ago. The cells can be laboratory size, running at currents between 10 and 50 A, or industrial size, with currents up to 15 000 A. Hydrogen fluoride gas must be bubbled into the cell continuously to replace that used in the process. Annual production is at least  $10^4$  tonnes. The cell contains a molten mixture of potassium fluoride and hydrogen fluoride in a 1:2 ratio and operates at about  $90^\circ\text{C}$ . The jacket of the apparatus is used to heat up the cell initially and then to cool it as the exothermic electrolysis occurs. At the central carbon anode, fluoride ion is oxidized to fluorine, and at the steel cathode walls of the container, hydrogen gas is produced (Figure 17.2):



**FIGURE 17.2** The cell used in the production of difluorine.

## The Fluoridation of Water

A dentist, Frederick McKay, noticed the remarkable lack of cavities in the population in the Colorado Springs, Colorado, area in 1902. He tracked down the apparent cause as the higher-than-average levels of fluoride ion in the drinking water. We now know that a concentration of about 1 ppm is required to convert the softer tooth material hydroxyapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , to the tougher fluoroapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . A higher concentration of 2 ppm results in a brown mottling of the teeth, and at 50 ppm, toxic health effects occur. As a means of minimizing dental decay, health authorities around the world, including the American Dental Association, have recommended that fluoride levels in drinking water supplies be optimized to a level of about 1 ppm. The first city in the world to add a controlled level of fluoride ion was Grand Rapids, Michigan, in 1945. Many parts of the world have natural fluoride levels in excess of the recommended value. For example, in parts of Texas, the natural levels are over 2 ppm, while water sources in parts of Africa and Asia have dangerous levels in excess of 20 ppm.

The major concern of most health experts is not fluoridated water but fluoride toothpaste. The toothpaste

contains high concentrations of fluoride ion designed to surface-coat the tooth with the fluoro compound. Unfortunately, young children have a predilection for swallowing toothpaste and thus massively exceeding the recommended fluoride intake. It is for this reason that toothpaste tubes carry such warnings as: “To prevent swallowing, children under six years of age should only use a pea-size amount and be supervised during brushing” and “Warning: Keep [tube] out of reach of children under six years of age.” It is commonly recommended that fluoride toothpaste not be used with children under two years of age since the lower the age, the higher the proportion of toothpaste swallowed. The overconsumption of fluoride toothpaste by children is generally believed to be responsible for a rise in dental fluorosis, a harmless but unsightly mottling of teeth.

It is the level of fluoridation that is most questionable. Formerly, a concentration of 1 ppm was recommended as being optimum if that was the only source of intake. Now, with other sources such as toothpaste and foodstuffs processed in fluoride-supplemented water, a lower concentration of about 0.7 ppm is generally considered preferable.

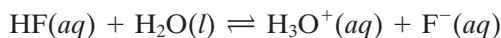
## 17.5 Hydrogen Fluoride and Hydrofluoric Acid

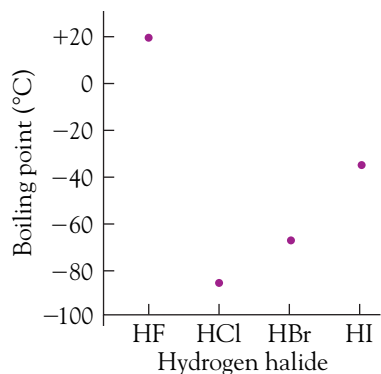
Hydrogen fluoride is a colorless, fuming liquid with a boiling point of  $20^\circ\text{C}$ . This is much higher than the boiling points of the other hydrogen halides, as can be seen from Figure 17.3.

The high boiling point of hydrogen fluoride is a result of the very strong hydrogen bonding between neighboring hydrogen fluoride molecules. Fluorine has the highest electronegativity of all the elements, so the hydrogen bond formed with fluorine is the strongest of all. The hydrogen bonds are linear with respect to the hydrogen atoms but are oriented at  $120^\circ$  with respect to the fluorine atoms. Thus, the molecules adopt a zigzag arrangement (Figure 17.4).

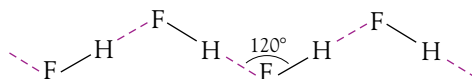
### Hydrofluoric Acid

Hydrogen fluoride dissolves in water, a small proportion ionizing to form the hydronium ion and the fluoride ion:



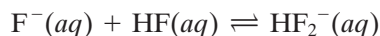


**FIGURE 17.3** Boiling points of hydrogen fluoride.



**FIGURE 17.4** Hydrogen bonding in hydrogen fluoride.

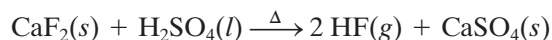
In more concentrated solutions, hydrofluoric acid ionizes to an even greater degree, the converse of the behavior of other acids. The cause of this behavior is well understood: a second equilibrium step that becomes more important at higher hydrogen fluoride concentrations and gives the linear hydrogen difluoride ion:



The hydrogen difluoride ion is so stable that alkali metal salts, such as potassium hydrogen difluoride,  $\text{KHF}_2$ , can be crystallized from solution. This acid anion is unique, for it involves a bridging hydrogen atom. It used to be regarded as a hydrogen fluoride molecule with a fluoride ion hydrogen bonded to it. However, recent studies have shown that the hydrogen is centrally located between the two fluorine atoms. The bonding is much better described in molecular orbital terms of a three-atom four-electron system.

### The Industrial Synthesis of Hydrofluoric Acid

About  $10^6$  tonnes of hydrofluoric acid are produced each year worldwide. Hydrogen fluoride is obtained by heating calcium fluoride, the mineral fluor-spar, with concentrated sulfuric acid:



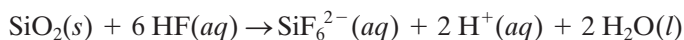
The product is either liquefied by refrigeration or added to water to give hydrofluoric acid. To lower the cost of this endothermic reaction, plants have been constructed next to sulfuric acid production facilities. The heat from the exothermic reactions in the sulfuric acid plant is then used for the hydrogen fluoride process.

Obviously, in the production of a substance as toxic as hydrofluoric acid, the flue gases have to be carefully “scrubbed” to prevent traces of hydrogen

fluoride from escaping into the environment. The other product in the reaction is the ubiquitous calcium sulfate. A simple stoichiometric calculation shows that, for every tonne of hydrogen fluoride, nearly 4 tonnes of calcium sulfate are produced. As with the other industrial processes that produce this by-product, some is utilized, but much of it is used as landfill.

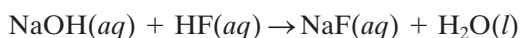
### Uses of Hydrofluoric Acid

Hydrofluoric acid is very corrosive, even though it is a weak acid. It is one of the few substances to attack glass, and for this reason hydrofluoric acid is always stored in plastic bottles. The reaction with glass produces the hexafluorosilicate ion,  $\text{SiF}_6^{2-}$ :

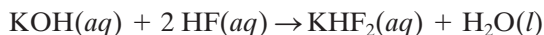


This property is used in the etching of glass. An object to be etched is dipped in molten wax, and the wax is allowed to harden. The required pattern is then cut through the wax layer. Dipping the glass in hydrofluoric acid enables the hydrofluoric acid to react with only those parts of the glass surface that are exposed. After a suitable depth of glass has been dissolved, the object is removed from the acid bath, rinsed with water, and the wax melted off, leaving the glass with the desired etched pattern.

Almost all of the hydrofluoric acid produced commercially is used as the starting material for the synthesis of other fluorine-containing chemicals. For example, sodium fluoride is produced by mixing hydrofluoric acid with sodium hydroxide solution:



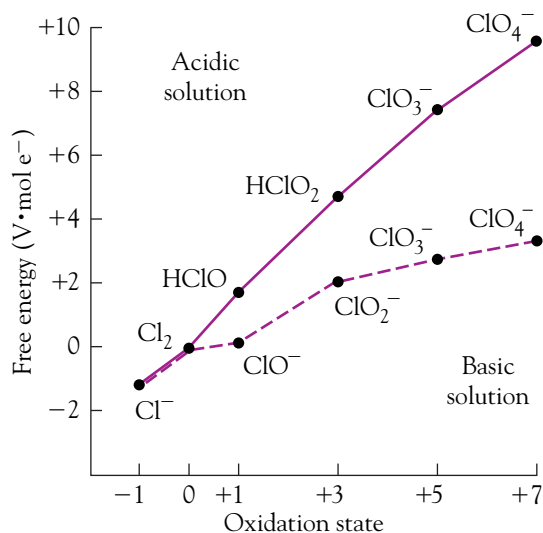
Evaporation gives sodium fluoride crystals, a compound used for water fluoridation. The reaction between hydrofluoric acid and potassium hydroxide solution, in a 2:1 mole ratio, gives the acid salt potassium hydrogen fluoride, which is used in the manufacture of fluorine gas:



## 17.6 Overview of Chlorine Chemistry

As the oxidation-state diagram in Figure 17.5 shows, the higher the oxidation state, the stronger the oxidizing ability. Whatever its positive oxidation state, a halogen atom is more oxidizing in an acidic solution than in a basic solution. The chloride ion is the most stable chlorine species because the dichlorine molecule can be reduced to the chloride ion in both acidic and basic solutions. In basic solution, the convex point on which the dichlorine molecule is located indicates that it will undergo disproportionation to the chloride and hypochlorite ions.

The highly oxidizing nature of the perchlorate ion makes it very different from its isoelectronic neighboring ions phosphate and sulfate. But the oxidizing



**FIGURE 17.5** Frost diagram for chlorine in acidic and basic solutions.

ability of the perchlorate ion is similar to that of the permanganate ion, providing more evidence for the Group ( $n$ ) and Group ( $n + 10$ ) similarities (see Chapter 9, Section 9.4).

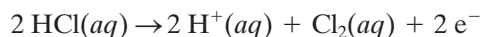
## 17.7 Chlorine

Chlorine gas is very poisonous; a concentration of over 30 ppm is lethal after a 30-minute exposure. It is the dense, toxic nature of dichlorine that led it to be used as the first wartime poison gas. In 1915, as a result of a German chlorine gas attack, 20 000 Allied soldiers were incapacitated and 5000 of them died.

By contrast, the toxicity of low concentrations of chlorine toward microorganisms has saved millions of human lives. It is through chlorination that waterborne disease-causing organisms have been virtually eradicated from domestic water supplies in Western countries. Curiously, there used to be a great enthusiasm for the benefits of chlorine gas. President Calvin Coolidge, among others, used sojourns in a “chlorine chamber” as a means of alleviating his colds. It is probable that many who tried this “cure” finished up with long-term lung damage instead.

### Preparation of Chlorine

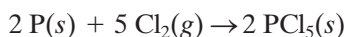
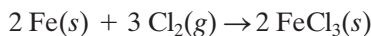
Chlorine gas is most easily prepared in the laboratory by adding concentrated hydrochloric acid to solid potassium permanganate. The chloride ion is oxidized to dichlorine and the permanganate ion is reduced to the manganese(II) ion:



The industrial preparation of chlorine is accomplished by electrolysis of aqueous sodium chloride solution (brine); the other product is sodium hydroxide. (This process was discussed in Chapter 11, Section 11.7.) Chlorine is produced on a vast scale, about  $10^8$  tonnes annually worldwide. Most of the product is used for the synthesis of organochlorine compounds. Appreciable quantities are used in the pulp and paper industry to bleach paper, in water treatment, and in the production of titanium(IV) chloride,  $\text{TiCl}_4$ , an intermediate step in the extraction of titanium from its ores.

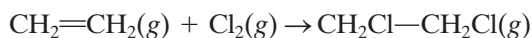
### Reactions of Chlorine

Although not as reactive as fluorine, chlorine reacts with many elements, usually to give the higher common oxidation state of the element. For example, iron burns to give iron(III) chloride, not iron(II) chloride; phosphorus burns in excess chlorine to give phosphorus pentachloride:



However, as discussed in Section 17.2, the highest oxidation state of an element with chlorine is usually much lower than its oxidation state in the equivalent fluoride.

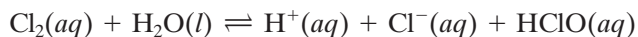
Dichlorine can act as an organic chlorinating agent. For example, mixing ethene,  $\text{C}_2\text{H}_4$ , with dichlorine gives 1,2-dichloroethane,  $\text{C}_2\text{H}_4\text{Cl}_2$ :



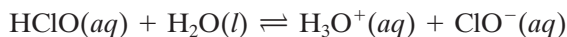
Dichlorine is also a strong oxidizing agent, having a very positive standard reduction potential (although much less than that of difluorine):



Dichlorine reacts with water to give a mixture of hydrochloric and hypochlorous acids:



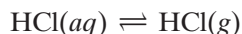
At room temperature, a saturated solution of chlorine in water contains about two-thirds hydrated dichlorine molecules and one-third of the acid mixture. It is the hypochlorite ion in equilibrium with the hypochlorous acid, rather than chlorine itself, that is used as an active oxidizing (bleaching) agent:



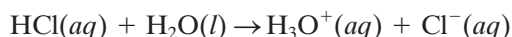
Before the discovery of the bleaching effect of aqueous chlorine, the only way to produce white linen was to leave it in the sun for weeks at a time. The cloth was placed over wooden frames in vast arrays, which were known as the bleach fields or bleachers—the origin of the name for the bench seats at ball games.

## 17.8 Hydrochloric Acid

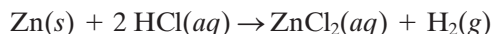
Hydrogen chloride is extremely soluble in water; in fact, concentrated hydrochloric acid contains about 38 percent by mass of hydrogen chloride, a concentration of  $12 \text{ mol} \cdot \text{L}^{-1}$ . This acid is a colorless liquid, although the technical-grade reagent often has a yellowish color from an iron(III) ion impurity. The solution has a pronounced acidic odor, which is due to the equilibrium between gaseous and aqueous hydrogen chloride:



In contrast to hydrofluoric acid, hydrochloric acid is a strong acid ( $\text{p}K_{\text{a}} = -7$ ), ionizing almost completely:



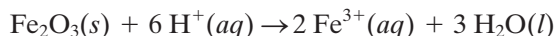
As the oxidation-state diagram shows (see Figure 17.1), the chloride ion is a very stable species. Hence, dilute hydrochloric acid is often the acid of choice over the oxidizing nitric acid and, to a lesser extent, sulfuric acid. For example, zinc metal will react with hydrochloric acid to give the zinc ion and hydrogen gas:



Hydrogen chloride is mostly produced industrially as a by-product from other industrial processes, such as the synthesis of carbon tetrachloride:



About  $10^7$  tonnes of hydrochloric acid are used worldwide every year. It has a wide range of uses: as a common acid, for removing rust from steel surfaces (a process called “pickling”), in the purification of glucose and corn syrup, in the acid treatment of oil and gas wells, and in the manufacture of chlorine-containing chemicals. The acid is available in many hardware stores under the archaic name of *muriatic acid*; its main home uses are the cleaning of concrete surfaces and rust removal. Representing rust as iron(III) oxide, we can write the process as:



## 17.9 Chlorine Oxides

Like nitrogen, there are chlorine oxides in which chlorine has every possible odd oxidation state. All of these oxides are thermodynamically unstable but kinetically stable. As a result of this and a low activation energy of decomposition, they are very unstable and have a tendency to explode. However, there are two oxides of importance, both of which have unpaired electrons; that is, they are free radicals. The first of these is chlorine monoxide, which is environmentally important even though it exists only in the upper atmosphere. The

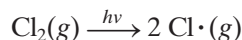


second is chlorine dioxide, a strong oxidizing agent, that is becoming increasingly important as a disinfectant.

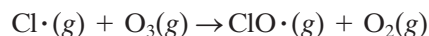
### Chlorine Monoxide

Many species that are too unstable to exist in significant concentrations at ambient temperature and pressure play important roles in atmospheric chemistry. For example, in Chapter 15, Section 15.8, we described how nitrogen trioxide acts as a nighttime tropospheric detergent. Another important atmospheric molecule is chlorine monoxide, ClO. Chlorine monoxide is a key stratospheric species responsible for causing the “ozone hole,” a decrease in ultraviolet-filtering ozone concentration over the south and, to a lesser extent, north polar regions during their respective spring seasons.

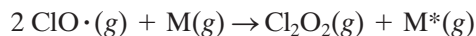
The saga is believed to begin with the buildup of chlorine molecules, predominantly from the breakdown of CFCs during the dark winter in the isolated air mass over the Antarctic. With the arrival of spring, sunlight causes the weakly bonded chlorine molecules (bond energy  $242 \text{ kJ}\cdot\text{mol}^{-1}$ ) to dissociate into chlorine atoms (a dot is used to indicate the lone electron on these free-radical species):



The chlorine atoms react with ozone (trioxygen) to give chlorine monoxide and dioxygen:



If the reaction terminated here, the damage to the ozone layer would be minimal. However, the chlorine monoxide takes part in a reaction cycle that regenerates the chlorine atoms, causing this process to be catalytic. That is, the chlorine atom acts as a catalyst for the conversion of ozone to dioxygen. The first step in this process is the combination of two chlorine monoxide radicals to form the ClOOCl dimer molecule. However, dissociation would immediately occur unless the two radicals simultaneously collide with a third body, M. It is the role of the species M to remove the excess energy. The identity of M is any molecule that can remove the energy—usually dinitrogen,  $\text{N}_2$ , or dioxygen,  $\text{O}_2$ , as these are the most common atmospheric molecules.



Sunlight again becomes involved, this time to fission the  $\text{Cl}_2\text{O}_2$  molecule asymmetrically:



The ClOO species is very unstable and rapidly breaks down to give a chlorine atom and a dioxygen molecule:



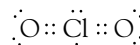
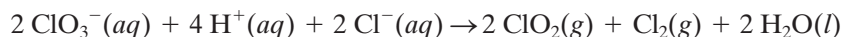
Then the chlorine atoms are again available to react with ozone molecules. It is this catalytic cycle that results in the severe polar ozone depletion.

## Chlorine Dioxide

Chlorine dioxide,  $\text{ClO}_2$ , is a yellow gas that condenses to a deep red liquid at  $11^\circ\text{C}$ . The compound is quite soluble in water, giving a fairly stable, green solution. Being a free radical species, chlorine dioxide is paramagnetic, like nitrogen dioxide. Yet unlike nitrogen dioxide, it shows no tendency to dimerize. The chlorine-oxygen bond length is only 140 pm, much shorter than the 170 pm that is typical for a single bond length, and it is very close to that of a typical chlorine-oxygen double bond. A possible electron-dot structure reflecting this bond order is shown in Figure 17.6 (this is not the same species as the transient  $\text{ClOO}\cdot$  radical formed in the upper atmosphere).

Chlorine dioxide, usually diluted with dinitrogen or carbon dioxide for safety, is a very powerful oxidizing agent. For example, to bleach flour to make white bread, chlorine dioxide is 30 times more effective than dichlorine. Large quantities of chlorine dioxide also are used as dilute aqueous solutions for bleaching wood pulp to make white paper. In this role, it is preferred over dichlorine because chlorine dioxide bleaches without significant formation of hazardous chlorinated wastes. Another advantage of chlorine dioxide is that, unlike dichlorine, it does not attack the cellulose structure, so it preserves the mechanical strength of paper. Similarly, chlorine dioxide is being used increasingly for domestic water treatment because, in this context too, it does not chlorinate hydrocarbon pollutants that are present in the water to any measurable extent. Hence, use of this reagent avoids the environmental problems discussed earlier.

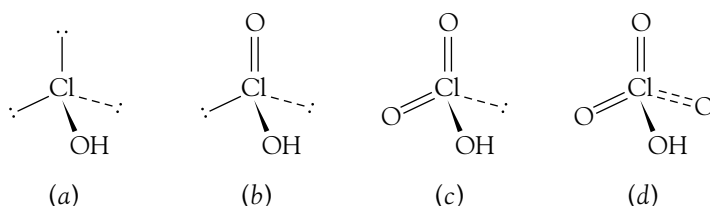
Thus, even though pure chlorine dioxide is explosive, it is of major industrial importance. About  $10^6$  tonnes are produced every year worldwide. It is difficult to determine the exact production total because the gas is so hazardous that it is generally produced in comparatively small quantities at the sites where it is to be used. The synthetic reaction involves the reduction of chlorine in the +5 ( $\text{ClO}_3^-$ ) oxidation state by chlorine in the  $-1$  ( $\text{Cl}^-$ ) oxidation state in very acid conditions to give chlorine in the +4 ( $\text{ClO}_2$ ) and 0 ( $\text{Cl}_2$ ) oxidation states:



**FIGURE 17.6** A possible electron-dot representation of the bonding in chlorine dioxide.

## 17.10 Chlorine Oxoacids and Oxoanions

Chlorine forms a series of oxoacids and oxoanions for each of its positive odd oxidation states from +1 to +7. The shapes of the ions (and related acids) are based on a tetrahedral arrangement around the chlorine atom (Figure 17.7). The short chlorine-oxygen bonds in each of the ions indicate that multiple bonding



**FIGURE 17.7** A possible representation of the bonding in (a) hypochlorous acid, (b) chlorous acid, (c) chloric acid, and (d) perchloric acid.

**TABLE 17.9** Comparative Strengths of the Chlorine Oxoacids

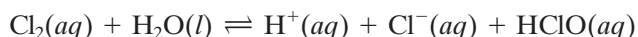
	Very Acidic	Acidic	Basic	Very Basic
Perchloric acid	$\text{ClO}_4^-(aq)$			
Chloric acid	$\text{ClO}_3^-(aq)$			
Chlorous acid	$\text{HClO}_2$	$\text{ClO}_2^-$		
Hypochlorous acid	$\text{HClO}$		$\text{ClO}^-$	

must be present, possibly involving some contribution to the  $\pi$  bonding by the full p orbitals on the oxygen atoms and empty d orbitals on the chlorine atom.

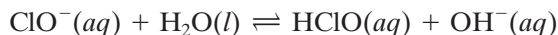
As discussed in Chapter 7, Section 7.4, acid strength increases as the number of oxygen atoms increases. Thus, hypochlorous acid is very weak; chlorous acid, weak; chloric acid, strong; and perchloric acid, very strong. The relative acid strengths can best be seen from the pH predominance diagram for the chlorine oxyacids (Table 17.9).

### Hypochlorous Acid and the Hypochlorite Ion

A mixture of hypochlorous acid and hydrochloric acid is formed when dichlorine is dissolved in cold water:



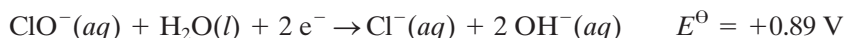
Hypochlorous acid is a very weak acid; thus, solutions of hypochlorites are very basic as a result of the hydrolysis reaction:



The two species are oxidizing agents but behave differently. Hypochlorous acid is a strong oxidizing agent and, in the process, is reduced to chlorine gas:



The hypochlorite ion, however, is a weaker oxidizing agent that is usually reduced to the chloride ion:

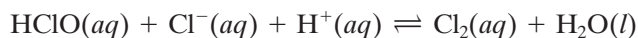
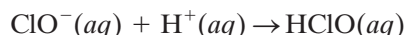


It is this oxidizing (bleaching and bactericidal) power that renders the hypochlorite ion useful.



The two compounds of industrial importance are sodium hypochlorite and calcium hypochlorite. Sodium hypochlorite is only stable in solution, not in the solid phase; thus, calcium hypochlorite is used as a solid source of hypochlorite ion. Sodium hypochlorite solution is used in commercial bleach solutions, such as Clorox and Javex, and for bleaching and decolorization of wood pulp and textiles. Both sodium and calcium hypochlorites are used in disinfection. Calcium hypochlorite is also used as a disinfectant in dairies, breweries, food processing, and bottling plants and in domestic mildew removers. Although the labels on sodium hypochlorite solution containers warn about the hazards of mixing cleansers, a

knowledge of chemistry is required to understand the problem. Commercial sodium hypochlorite solution contains chloride ion. In the presence of hydrogen (hydronium) ion such as that in a sodium hydrogen sulfate-based cleanser, the hypochlorous acid reacts with the chloride ion to produce chlorine gas:



## The Chlorate Ion

Although chlorites are of little interest, chlorates have several uses. Sodium chlorate can be prepared by bubbling dichlorine into a hot solution of sodium hydroxide. The sodium chloride, which is less soluble than sodium chlorate, precipitates:



Potassium chlorate is used in large quantities to make matches and fire-works. Like all chlorates, it is a strong oxidizing agent that can explode unpredictably when mixed with reducing agents. Considerable amounts of sodium chlorate are consumed in the production of chlorine dioxide.

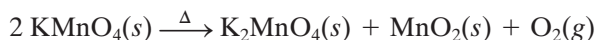
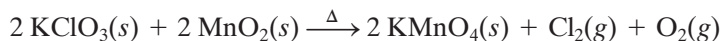
Chlorates decompose when heated, although in an unusual manner. The route for producing potassium chlorate has been studied in the most detail. When potassium chlorate is heated to temperatures below 370°C, disproportionation occurs to give potassium chloride and potassium perchlorate:



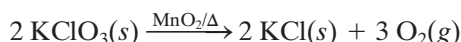
This is a synthetic route for the perchlorate. When potassium chlorate is heated above 370°C, the perchlorate that is formed by disproportionation decomposes:



The pathway for the slow, uncatalyzed reaction is different from that for the reaction catalyzed by manganese(IV) oxide. When catalyzed, the pathway giving potassium chloride and dioxygen involves potassium permanganate (which produces a purple color) and potassium manganate(VI),  $\text{K}_2\text{MnO}_4$ . The mechanism is a nice illustration of the chemical participation of a catalyst:



If these reaction steps are combined, we see that the overall reaction is:



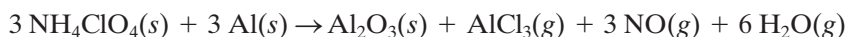
Thus, the oxygen is oxidized from the oxidation state of  $-2$  to  $0$ , the manganese cycles from  $+4$  through  $+7$  and  $+6$  back to  $+4$ , and the chlorine is reduced from  $+5$  to  $0$  to  $-1$ . Additional evidence for this mechanism is a faint odor of dichlorine, which is released during the first step.

### Perchloric Acid and the Perchlorate Ion

The strongest simple acid of all is perchloric acid. The pure acid is a colorless liquid that can explode unpredictably. As a result of its oxidizing nature and high oxygen content, contact with organic materials such as wood or paper causes an immediate fire. Concentrated perchloric acid, usually a 60 percent aqueous solution, is rarely used as an acid but is far more often used as a very powerful oxidizing agent; for example, to oxidize metal alloys to the metal ions so that they can be analyzed. Special perchloric acid fume hoods should be used when these oxidations are performed. Cold dilute solutions of perchloric acid are reasonably safe, however.

The solubility of the alkali metal salt decreases with increasing cation size. That is, the increasing size (decreasing charge densities) of the ions will reduce the hydration energies to the point that they are exceeded by the lattice energy. Thus, potassium perchlorate is only slightly soluble ( $20 \text{ g} \cdot \text{L}^{-1}$  of water). By contrast, silver perchlorate is amazingly soluble, to the extent of  $5 \text{ kg} \cdot \text{L}^{-1}$  of water. The high solubility of silver perchlorate in low-polarity organic solvents as well as water suggests that its bonding in the solid phase is essentially covalent rather than ionic. That is, only dipole attractions need to be overcome to solubilize the compound rather than the much stronger electrostatic attractions in an ionic crystal lattice, which can be overcome only by a very polar solvent.

Potassium perchlorate is used in fireworks and flares, but about half the commercially produced perchlorate is used in the manufacture of ammonium perchlorate. This compound is the oxidant, together with the reducing agent aluminum in solid booster rockets for spacecraft. At the high temperature produced (over  $5000^\circ\text{C}$ ) by the very exothermic reaction, a wide range of products is formed, including the following:

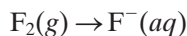
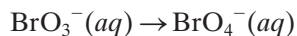


#### WORKED EXAMPLE 17.2

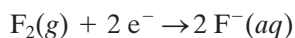
The perbromate ion is synthesized by reacting aqueous bromate ion with fluorine gas. Write a balanced ionic equation for the reaction.

#### Answer

If bromate ion,  $\text{BrO}_3^-$ , is oxidized to perbromate ion,  $\text{BrO}_4^-$ , then the fluorine must be reduced to fluoride ion. The two skeletal half-reactions can be written as:



Balancing each half-reaction:

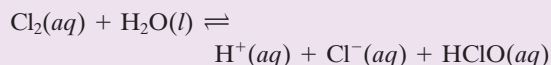


Combining the half-reactions:

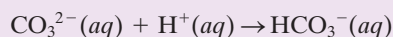


## Swimming Pool Chemistry

In North America, we usually rely on dichlorine- or chlorine-based compounds, such as calcium hypochlorite, to destroy the microorganisms in our swimming pools. In fact, the most potent disinfectant is hypochlorous acid. In many public pools, this compound is formed when dichlorine reacts with water:

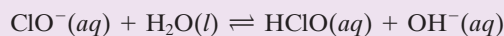


To neutralize the hydronium ion, sodium carbonate (soda ash) is added:

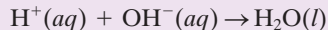


As a secondary result of this addition, the chlorine equilibrium shifts to the right, thus providing more hypochlorous acid.

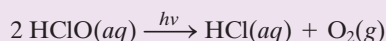
In smaller pools, the hydrolysis of the hypochlorite ion provides the hypochlorous acid:



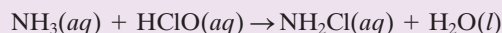
Acid must then be added to reduce the pH:



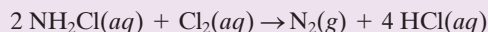
It is important to keep the hypochlorous acid concentrations at levels high enough to protect against bacteria and other pool organisms. This is a particularly difficult task in outdoor pools because hypochlorous acid decomposes in bright light and at high temperatures:



The production of stinging eyes in a swimming pool is usually blamed on “too much chlorine.” In fact, it is the converse problem, for the irritated eyes can be caused by the presence of chloramines in the water, such as  $\text{NH}_2\text{Cl}$ . These nasty compounds are formed through the reaction of hypochlorous acid with ammonia-related compounds, such as urea from urine, provided by the bathers:



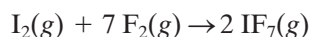
To destroy chloramines, we need to add more dichlorine, a process known as *superchlorination*. This additional dichlorine will react with the chloramines, decomposing them to give hydrochloric acid and dinitrogen:

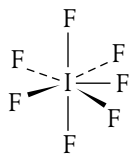


## 17.11 Interhalogen Compounds and Polyhalide Ions

There is an enormous number of combinations of pairs of halogens forming interhalogen compounds and polyhalide ions. These molecules and ions are of particular interest to inorganic chemists because of their geometries. The neutral compounds fit the formulas  $\text{XY}$ ,  $\text{XY}_3$ ,  $\text{XY}_5$ , and  $\text{XY}_7$ , where X is the halogen of higher atomic mass and Y, that of lower atomic mass. All permutations are known for  $\text{XY}$  and  $\text{XY}_3$ , but  $\text{XY}_5$  is only known where Y is fluorine. Thus, once again, it is only with fluorine that the highest oxidation states are obtained. The formula  $\text{XY}_7$ , in which X would have the oxidation state of +7, is found only in  $\text{IF}_7$ . The common argument for the lack of chlorine and bromine analogs is simply that of size: only the iodine atom is large enough to accommodate seven fluorine atoms.

All of the interhalogens can be prepared by combination reactions of the constituent elements. For example, heating purple iodine and yellow fluorine in a 1:7 ratio gives colorless iodine heptafluoride,  $\text{IF}_7$  which has the rare pentagonal bipyramidal shape of a seven-coordinate species (Figure 17.8):

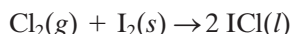




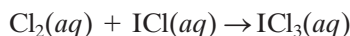
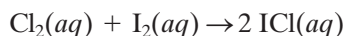
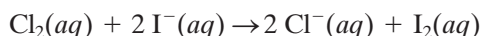
**FIGURE 17.8** The shape of the iodine heptafluoride molecule, which has a pentagonal arrangement in the horizontal plane.

### Iodine Monofluoride

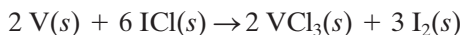
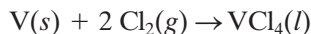
Iodine monochloride is a black solid (red by transmitted light) which forms a dark brown liquid on warming. The compound can be considered as a “combo” element (Chapter 9, Section 9.9) analog of bromine as it has the same number of combined valance electrons and total number of electrons as  $\text{Br}_2$ . The compound can be prepared by mixing equimolar quantities of the two halogens:



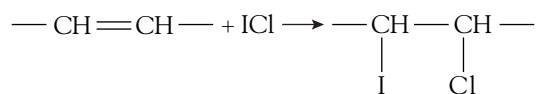
A solution of iodine monochloride can be prepared by bubbling chlorine gas through an aqueous solution of iodide ion. First, a brown-black solution of iodine is formed, then additional chlorine results in the synthesis of dark brown iodine monochloride. However, if more chlorine is bubbled through the solution, pale yellow iodine trichloride results:



More important, the chemical reactivity of an interhalogen compound is usually similar to that of the more reactive parent halogen. To chlorinate an element or compound, it is often more convenient to use solid iodine monochloride than chlorine gas, although sometimes the nonhalogen atom in the two products has different oxidation states. This outcome can be illustrated for the chlorination of vanadium:



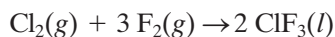
Ruby red, solid iodine monochloride, is used in biochemistry as the *Wij reagent* for the determination of the number of carbon-carbon double bonds in an oil or fat. When we add the brown solution of the interhalogen to the unsaturated fat, decolorization occurs as the halogens add across the double bond:



When a permanent brown color remains, the reaction has been completed. The results are reported as the iodine number—the volume (milliliters) of a standard iodine monochloride solution needed to react with a fixed mass of fat.

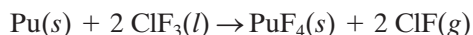
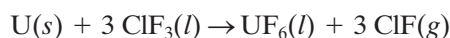
### Chlorine Trifluoride

The only interhalogen compound produced on an industrial scale is chlorine trifluoride. It is prepared by the reaction of chlorine with fluorine in a 1:3 ratio:



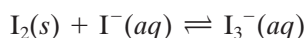
This colorless, poisonous, highly corrosive, and extremely reactive gas condenses to a yellow liquid at 12°C. It has a T-shaped structure which can be understood in the context of valence-shell electron-pair repulsion (VSEPR) theory as resulting from two equatorial lone pairs of electrons (Figure 17.9). Chlorine trifluoride is a convenient and extremely powerful fluorinating agent as a result of its high fluorine content and high bond polarity. The compound will react with almost anything, including sand and asbestos. In an industrial accident, a spill of 900 kg of chlorine trifluoride reacted its way through 30 cm of concrete and 90 cm of gravel.

Chlorine trifluoride is particularly useful in the separation of uranium from most of the fission products in used nuclear fuel. At the reaction temperature of 70°C, uranium forms liquid uranium(VI) fluoride. However, most of the major reactor products, such as plutonium, form solid fluorides, thus the uranium compound can then be separated from the mixture by distillation:



### The Triiodide(1−) Ion

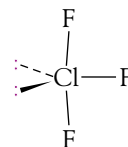
The halogens also form polyatomic ions. Iodine is the only halogen to readily form polyhalide anions by itself. The triiodide(1−) ion,  $\text{I}_3^-$ , is important because its formation provides a means of “dissolving” molecular iodine in water by using a solution of the iodide ion:



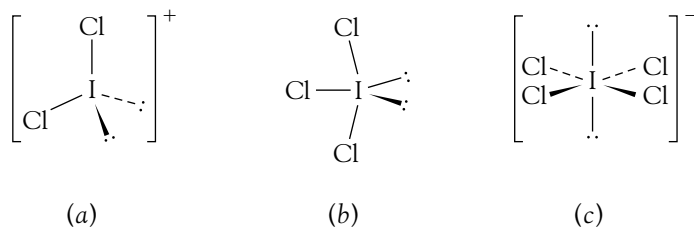
The ion is linear and has equal iodine-iodine bond lengths of about 293 pm; these bonds are slightly longer than the single bond in the diiodine molecule (272 pm). There are many other polyiodide ions, including  $\text{I}_5^-$  and  $\text{I}_7^-$ , but these are less stable than the triiodide ion. The large, low-charge triiodide ion will actually form solid compounds with low-charge-density cations such as rubidium, with which it forms rubidium triiodide,  $\text{RbI}_3$ .

### Interhalogen Ions

There also are a wide variety of interhalogen cations and anions, for example, the dichloroiodine ion,  $\text{ICl}_2^+$ , and the tetrachloroiodate ion,  $\text{ICl}_4^-$ . VSEPR theory can be used to predict the shapes of the interhalogen molecules and ions (Figure 17.10).



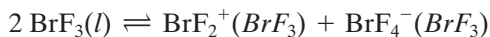
**FIGURE 17.9** The shape of the chlorine trifluoride molecule.



**FIGURE 17.10** The shapes of (a) the dichloroiodine ion,  $\text{ICl}_2^+$ ; (b) the iodine trichloride molecule,  $\text{ICl}_3$ ; and (c) the tetrachloroiodate ion,  $\text{ICl}_4^-$ .



Interhalogens can be used as aprotic solvents. For example, in Chapter 7, Section 7.1, we described how bromine trifluoride acts as a solvent by means of self-ionization to the difluorobromine cation and tetrafluorobromate anion:

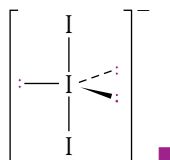


### WORKED EXAMPLE 17.3

Use VSEPR theory to predict the shape of the triiodide(1−) ion.

#### Answer

There are a total of 22 electrons to consider. Forming single bonds will leave 10 electrons on the central iodine atom, to give three lone pairs. The electron-pair arrangement will be trigonal bipyramidal, with the two attached iodine atoms in the axial positions.



### WORKED EXAMPLE 17.4

Predict which main-group (groups 13 to 18) ion might form a stable compound with the triiodide(1−) ion.

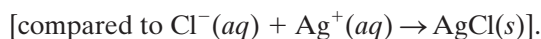
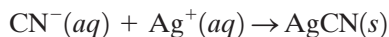
#### Answer

To form a stable solid triiodide(1−) compound, a large, low-charge cation is necessary. In Chapter 9, Section 9.6, we showed that the thallium(I) ion,  $\text{Tl}^+$ , closely resembled the larger alkali-metal cations in its behavior. Thus, thallium(I) triiodide(1−),  $\text{TlI}_3$ , might exist (and, in fact, it does). ■

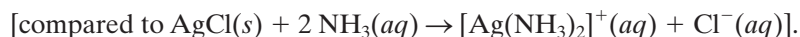
## 17.12 Cyanide Ion as a Pseudo-halide Ion

In Chapter 11, Section 11.14, we described how the ammonium ion, despite being a polyatomic ion, behaved much like an alkali metal ion. However, the best example of a pseudo-element ion is cyanide. Not only does it behave very much like a halide ion but also the parent pseudo-halogen, cyanogen,  $(\text{CN})_2$ , exists. The cyanide ion resembles a halide ion in a remarkable number of ways:

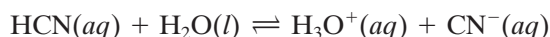
1. Salts of cyanide ion with silver, lead(II), and mercury(I) are insoluble, as are those of chloride, bromide, and iodide ions. For example:



2. Like silver chloride, silver cyanide reacts with ammonia to give the diamminesilver(I) cation:

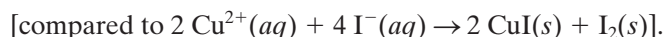
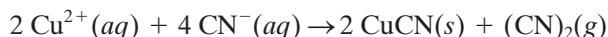


3. The cyanide ion is the conjugate base of the weak acid hydrocyanic acid, HCN, parallel to fluoride ion and hydrofluoric acid:

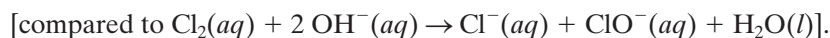


4. The cyanide ion forms numerous complex ions with transition metals, such as  $[\text{Cu}(\text{CN})_4]^{2-}$ , which is similar to its chloride analog,  $[\text{CuCl}_4]^{2-}$ .

5. Cyanide ion can be oxidized to the parent pseudo-halogen, cyanogen, similar to the oxidation of halides to halogens. The parallel is particularly close with iodide ion since they can both be oxidized by very weak oxidizing agents such as the copper(II) ion:



6. Cyanogen reacts with base to give the cyanide and cyanate ions:



7. Cyanogen forms pseudo-interhalogen compounds such as iodineonocyanide, ICN, in the same way that halogens form interhalogen compounds such as iodine monochloride, ICl (see Section 17.11).

## 17.13 Biological Aspects

The halogens are unique in that every stable member of the group has a biological function.

### Fluorine and Killer Plants

In several regions of the world, cattle ranchers have a major problem from toxic plants. Australia suffers particularly severely since about a thousand plant species there are known to be toxic to animals and humans. A significant number of these plants produce the fluoroacetate ion,  $\text{CH}_2\text{FCOO}^-$ . Although acetate ion is harmless (unless consumed in enormous quantities), the substitution of one fluorine for a hydrogen changes the properties of the ion substantially. For example, fluoroacetic acid is a strong acid with a  $\text{p}K_a$  of 2.59 compared to a value of 4.76 for acetic acid. The fluoroacetate ion acts by blocking the Krebs cycle in mammals, causing a buildup of citric acid and resulting in heart failure.

The plants absorb traces of fluoride ion from the soil and then incorporate it into their biochemical pathways. It is thought that these plants produce the fluoroacetate ion as a defense mechanism against predators. Although Australia probably has the most fluoroacetate-producing species, South Africa has a plant that produces the fluoroacetate ion to a concentration of 1 percent, meaning that the ingestion of one leaf of the plant is sufficient to kill a cow.

Sodium fluoroacetate is used by some in the United States and elsewhere as a poison for unwanted mammals such as coyotes. One of Australia's most famous double-murder cases (the Bogle-Chandler case) is believed to have been caused by deliberate fluoroacetate poisoning.

### Chlorine: The Challenge of Trihalomethanes

The chloride ion has a vital role in the ion balance in our bodies. It does not appear to play an active role but simply acts to balance the positive ions of sodium and potassium. However, covalently bonded chlorine is far less benign. Many of the toxic compounds with which we are currently concerned—for example, DDT and PCBs—are chlorine-containing molecules. The argument has been made to completely ban the production of chlorine-containing covalently bonded compounds. However, this would result in the elimination of many useful materials such as polyvinylchloride (PVC). It is important to recognize that there are organochloro compounds produced by a variety of organisms; thus, banning synthetic chloro compounds would not totally eliminate chloro compounds from the planet.

A group of compounds of particular concern are the trihalomethanes (THMs). These are produced when water rich in organic matter is chlorinated to disinfect it for human consumption. The organic matter is found in surface waters that have dissolved humic and fulvic acids from rotting vegetation. The acids themselves are comparatively harmless, although they do cause the water to have a brownish tint. It is the chlorination process that results in the fragmentation of the complex organic molecules to give small chloro molecules such as trichloromethane,  $\text{CHCl}_3$ . The existence of THMs in some tap-water samples was discovered in the 1970s, and regulations limiting the allowable level were introduced in the early 1980s. At that time, a maximum level of 100 ppb was generally considered safe, but now there is evidence of a weak correlation between drinking more than five glasses of water of high THM (over 75 ppb) per day and miscarriages. For this reason, there are proposals to reduce the permissible THM levels. One way to accomplish this is to use ozone (trioxygen; see Chapter 16, Section 16.3) or chlorine dioxide (see Section 17.9) as the primary disinfectant of the water supply. These compounds decompose the organic acids without significant generation of THMs. However, because ozone decomposes within a short time, a small concentration of chlorine needs to be added to water supplies to maintain potability because the water travels many kilometers through the aging, leaky pipes of most of our cities to its destination in your home.

### Bromine: The Methyl Bromide Problem

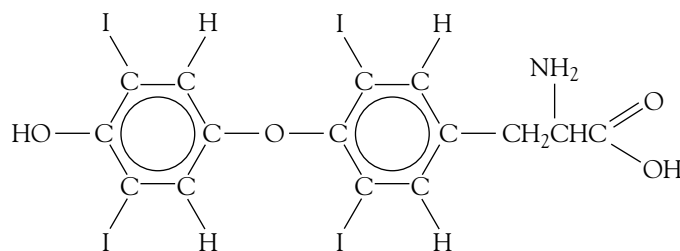
The most contentious bromine-containing compound is bromomethane, more commonly called *methyl bromide*. Methyl bromide,  $\text{CH}_3\text{Br}$ , is a broad-spectrum fumigant used in control of pest insects, nematodes, weeds, pathogens, and rodents. Apart from its unmatched range, it has a high volatility and hence leaves little residue. About 80 000 tonnes are used every year: about 75 percent as soil fumigant; 22 percent, postharvest; and 3 percent, structural pest control tool. Methyl bromide is important to the agricultural community because it controls a wide variety of pests at low cost. In fact, there is no one chemical that can currently be found to replace all of its roles.

Because seawater contains relatively high concentrations of bromide ion, it is not surprising that many marine organisms synthesize organobromine compounds. The function of most of these unique molecules is unknown at present. However, we do know that some of the metabolic pathways result in the production of methyl bromide. Thus, a significant proportion of the atmospheric burden of methyl bromide—probably about half—comes from natural sources.

There are two concerns with methyl bromide. First, it is an ozone-depleting substance (ODS); bromine being 50 times more efficient at destroying ozone than chlorine. The first global controls on methyl bromide emissions were established in 1995, although the compound is still in widespread agricultural use. The second concern is that methyl bromide is lethal against nontarget organisms. For example, in humans, low doses can cause headaches and nausea; then, in higher doses, muscle spasms, coma, convulsions, and death ensue. Thus, farm workers are at risk from handling the compound.

### Iodine: The Thyroid Element

About 75 percent of the iodine in the human body is found in one location—the thyroid gland. Iodine is utilized in the synthesis of the hormones thyroxine (Figure 17.11) and triiodothyronine. These hormones are essential for growth, for the regulation of neuromuscular functioning, and for the maintenance of male and female reproductive functions. Yet goiter, the disease resulting from a deficiency of the thyroid hormones, is found throughout the world, including a band across the northern United States, much of South America, and Southeast Asia; there are localized areas of deficiency in most other countries of the world. One common cause of the disease is a lack of iodide ion in the diet. To



**FIGURE 17.11** The structure of the thyroxine molecule.

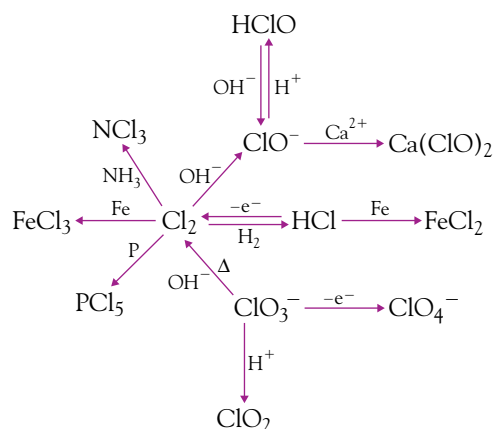
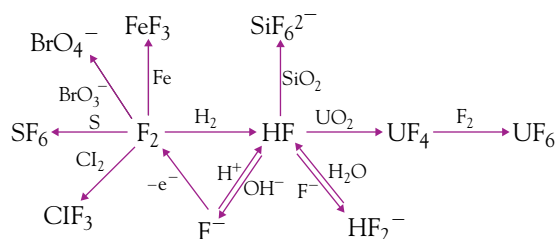
remedy the iodine deficiency, potassium iodide is added to common household salt (iodized salt).

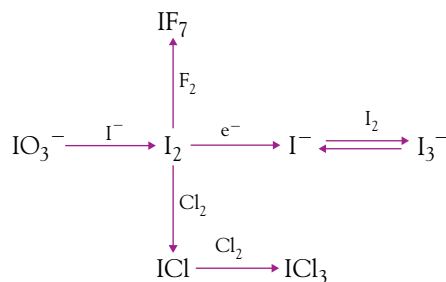
A symptom of goiter, which can have causes other than simple iodide deficiency, is a swollen lower part of the neck. The enlargement is the attempt of the thyroid gland to maximize absorption of iodide in iodine-deficient circumstances. In previous centuries, upperclass women with mild goiter were favored as marriage partners because their swollen necks enabled them to display their expensive and ornate necklaces more effectively.

Why is iodine essential? Bound to carbon, the iodine cannot take part in any redox function, nor is it chemically available for covalent bonding to other molecules. Because its electronegativity is close to that of carbon, it is unlikely that the iodine atoms make any significant change to the overall electronic structure of the molecule and hence the molecular properties. The clue seems to be in the very large covalent radius of the iodine atom—133 pm—about twice the radius of carbon, nitrogen, and oxygen. This corresponds to an eightfold greater volume. The iodine atoms of the iodo-organic molecules seem to be designed to fit in certain large cavities in a matching enzyme site, holding the enzyme in a unique conformation. Evidence for this role is provided by the fact that substituting the large isopropyl unit,  $(\text{CH}_3)_2\text{CH}-$ , for iodine results in a molecule with similar hormonal activity. Of course, this raises the question as to why a biological system should choose such a rare element for an essential pathway. The only obvious answer relates to the presumed marine origin of life. The seas are iodine-rich, and, in such an environment, incorporation of iodine would have provided a simple pathway to addition of a bulky substituent. Land organisms then became stuck with a process that necessitated an element much less common in the nonaquatic environment.

### 17.14 Element Reaction Flowcharts

Flowcharts are shown for fluorine, chlorine, and iodine.





## KEY IDEAS

- Fluorine is the most reactive element in the periodic table.
- Fluorine chemistry is influenced by the weakness of the fluorine-fluorine bond.
- Chlorine oxyacids are strongly oxidizing.
- Chlorine is an important industrial chemical.
- Ionic and covalent halides have very different properties.
- There is a wide range of interhalogen compounds and polyhalide ions.
- Cyanide ion behaves in many ways as a pseudo-halide ion.

## EXERCISES

**17.1** Write balanced chemical equations for the following chemical reactions:

- (a) uranium(IV) oxide with hydrogen fluoride
- (b) calcium fluoride with concentrated sulfuric acid
- (c) liquid sulfur tetrachloride with water
- (d) aqueous dichlorine and hot sodium hydroxide solution
- (e) diiodine with difluorine in a 1:5 mole ratio
- (f) bromine trichloride and water

**17.2** Write balanced chemical equations for the following chemical reactions:

- (a) lead metal with excess dichlorine
- (b) magnesium metal with dilute hydrochloric acid
- (c) the hypochlorite ion with sulfur dioxide gas
- (d) mild heating of potassium chlorate
- (e) solid iodine monobromide with water
- (f) phosphorus and iodine monochloride

**17.3** Summarize the unique features of fluorine chemistry.

**17.4** What are the shapes of the following species?

- (a)  $\text{BrF}_2^+$ ; (b)  $\text{BrF}_3$ ; (c)  $\text{BrF}_4^-$

**17.5** Suggest an explanation for why difluorine is so reactive toward other nonmetals.

**17.6** For chlorine, the only two naturally occurring isotopes are chlorine-35 and chlorine-37, while for bromine, they are bromine-79 and bromine-81. Suggest why chlorine-36 and bromine-80 are not stable isotopes.

**17.7** Use the formation of solid iodine heptafluoride to indicate why entropy cannot be a driving force in the reactivity of fluorine.

**17.8** Why cannot difluorine be produced electrolytically from an aqueous solution of sodium fluoride by a similar process to that used to produce dichlorine from sodium chloride solution?

**17.9** In the Frost diagram for chlorine, the  $\text{Cl}_2/\text{Cl}^-$  lines are identical for acidic and basic solution. Explain why.

**17.10** Why, in the Frost diagram (see Figure 17.1), is the acid species of chloric acid written as  $\text{ClO}_3^-$ , while that of chlorous acid is written  $\text{HClO}_2$ ?

**17.11** Suggest a reason why hydrofluoric acid is a weak acid, whereas the binary acids of the other halogens are all strong acids.

**17.12** Explain why, as the solution becomes more concentrated, hydrofluoric acid ionizes to a lesser extent at first, then to a greater extent at high concentrations.

**17.13** If annual hydrogen fluoride production is  $1.2 \times 10^6$  tonnes per year, calculate the mass of calcium sulfate produced per annum by this process.

**17.14** Why would you expect the hydrogen difluoride ion to form a solid compound with potassium ion?

**17.15** Deduce the oxidation number for oxygen in hypofluorous acid, HOF.

**17.16** Why is hydrochloric acid used as a common laboratory acid in preference to nitric acid?

**17.17** Suggest how you would prepare (a) chromium(III) chloride,  $\text{CrCl}_3$ , from chromium metal; and (b) chromium(II) chloride,  $\text{CrCl}_2$ , from chromium metal.

**17.18** Suggest how you would prepare (a) selenium tetrachloride,  $\text{SeCl}_4$ , from selenium; and (b) diselenium dichloride,  $\text{Se}_2\text{Cl}_2$ , from selenium.

**17.19** Explain why iron(III) iodide is not a stable compound.

**17.20** Describe the tests used to identify each of the halide ions.

**17.21** Calculate the enthalpy of reaction of ammonium perchlorate with aluminum metal. Apart from the exothermicity of the reaction, what other factors would make it a good propellant mixture?

**17.22** Construct an electron-dot formula for the triiodide ion. Thus, deduce the shape of the ion.

**17.23** The concentration of hydrogen sulfide in a gas supply can be measured by passing a measured volume of gas over solid diiodine pentoxide. The hydrogen sulfide reacts with the diiodine pentoxide to give sulfur dioxide, diiodine, and water. The diiodine can then be titrated with thiosulfate ion and the hydrogen sulfide concentration calculated. Write chemical equations corresponding to the two reactions.

**17.24** Carbon tetrachloride has a melting point of  $-23^\circ\text{C}$ ; carbon tetrabromide,  $+92^\circ\text{C}$ ; and carbon tetraiodide,  $+171^\circ\text{C}$ . Provide an explanation for this trend. Estimate the melting point of carbon tetrafluoride.

**17.25** The highest fluoride of sulfur is sulfur hexafluoride. Suggest why sulfur hexaiodide does not exist.

**17.26** Construct electron-dot structures of chlorine dioxide that have zero, one, and two double bonds (one of each) and decide which would be preferred on the basis of formal charge assignments.

**17.27** Another compound of chlorine and oxygen,  $\text{Cl}_2\text{O}_4$ , is more accurately represented as chlorine perchlorate,  $\text{ClOClO}_3$ . Draw the electron-dot structure of this compound and determine the oxidation number of each chlorine in the compound.

**17.28** Describe the uses of (a) sodium hypochlorite; (b) chlorine dioxide; (c) ammonium perchlorate; (d) iodine monochloride.

**17.29** Predict some physical and chemical properties of astatine as an element.

**17.30** Explain why the cyanide ion is often considered a pseudo-halogen.

**17.31** The thiocyanate ion,  $\text{SCN}^-$ , is linear. Construct reasonable electron-dot representations of this ion by assigning formal charges. The carbon-nitrogen bond length is known to be close to that of a triple bond. What does this tell you about the relative importance of each representation?

**17.32** How does fluoride ion affect the composition of teeth?

**17.33** Write balanced chemical equations corresponding to each transformation in the element reaction flowcharts for fluorine, chlorine, and iodine (pages 502–503).

**17.34** Iodine forms an oxide, diiodine pentoxide, that resembles dinitrogen pentoxide in structure. Construct the electron-dot structure of the iodine compound and contrast the bonding with that in  $\text{N}_2\text{O}_5$  (see Chapter 15, Section 15.8). Explain why the bonding differs. What is the oxidation state of each iodine atom, of the bridging oxygen atom, of each terminal oxygen atom?

**17.35** Draw the electron-dot structure of the dichlorine dioxide,  $\text{ClOOC}$ , molecule. Deduce the oxidation state of the chlorine atoms and of the oxygen atoms.

**17.36** Explain why ammonium fluoride adopts the wurtzite structure, whereas ammonium chloride adopts the sodium chloride lattice.

**17.37** Explain why, of the tetraphosphonium halides,  $[\text{PH}_4]\text{I}$  is the most stable toward decomposition.

**17.38** Tetramethylammonium fluoride,  $(\text{CH}_3)_4\text{NF}$ , reacts with iodine heptafluoride,  $\text{IF}_7$ , to give an electrically conducting solution. Write a chemical equation for the reaction.

**17.39** We noted that iodine monochloride can be considered as a “combo” element analog of bromine. Which other halogen pair can be considered as a combo element analog of another halogen?

**17.40** Give one example of how the cyanide ion resembles (a) the fluoride ion; (b) the chloride ion; (c) the iodide ion.



**17.41** The thiocyanate ion,  $\text{SCN}^-$ , also behaves as a pseudo-halide ion.

- Write the formula of the parent pseudo-halogen.
- Deduce an insoluble compound of the thiocyanate ion.

**17.42** Deduce an electron-dot structure of the cyanogen,  $(\text{CN})_2$ , molecule and draw the molecular shape. Experimental

measurements of the carbon-carbon bond length show it to be shorter than the simple bonding model predicts. Suggest an explanation.

**17.43** Phosphorus forms halide and pseudo-halide compounds of the form  $\text{PX}_3$ . Write the formula for the compound with cyanide.

## BEYOND THE BASICS

**17.44** Iodine pentafluoride undergoes self-ionization. Deduce the formulas of the cation and anion formed in the equilibrium and write a balanced equation for the equilibrium. Construct electron-dot diagrams for the molecule and the two ions. Which ion is the Lewis acid, and which is the Lewis base? Explain your reasoning.

**17.45** The melting point of ammonium hydrogen difluoride,  $(\text{NH}_4)^+(\text{HF}_2)^-$ , is only  $+26^\circ\text{C}$ . This is much lower than what one would expect for an ionic lattice. Suggest what might be happening.

**17.46** Calculate the enthalpy of formation of the chlorine molecular ion,  $\text{Cl}_2^+$ , given that the bond energy of molecular chlorine is  $240\text{ kJ}\cdot\text{mol}^{-1}$ , while the first ionization energy of the chlorine atom is  $1250\text{ kJ}\cdot\text{mol}^{-1}$  and that of the chlorine molecule is  $1085\text{ kJ}\cdot\text{mol}^{-1}$ . Comment on the bond strength in the molecular ion compared to that in the neutral molecule.

**17.47** Construct an approximate molecular-orbital-energy-level diagram to depict the bonding in chlorine monofluoride.

**17.48** Use the principle of formal charge to determine the average bond order in the phosphate ion and the perchlorate ion. Use these two results to suggest the average bond order in the sulfate ion.

**17.49** Which of dichlorine oxide and dichlorine heptaoxide is likely to be the more acidic oxide? Give your reasoning.

**17.50** Dichlorine heptaoxide,  $\text{Cl}_2\text{O}_7$ , is a colorless, oily liquid.

- Calculate the oxidation state of chlorine in the compound.
- Draw the probable structure of the compound.
- Write a balanced chemical equation for the reaction of this compound with water.
- Write the formula of an analogous compound of a metallic element. Give your reasoning.
- Write the formula of two probable isoelectronic and isostructural ions.

**17.51** Draw a probable structure of the dichlorine trioxide molecule. Will it be completely linear or bent? If bent, suggest an approximate bond angle.

**17.52** As we discussed, there are strong parallels between the chemistry of the pseudo-halogens and the halogens. On this assumption, write balanced chemical equations for the reactions between:

- cyanogen,  $(\text{CN})_2$ , and cold sodium hydroxide solution
- thiocyanate ion,  $\text{NCS}^-$ , and acidified permanganate ion solution

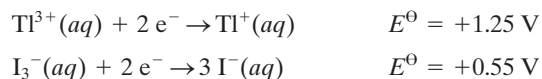
**17.53** Why is ammonium perchlorate an explosive hazard while sodium perchlorate is much less hazardous? Use a balanced equation to illustrate your argument and identify which elements undergo a change in oxidation state.

**17.54** Diiodine reacts with an excess of dichlorine to form a compound of formula  $\text{ICl}_x$ . One mole of  $\text{ICl}_x$  reacts with an excess of iodide ion to produce chlorine gas and 2 moles of diiodine. What is the empirical formula of  $\text{ICl}_x$ ?

**17.55** Fluorine, chlorine, and oxygen form a series of polyatomic ions:  $(\text{F}_2\text{ClO}_2)^-$ ,  $(\text{F}_4\text{ClO})^-$ ,  $(\text{F}_2\text{ClO})^+$ , and  $(\text{F}_2\text{ClO}_2)^+$ . Deduce the molecular shape of each of these ions.

**17.56** Fluorine forms only one oxide,  $\text{F}_2\text{O}$ . Draw the electron-dot structure of the compound and determine the oxidation state of fluorine and of oxygen in the compound. Explain why the oxidation state of oxygen is unusual. Suggest why one would not expect any other fluorine oxides. Use as comparisons the compounds  $\text{Cl}_2\text{O}$  and  $\text{Cl}_2\text{O}_7$ .

**17.57** Thallium forms an iodide,  $\text{TlI}_3$ . Suggest the actual formulation of the compound given the following information:



Why would this formulation be expected?



**17.58** Refer to the discussion of chlorine monoxide in Section 17.8. Sum together the reaction steps for the ozone destruction process and write the overall reaction. Identify catalytic and intermediate species.

**17.59** The ion  $[\text{I}(\text{N}_3)_2]^-$  is known.

- (a) Why should the existence of this ion be expected?
- (b) Deduce whether the electronegativity of the azide unit is higher or lower than that of iodine.
- (c) Deduce the geometry of the azide units about the iodine atom.
- (d) Suggest how the ion was stabilized.

**17.60** The standard enthalpy of formation of gaseous iodine monochloride is  $+18 \text{ kJ}\cdot\text{mol}^{-1}$ .

- (a) Write a balanced chemical equation for the process.

(b) Using  $\text{Cl}-\text{Cl}$  and  $\text{I}-\text{I}$  bond energy data (Appendix 3) and the enthalpy of sublimation of diiodine ( $62 \text{ kJ}\cdot\text{mol}^{-1}$ ), calculate the  $\text{I}-\text{Cl}$  bond energy.

(c) If the standard free energy of formation is  $-5 \text{ kJ}\cdot\text{mol}^{-1}$ , calculate the entropy change for the reaction. Why would you expect the value to have the sign that it does (two reasons)?

**17.61** (a) Chlorine trifluoride reacts with boron trifluoride to give an ionic product in which the chlorine is in the polyatomic cation. Write a chemical equation for the reaction.

(b) Chlorine trifluoride reacts with potassium fluoride to give an ionic product in which the chlorine is in the polyatomic cation. Write a chemical equation for the reaction.

(c) Comment on the difference in reactions.

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

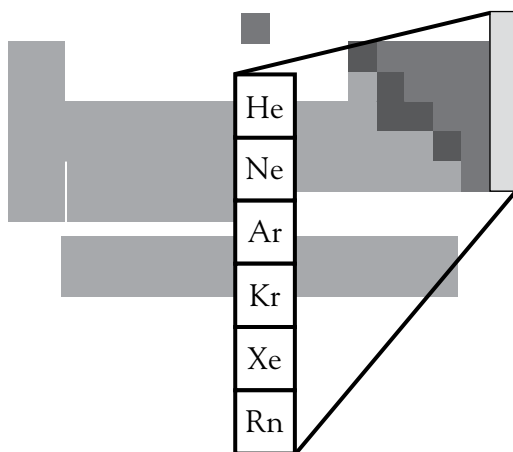


For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# THE GROUP 18 ELEMENTS:

## The Noble Gases

## CHAPTER 18



He
Ne
Ar
Kr
Xe
Rn

The noble gases make up the least reactive group in the periodic table. In fact, xenon is the only noble gas to form a wide range of compounds—and then only with highly electronegative elements. It is doubtful that stable chemical compounds will ever be made of helium and neon.

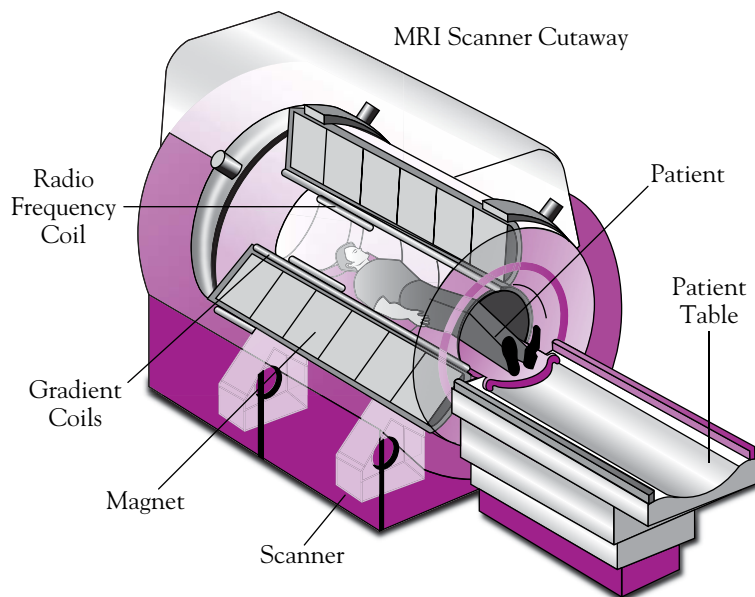
### Context: Helium—An Increasingly Rare Gas

It is not only the metallic elements which we are squandering. For we are using up helium, as the phrase goes, “like there’s no tomorrow.” Helium is the most widely used of all the noble gases. All of us will be familiar with its everyday use in helium-filled party balloons. As described in this chapter, with a uniquely low boiling point, liquid helium is used to cool nuclear reactors and the superconducting magnets that are used in magnetic resonance imaging (MRI). One of the largest uses of liquid helium is the Large Hadron Collider (LHC) at CERN in Switzerland. The LHC, used to generate and research subatomic particle, uses 96 tonnes of liquid helium to cool the LHC superconducting magnets (see Context section, Chapter 5).

The demand for helium is now outstripping supply, and it has been predicted that helium will run out in 20 to 30 years. Helium accumulates in underground deposits of natural gas. In fact, the discovery of the deposits in the 1920s caused the price of helium gas to drop from \$88 per liter (1915) to \$0.05 per liter (1926). In 1925, the United States

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 18.1** Group Trends
- 18.2** Helium
- 18.3** Compounds of Helium, Argon, and Krypton
- 18.4** Xenon Fluorides
- 18.5** Xenon Oxides
- 18.6** Other Xenon Compounds
- 18.7** Biological Aspects
- 18.8** Element Reaction Flowchart



An MRI is essentially a giant superconducting magnet, cooled with liquid helium.

established the National Helium Reserve, a massive storage facility holding over a billion cubic meters of helium, initially for use in airships, and then as a coolant during the Space Race and the Cold War. Then, in 1996, U.S. federal legislation was passed which required that the Reserve be depleted as the Reserve was a money-loser. When the helium in the reservoir was put on the market, the price again fell, making recycling uneconomical.

Once helium is released, it diffuses throughout the atmosphere. With its low atomic mass and resulting high average atomic velocity of the gas, over time, helium readily escapes Earth's gravity. As mentioned later, the concentration of helium in the atmosphere is extremely low, making it challenging to provide any large supply from that source. Thus, there is now a real danger that the world's store of helium will run out. The lack of inexpensive helium will have a major negative impact on MRI imaging, space technology, and many other applications, including those celebratory balloons.

## 18.1 Group Trends

All the elements in Group 18 are colorless, odorless, monatomic gases at room temperature. They neither burn nor support combustion; in fact, they make up the least reactive group in the periodic table. The very low melting and boiling points of the noble gases indicate that the dispersion forces holding the atoms together in the solid and liquid phases are very weak. The trend in the melting and boiling points, shown in Table 18.1, corresponds to the increasing number of electrons and, hence, greater polarizability.

**TABLE 18.1** Melting and boiling points of the noble gases

Noble gas	Melting point (°C)	Boiling point (°C)	Number of electrons
He	—	−269	2
Ne	−249	−245	10
Ar	−189	−186	18
Kr	−157	−152	36
Xe	−112	−109	54
Rn	−71	−62	86

### Densities of Noble Gases

Because the elements are all monatomic gases, there is a well-behaved trend in densities at the same pressure and temperature. The trend is a simple reflection of the increase in molar mass (Table 18.2). Air has a density of about  $1.3 \text{ g}\cdot\text{L}^{-1}$ ; so, relative to air, helium has an extremely low density. Conversely, radon is among the densest of gases.

The denser noble gases, particularly argon, have been used to fill the air space between the glass layers of thermal insulating windows. This use is based on the low thermal conductivities of these gases; for example, that of argon at  $0^\circ\text{C}$  is  $0.017 \text{ J}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . Dry air at the same temperature has a thermal conductivity of  $0.024 \text{ J}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ .

### Noble Gas Clathrates

As we discussed in Chapter 10, Section 10.6, until 1962, the only known species involving the noble gases were the clathrates, in which the noble gas atoms are trapped within ice cages. These clathrates have now become of interest again to explain why the atmosphere of Saturn's moon Titan lacks the krypton and xenon that should be present from the forming of this large moon. Cosmochemists currently think that these gases have been trapped within ice clathrates on Titan's surface ever since the solar system formed and the moon's surface cooled.

### Atmospheric Concentrations of the Noble Gases

All the stable noble gases are found in the atmosphere, although only argon is present in a high proportion (Table 18.3). The high abundance of argon in the

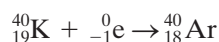
**TABLE 18.2** Densities of the noble gases (at SATP)

Noble gas	Density ( $\text{g}\cdot\text{L}^{-1}$ )	Molar mass ( $\text{g}\cdot\text{mol}^{-1}$ )
He	0.2	4
Ne	1.0	20
Ar	1.9	39
Kr	4.1	84
Xe	6.4	131
Rn	10.6	222

**TABLE 18.3** Abundance of the noble gases in the dry atmosphere

Noble gas	Abundance (% by moles)
He	0.000 52
Ne	0.001 5
Ar	0.93
Kr	0.000 11
Xe	0.000 008 7
Rn	Trace

atmosphere is largely the result of the radioactive decay of potassium-40, the naturally occurring radioactive isotope of potassium. As mentioned in Chapter 11, Section 11.6, this isotope has two decay pathways, one of which involves the capture of a core electron to form argon-40:



All the noble gases, except helium, are obtained as by-products of the production of dioxygen and dinitrogen from air. Some argon also is obtained from industrial ammonia synthesis, where it accumulates during the recycling of the unused atmospheric gases. Argon production is quite large, approaching  $10^6$  tonnes per year. Its major use is as an inert atmosphere for high-temperature metallurgical processes. Argon and helium are both used as an inert atmosphere in welding; neon, argon, krypton, and xenon are used to provide different colors in “neon” lights.

## 18.2 Helium

Helium is still a liquid at the lowest temperatures we can reach. In fact, even at a temperature of 1.0 K, a pressure of about 2.5 MPa is required to cause it to solidify. However, liquid helium is an amazing substance. At a pressure of 100 kPa, the gas condenses at 4.2 K to form an ordinary liquid (referred to as *helium I*), but when cooled below 2.2 K, the properties of the liquid (now *helium II*) are dramatically different. For example, helium II is an incredibly good thermal conductor;  $10^6$  times greater than helium I and much better than even silver, the best metallic conductor at room temperature. Thus, helium is ideal for keeping superconducting magnets cool, both from the perspective of the enthalpy of vaporization and the high thermal conductivity. Hence, the crucial use to cool the magnets of MRIs and other scientific equipment.

Because it is the gas with the second-lowest density (dihydrogen having the lowest), helium is used to fill balloons. Dihydrogen would provide more “lift,” but its flammability is a major disadvantage. Today, the public thinks of airships solely in their advertising role. However, they have also been employed as long-endurance flying radar posts by the U.S. Coast Guard to identify illegal drug-carrying flights. An airship has also been used to study the upper canopy of the rain forest in the Amazon basin, a vital task that would be very difficult to do by

any other means. Using modern technology, new designs of airships are being constructed for a variety of tasks, such as ecotourism and heavy lifting.

Helium is used in deep-sea-diving gas mixtures as a replacement for the more blood-soluble nitrogen gas in air. The velocity of sound is much greater in low-density helium than in air. As many people know, this property gives breathers of helium “Mickey Mouse” voices. It should be added that the combination of dry helium gas and the higher frequency of vibrations in the larynx can cause voice damage to those who frequently indulge in the gas for fun.

## 18.3 Compounds of Helium, Argon, and Krypton

### Hydridohelium(1+)

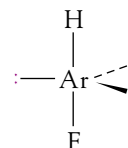
Why are there no chemical compounds of helium, neon, or argon? In fact, this statement is not quite correct. The gas-phase ion  $\text{HeH}^+$  was first synthesized in 1925, but it only exists for a very short time. Hydridohelium(1+) is believed to have been the first compound to have formed in the Universe, after the Big Bang.

This ion is spontaneously formed as a result of radioactive decay of hydrogen molecules in which one atom is tritium, the hydrogen isotope with two neutrons. As mentioned in Chapter 10, Section 10, tritium decays to helium-3. Thus, the hydridohelium(1+) ion is generated in the decay process:



### Argon Fluoridohydride

At the time of writing, only one argon compound has been synthesized and conclusively identified:  $\text{HArF}$ . It can be formed by irradiating a mixture of argon and hydrogen fluoride at about  $-255^\circ\text{C}$ . Infrared spectroscopy shows that the compound does indeed contain  $\text{H}-\text{Ar}$  and  $\text{Ar}-\text{F}$  covalent bonds and that it is linear as valence-shell electron-pair repulsion (VSEPR) theory predicts (Figure 18.1). Unfortunately, the compound decomposes above  $-245^\circ\text{C}$ . Nevertheless, it shows that there is some very low-temperature argon chemistry. Such species may occur on the very cold outer planets of our solar system.



**FIGURE 18.1** The structure of argon hydrofluoride.

### Krypton Compounds

The only known binary compound of krypton is krypton difluoride, formed by the reaction of krypton and fluorine in ultraviolet light at  $-196^\circ\text{C}$ . The compound decomposes at about  $-20^\circ\text{C}$ . Krypton difluoride is an extremely strong oxidizing agent. For example, it will oxidize/fluorinate metallic gold to give  $(\text{KrF})^+[\text{AuF}_6]^-$ . The fluoridokrypton cation is quite stable and will undergo reactions as a Lewis acid.

## 18.4 Xenon Fluorides

All three xenon fluorides are white solids and are stable with respect to dissociation into elements at ordinary temperatures; that is, they have negative free energies of formation at  $25^\circ\text{C}$ . As noted earlier, it is not necessary to invoke

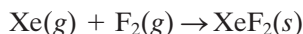
**TABLE 18.4** Xenon halides and isoelectronic iodine polyfluoride anions

Number of electron pairs	Xenon halides	Iodine polyfluoride anions
5	XeF <sub>2</sub>	IF <sub>2</sub> <sup>−</sup>
6	XeF <sub>4</sub>	IF <sub>4</sub> <sup>−</sup>
7	XeF <sub>6</sub>	IF <sub>6</sub> <sup>−</sup>

any novel concepts to explain the bonding; in fact, the three compounds are isoelectronic with well-established iodine polyfluoride anions. Table 18.4 shows the formulas of the compounds and the number of electron pairs around the central atom.

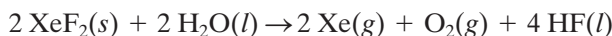
### Xenon Difluoride

Xenon difluoride is a colorless solid with a high vapor pressure, giving a nauseating odor. It is synthesized by reacting xenon with fluorine in a 1:2 mole ratio:



The linear shape of xenon difluoride is consistent with that predicted from VSEPR theory for a molecule with three lone pairs (Figure 18.2).

Xenon difluoride reacts with water:

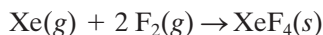


The fluorides are strong fluorinating agents. For example, xenon difluoride can be used to fluorinate double bonds in organic compounds. It is a very “clean” fluorinating agent, in that the inert xenon gas can be easily separated from the required product:



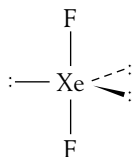
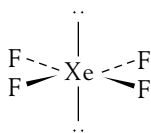
### Xenon Tetrafluoride

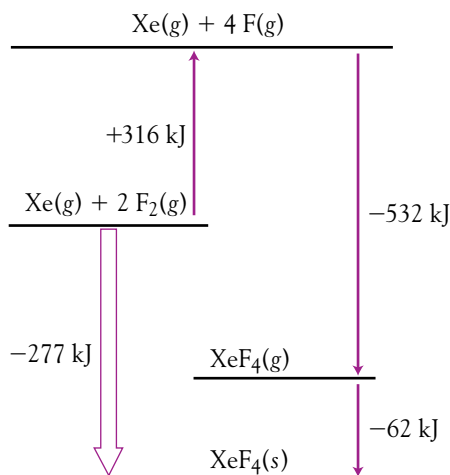
To synthesize xenon tetrafluoride, a xenon to fluorine mole ratio of about 1:3 is required:



The molecule has a square planar geometry and this structure, too, is consistent with the VSEPR prediction for six electron pairs, and hence two lone pairs, around the central xenon atom (Figure 18.3).

What is the driving force in the formation of the xenon fluorides? Using xenon tetrafluoride as an example, from the equation for the formation of the compound from its elements (see earlier), we see that the entropy change must be negative, considering that 1 mole of solid is being formed from 3 moles of gas. The negative free energy must, therefore, result from a negative enthalpy change—an exothermic reaction. Figure 18.4 shows the enthalpy cycle for the

**FIGURE 18.2** The structure of xenon difluoride.**FIGURE 18.3** The structure of xenon tetrafluoride.

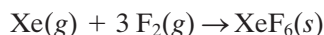


**FIGURE 18.4** Enthalpy cycle for the formation of xenon tetrafluoride.

formation of this compound from its elements. In the cycle, 2 moles of difluorine are dissociated into atoms, then 4 moles of xenon-fluorine bonds are formed, followed by solidification of the product. The stability of this compound clearly depends on the moderately high Xe—F bond energy and the low dissociation energy of the fluorine molecule.

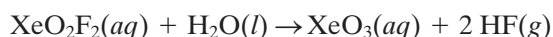
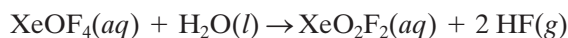
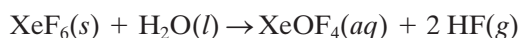
### Xenon Hexafluoride

Xenon hexafluoride, a colorless solid which sublimes into an intensely yellow gas, can be prepared at high pressures and temperatures or, at 120°C, using a catalyst:

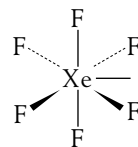


With six bonding pairs and one lone pair around the xenon atom, seven bonding directions are predicted (one having the lone pair). As discussed in Chapter 3, Section 3.4, there are three possible arrangements: pentagonal bipyramid, capped trigonal prism, and capped octahedron. In fact, the structural studies of xenon hexafluoride in the gas phase indicate that it adopts a distorted octahedral arrangement with a mobile lone pair (Figure 18.5).

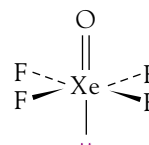
Upon addition to water, xenon hexafluoride is first hydrolyzed to xenon oxidotetrafluoride,  $\text{XeOF}_4$  (Figure 18.6), then xenon dioxidodifluoride, and finally xenon trioxide:



Xenon oxidotetrafluoride has a square-based pyramidal shape with a short Xe—O bond consistent with multiple-bond character. The structure can be understood using the VSEPR concept, as a lone pair would be expected to occupy the sixth bonding direction of an octahedron (Figure 18.6).



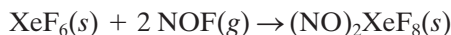
**FIGURE 18.5** Probable structure of xenon hexafluoride in the gas phase.



**FIGURE 18.6** A possible representation of the bonding in the xenon oxotetrafluoride molecule.



From xenon hexafluoride, the octafluoridoxenate(VI) ion can be synthesized. For example, reaction of xenon hexafluoride with nitrosyl fluoride, NOF, gives the compound with the nitrosonium cation,  $\text{NO}^+$  (isoelectronic with the  $\text{N}_2$  molecule):

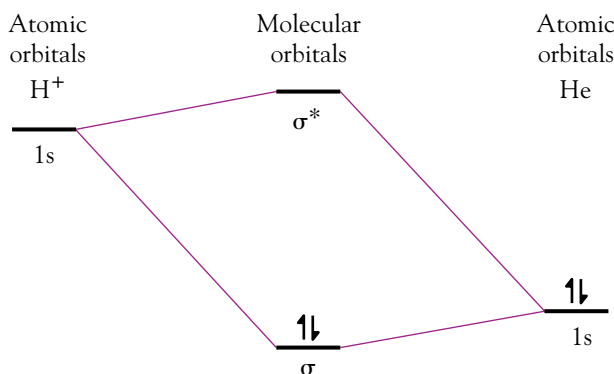


### WORKED EXAMPLE 18.1

Use a molecular orbital diagram to show how the  $\text{HeH}^+$  ion would have a single bond as does isoelectronic dihydrogen. The bond energy of the  $\text{He—H}$  bond is  $178 \text{ kJ}\cdot\text{mol}^{-1}$ , compared with  $436 \text{ kJ}\cdot\text{mol}^{-1}$  for the  $\text{H—H}$  bond.

#### Answer

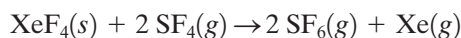
The molecular orbital diagram is shown in the following figure (for the atomic orbitals, one electron could have been assigned to each atom). As the helium nucleus has two protons, the attraction for the 1s electrons is much stronger, and the 1s level for helium must be shown much lower. The bond order is 1 as it is for dihydrogen.



We can suggest that the weakness of the  $\text{He—H}$  bond is a result of the significant energy difference between the hydrogen and helium atomic orbitals, so that the electron pair of the formed molecular orbital is essentially residing on the helium atom, and not significantly shared with the hydrogen atom. As a result, it would be a much weaker covalent bond. ■

### WORKED EXAMPLE 18.2

Use the bond energy data given to calculate the enthalpy of reaction for the following:



Xe—F	159 $\text{kJ}\cdot\text{mol}^{-1}$
S—F in $\text{SF}_4$	340 $\text{kJ}\cdot\text{mol}^{-1}$
S—F in $\text{SF}_6$	329 $\text{kJ}\cdot\text{mol}^{-1}$

We can use  $\Delta H^\circ = \Sigma(\text{Bonds broken}) - \Sigma(\text{Bonds formed})$  to calculate the enthalpy of formation. We are breaking four Xe—F bonds and eight S—F(SF<sub>4</sub>) bonds. We are forming 12 S—F(SF<sub>6</sub>) bonds. So the enthalpy of reaction will be:

$$[(4 \times 159) + (8 \times 340) - (12 \times 329)] \text{ kJ} \cdot \text{mol}^{-1} = -592 \text{ kJ} \cdot \text{mol}^{-1} \blacksquare$$

## 18.5 Xenon Oxides

Xenon forms two common oxides: xenon trioxide and xenon tetroxide. As discussed in Chapter 16, Section 16.5, higher oxidation states are often found for elements with oxygen than with fluorine. This is also the case with xenon, where the highest fluoride, XeF<sub>6</sub>, has xenon in the +6 oxidation state, while the highest oxide, XeO<sub>4</sub>, has xenon in the +8 oxidation state.

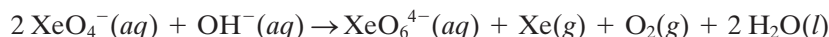
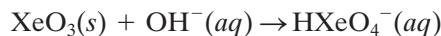
### Xenon Dioxide

Xenon dioxide is a yellow-orange solid which readily disproportionates to xenon and xenon trioxide. The compound has a polymeric structure with four-coordinate xenon and two-coordinate oxygen atoms. It is possible that xenon dioxide exists deep within the Earth. For decades, geochemists and atmospheric chemists have sought an explanation for the low level of xenon in the atmosphere (the “xenon deficit”). It has been postulated that some of the xenon formed by radioactive decay within the Earth, instead of diffusing to the surface, has substituted for silicon in the tetrahedrally bonded silicate structures under the extreme temperatures and pressures within the Earth’s crust. By experiment under extreme conditions, reaction of xenon with silicates and silicon dioxide has indeed been shown to occur.

### Xenon Trioxide

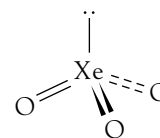
Xenon trioxide is a colorless, deliquescent solid that is quite explosive. The oxide is an extremely strong oxidizing agent, although its reactions are often kinetically slow. Because of its lone pair, it is a trigonal pyramidal molecule, as predicted by VSEPR theory (Figure 18.7). The bond length indicates that, as discussed before for silicon, phosphorus, and sulfur, there is some degree of multiple bonding.

Xenon trioxide reacts with dilute base to give the hydrogen xenate ion, HXeO<sub>4</sub><sup>−</sup>. However, this ion is not stable, and disproportionation to xenon gas and the yellow perxenate ion, XeO<sub>6</sub><sup>4−</sup>, occurs:

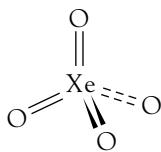


### Xenon Tetroxide

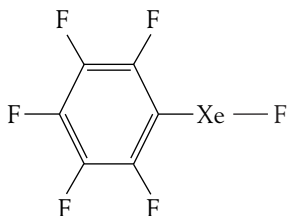
Xenon tetroxide is a yellow solid, only stable below −36°C, prepared by adding concentrated sulfuric acid to solid barium perxenate:



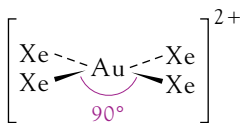
**FIGURE 18.7** A possible representation of the bonding in the xenon trioxide molecule.



**FIGURE 18.8** A possible representation of the bonding in the xenon tetroxide molecule.



**FIGURE 18.9** The structure of the  $\text{C}_6\text{F}_5\text{XeF}$  molecule.



**FIGURE 18.10** The structure of the  $[\text{AuXe}_4]^{2+}$  ion.

This oxide, also with xenon in the oxidation state of +8, is an explosive gas. Its structure has been shown to be tetrahedral (Figure 18.8), a geometry expected from VSEPR theory. As for xenon trioxide, there appears to be significant multiple-bond character in the  $\text{Xe}-\text{O}$  bond. In Chapter 9, Section 9.4, we showed the similarities of xenon tetroxide in Group 18 with osmium(VIII) oxide of Group 8.

## 18.6 Other Xenon Compounds

Finding compounds of noble gases with elements other than fluorine and oxygen has become close to an obsession with chemists. Descriptions of two of these, pentafluorophenylxenonfluoride and the tetraxenongold(II) ion, follow.

### Pentafluorophenylxenonfluoride

The most stable xenon compound containing a xenon-carbon bond is pentafluorophenylxenonfluoride (Figure 18.9). This can be used as a starting material for producing other organoxenon compounds.

### The Tetraxenongold(II) Ion

Probably the most surprising xenon-containing compound is the dark red ion  $[\text{AuXe}_4]^{2+}$  (Figure 18.10). This square-planar cation is stabilized by very large fluorine-containing anions, such as  $[\text{Sb}_2\text{F}_{11}]^{2-}$ .

## 18.7 Biological Aspects

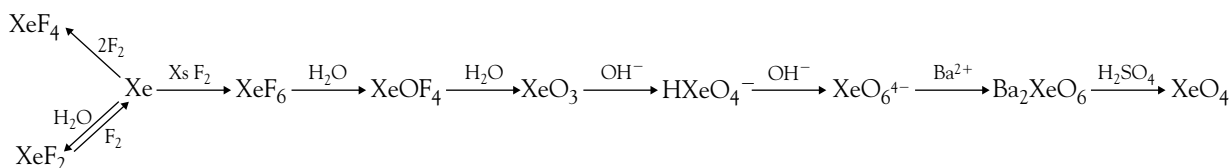
None of the noble gases has any positive biological functions. Radon, however, has been in the news because it accumulates inside buildings. The radiation it releases as it decays may be a significant health hazard. Radon isotopes are produced during the decay of uranium and thorium. Only one isotope, radon-222, has a half-life long enough (3.8 days) to cause major problems, and this particular isotope is produced in the decay of uranium-238. This process is happening continuously in the rocks and soils, and the radon produced normally escapes into the atmosphere.

However, the radon formed beneath dwellings permeates through cracks in concrete floors and basement walls, a process that is enhanced when the pressure inside the house is lower than the external value. This pressure differential occurs when ventilation fans, clothes dryers, and other mechanical devices pump air out of the house. Furthermore, our concern about saving energy has prompted us to build houses that are more airtight, thereby preventing exchange of radon-rich interior air with exterior fresh air. For existing homes, two approaches are used. First, the basement is vented continuously. Second, it is possible to install drain tile under the basement floor and tie that into an exterior ventilation fan. Because the latter design is done outside the ventilation “envelope” of the house, it is more energy efficient.

It is not actually the radon that is the problem but the solid radioactive isotopes produced by its subsequent decay, such as polonium-218. These solid particles attach themselves to lung tissue, subsequently irradiating it with  $\alpha$ -particles (helium nuclei) and  $\beta$ -particles (electrons), disrupting the cells and even initiating lung cancer.

## 18.8 Element Reaction Flowchart

Following is a flowchart for xenon, the only noble gas with a significant chemistry.



## KEY IDEAS

- No stable chemical compounds of helium or neon have yet been synthesized.
- The three fluorides of xenon are strong fluorinating agents.
- The two oxides of xenon are strong oxidizing agents.

## EXERCISES

**18.1** Write balanced chemical equations for the following chemical reactions:

- (a) xenon with difluorine in a 1:2 mole ratio;  
(b) xenon tetrafluoride with phosphorus trifluoride.

**18.2** Write balanced chemical equations for the following chemical reactions:

- (a) xenon difluoride with water;  
(b) solid barium perxenate with sulfuric acid.

**18.3** Describe the trends in the physical properties of the noble gases.

**18.4** Why is argon (thermal conductivity  $0.017 \text{ J}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at  $0^\circ\text{C}$ ) more commonly used as a thermal insulation layer in glass windows than xenon (thermal conductivity  $0.005 \text{ J}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at  $0^\circ\text{C}$ )?

**18.5** What are the unusual features of liquid helium?

**18.6** Why would we expect noble gas compounds to exist?

**18.7** A bright green ion,  $\text{Xe}_2^+$ , has been identified. Suggest the bond order for this ion, showing your reasoning.

**18.8** The  $\text{XeF}^+$  ion is known. Construct the electron-dot formula for this ion. By comparison with interhalogen chemistry, would this ion be predicted to exist?

**18.9** What are the key thermodynamic factors in the formation of xenon-fluorine compounds?

**18.10** For the formation of xenon tetrafluoride,  $\Delta_f G^\ominus = -121.3 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H^\ominus = -261.5 \text{ kJ}\cdot\text{mol}^{-1}$ . Determine the value for the standard entropy of formation of this compound. Why do you expect the sign of the entropy change to be negative?

**18.11** Estimate the enthalpy of formation of xenon tetrachloride from the following data: bond energy (Xe—Cl) [estimated] = 86 kJ·mol<sup>-1</sup>; enthalpy of sublimation of solid xenon tetrachloride [estimated] = 60 kJ·mol<sup>-1</sup>. Obtain any other required data from the data tables in the appendices.

**18.12** One of the few krypton compounds known is krypton difluoride,  $\text{KrF}_2$ . Calculate the enthalpy of formation of this compound using the data in the appendices (the  $\text{Kr}-\text{F}$  bond energy is  $50 \text{ kJ}\cdot\text{mol}^{-1}$ ).

**18.13** Construct an electron-dot structure for  $\text{XeOF}_4$  with a xenon-oxygen (a) single bond; (b) double bond. Decide which is more significant on the basis of formal charge.

**18.14** Determine the shapes of the following ions: (a)  $\text{XeF}_3^+$ ; (b)  $\text{XeF}_5^+$ ; (c)  $\text{XeO}_6^{4-}$ .

**18.15** Determine the oxidation number of xenon in each of the compounds in Exercise 18.14.

**18.16** Which of the noble gases would you choose as:  
 (a) the lowest-temperature liquid refrigerant?  
 (b) the least-expensive inert atmosphere?  
 (c) an electric discharge light source requiring a safe gas with the lowest ionization energy?

**18.17** It is possible to prepare a series of compounds of formula  $\text{MXeF}_7$ , where M is an alkali metal ion. Which alkali metal ion should be used in order to prepare the most stable compound?

**18.18** Suggest an explanation why xenon forms compounds with oxygen in the +8 oxidation state but with fluorine only up to an oxidation state of +6.

**18.19** Write a balanced chemical equation for the reaction of krypton difluoride with gold to give  $(\text{KrF})^+[\text{AuF}_6]^-$  (the other product is krypton gas).

**18.20** Briefly discuss why radon is a health hazard.

**18.21** Write balanced chemical equations corresponding to each transformation in the element reaction flowchart for xenon (page 517).

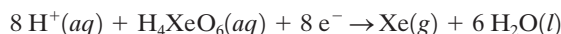
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## BEYOND THE BASICS

**18.22** Why is  $\text{XeCl}_2$  likely to be much less stable than  $\text{XeF}_2$ ?

**18.23** Xenon difluoride reacts with antimony pentafluoride,  $\text{SbF}_5$ , to give an electrically conducting solution. Write a chemical equation for the reaction.

**18.24** The reduction potential for the  $\text{H}_4\text{XeO}_6(\text{aq})/\text{XeO}_3(\text{aq})$  reduction half-reaction is +2.3 V, whereas that for the  $\text{XeO}_3(\text{aq})/\text{Xe}(\text{g})$  reduction half-reaction is +1.8 V. Calculate a value for the half-cell potential of



**18.25** The fact that argon difluoride has not been prepared despite strenuous efforts suggests that the argon-fluorine bond must be very weak. Use a theoretical enthalpy cycle to determine an approximate maximum value that the  $\text{Ar}-\text{F}$  bond energy could have. Do entropy factors favor or oppose the formation of argon difluoride? Give your reasoning.

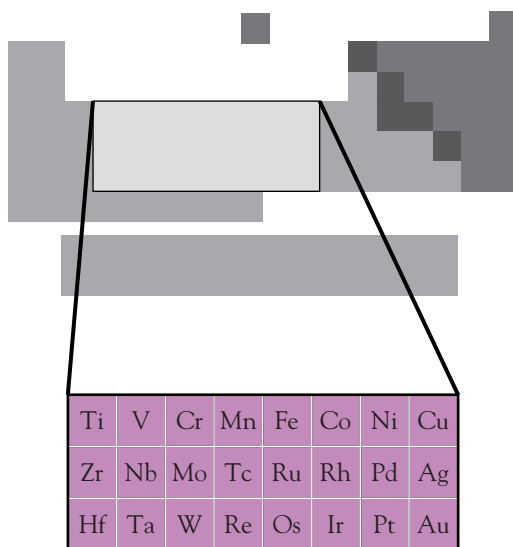
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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# TRANSITION METAL COMPLEXES

## CHAPTER 19



Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

An obvious feature of the transition metals is the enormous number of compounds. We will see the ways in which transition metals can form this galaxy of species, introduce the naming system used for them, and discuss the modern theories of bonding that are used to explain their diversity. In addition, we will revisit hard-soft acid-base concepts in the context of transition metal compounds.

### Context: Platinum Complexes and Cancer Treatment

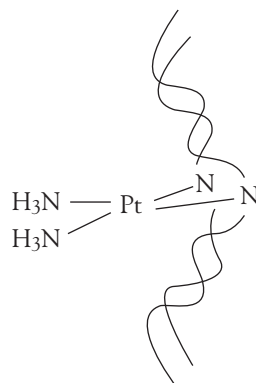
It is a common misconception that scientific research works the same way as does technology, where goals are set and the appropriate solutions found. In science, however, so much is not known that we still rely to a large extent on observing the unexpected. It was in 1965 that Barnett Rosenberg, of Michigan State University, was studying the rate of bacterial growth in the presence of electric fields. He and his co-researchers were surprised to find that the bacteria in electric fields were growing without dividing. The group spent a considerable amount of time looking for possible causes of this, such as pH and temperature changes. Having excluded every probable cause, they examined the

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 19.1 Transition Metals
- 19.2 Introduction to Transition Metal Complexes
- 19.3 Stereochemistries
- 19.4 Isomerism in Transition Metal Complexes
- 19.5 Naming Transition Metal Complexes
- 19.6 An Overview of Bonding Theories of Transition Metal Compounds
- 19.7 Crystal Field Theory
- 19.8 Successes of Crystal Field Theory
- 19.9 More on Electronic Spectra
- 19.10 Ligand Field Theory
- 19.11 Thermodynamic versus Kinetic Factors
- 19.12 Synthesis of Coordination Compounds
- 19.13 Reaction Mechanisms
- 19.14 Coordination Complexes and the Hard-Soft Acid-Base (HSAB) Concept
- 19.15 Biological Aspects

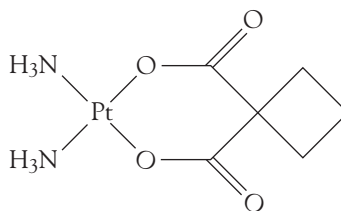
electrodes that they were using to generate the electric charge. These were made of platinum, a metal that was “well known” to be extremely unreactive.

However, their tests showed that some of the platinum metal was being oxidized, and it was the oxidation products, particularly  $[\text{PtCl}_2(\text{NH}_3)_2]$ , that were causing the bacterial abnormalities. Further, it was only one geometric arrangement around the platinum ion, the *cis* form (see Section 19.4) which was active. This biological activity of platinum compounds was completely unexpected. Because they prevented cell division, the compounds were tested for antitumor activity, and the *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$  seemed particularly effective. The compound is now available for cancer treatment under the name *cisplatin*. The key to this compound’s effectiveness seems to be the ability of the *cis*-( $\text{H}_3\text{N}$ ) $_2$ Pt unit to cross-link DNA units, bending and partially unwinding the double helix, thereby preventing further DNA synthesis. The following figure shows the cross-linking of ( $\text{H}_3\text{N}$ ) $_2$ Pt to a nitrogen atom on each strand.



The cross-linking of cisplatin across DNA strands.

Although cisplatin was a breakthrough in finding a whole new way of inhibiting tumor growth, it had side effects, sometimes severe, and also its effect sometimes diminished with repeated doses. So chemists looked at other compounds (called *ligands*; see Section 19.2) which could be affixed to the platinum to see if they had lower toxicity or other improved outcomes. As hoped, changing the chloride ligands for other species has opened up whole new avenues of possibilities. The structure of one of the newer and less toxic compounds, carboplatin, is shown in the following figure.



The structure of the antitumor agent, carboplatin.

## 19.1 Transition Metals

Although some people use the terms *d-block elements* and *transition metals* interchangeably, this is not strictly correct. Inorganic chemists generally restrict the term *transition metal* to an element that has at least one simple ion with an incomplete outer set of d electrons. For example, chromium has two common oxidation states (plus several other less common ones). The +3 oxidation state has a partially filled d set even though the +6 state has an empty d set. Thus, chromium is considered to be a transition metal. Note that the 4s electrons are lost before the 3d electrons.

Atom	Electron configuration	Ion	Electron configuration
Cr	[Ar]4s <sup>1</sup> 3d <sup>5</sup>	Cr <sup>3+</sup>	[Ar]3d <sup>3</sup>
		Cr <sup>6+</sup>	[Ar]

### The Exclusion of Group 3

By contrast, the only common oxidation state of scandium is +3. Because this state has an empty d set, scandium (and the other members of Group 3) is excluded from the transition metal designation. In fact, as we mentioned in Chapter 9, Section 9.4, scandium closely resembles the main group metal aluminum in its chemical behavior. The Group 3 elements also resemble the 4f-block elements in their chemistry and hence are discussed together with them in Chapter 24.

Atom	Electron configuration	Ion	Electron configuration
Sc	[Ar]4s <sup>2</sup> 3d <sup>1</sup>	Sc <sup>3+</sup>	[Ar]

### The Exclusion of Group 12

At the other end of the d-block, we have to consider the elements that retain a full d set in their oxidation states. The Group 12 elements—zinc, cadmium, and mercury—fit this category. Their common oxidation state is +2. Thus, these elements are not considered as transition metals. For this reason, the Group 12 elements are covered in a separate chapter—Chapter 22.

Atom	Electron configuration	Ion	Electron configuration
Zn	[Ar]4s <sup>2</sup> 3d <sup>10</sup>	Zn <sup>2+</sup>	[Ar]3d <sup>10</sup>

### The Period 7 Transition Elements

The elements from rutherfordium (element 104) to roentgenium (element 111) are also transition metals. However, because they are all short-lived radioactive elements, it is common to discuss them together with the actinoid metals



**FIGURE 19.1** A periodic table with the elements usually defined as transition metals, shown in dark mauve, and corresponding postactinoid transition metals, in light mauve.

																H								He
Li	Be																	B	C	N	O	F	Ne	
Na	Mg																	Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr							
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe							
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn							
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo							
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb											
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No											

(see Chapter 24). To summarize, the elements commonly considered as transition metals are shown in Figure 19.1.

### WORKED EXAMPLE 19.1

Predict the electron configuration of the  $\text{Fe}^{3+}$  ion.

#### Answer

The electron configuration of Fe is  $[\text{Ar}]4s^23d^6$ .

Removing three electrons to form  $\text{Fe}^{3+}$  gives  $[\text{Ar}]3d^5$ . ■

## 19.2 Introduction to Transition Metal Complexes

We rarely encounter a “naked” transition metal ion because the ion is usually covalently bonded to other ions or molecules. These groupings are called metal *complexes*, and it is the number and diversity of the metal complexes that provide the wealth of transition metal chemistry.

There is a specific number of molecules or ions with which a transition metal will combine. We refer to this number (or numbers) as the *coordination number(s)* of the metal ion, and it is usually four or six. The molecules or ions that are covalently bonded to the central metal ion are called *ligands*.

One of the best illustrations of the concept is shown by the series of compounds that can be prepared from platinum(II) and ammonia, chloride ions, and potassium ions. These compounds are shown in Table 19.1. The key to understanding this multiplicity of compounds was provided by measurements of the electrical conductivity of their solutions and by gravimetric analysis using silver nitrate solution. Thus, the presence of three ions in solution and 2 moles of precipitating silver chloride in the first case can only be explained if the two chloride ions are not covalently bonded to the platinum. In the second

**TABLE 19.1** Formulas and structures of a series of platinum(II) complexes

Composition	Number of ions	Modern formulation
$\text{PtCl}_2 \cdot 4\text{NH}_3$	3	$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
$\text{PtCl}_2 \cdot 3\text{NH}_3$	2	$[\text{PtCl}(\text{NH}_3)_3]\text{Cl}$
$\text{PtCl}_2 \cdot 2\text{NH}_3$	0	$[\text{PtCl}_2(\text{NH}_3)_2]$ (two forms)
$\text{KPtCl}_3 \cdot \text{NH}_3$	2	$\text{K}[\text{PtCl}_3(\text{NH}_3)]$
$\text{K}_2\text{PtCl}_4$	3	$\text{K}_2[\text{PtCl}_4]$

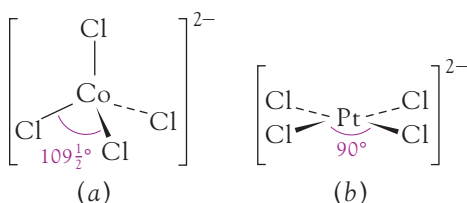
complex, the presence of two ions and only 1 mole of free chloride ion that can be precipitated as silver chloride shows that only one chloride ion is ionic and that the other must be part of the coordination sphere of the platinum. Similar arguments can be made for the other compounds.

### 19.3 Stereochemistries

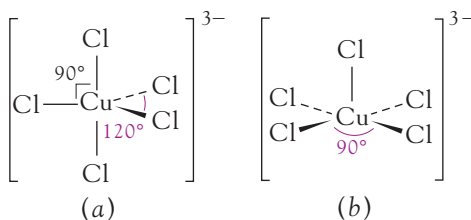
Transition metal complexes have a wide range of shapes. With four ligands, there are two alternatives: tetrahedral and square planar. Tetrahedra are more common in Period 4 transition metals, and square planar complexes are more prevalent among Periods 5 and 6. Figure 19.2a shows the tetrahedral geometry of the tetrachloridocobaltate(II) ion,  $[\text{CoCl}_4]^{2-}$ , and Figure 19.2b shows the square planar configuration of the tetrachloridoplatinate(II) ion,  $[\text{PtCl}_4]^{2-}$ .

There are few simple complexes with five ligands, but it is interesting to find that, like the four-ligand situation, these complexes have two stereochemistries: trigonal bipyramidal, like the main group compounds, and square-based pyramidal (Figure 19.3). The energy difference between these two configurations must be very small because the pentachloridocuprate(II) ion,  $[\text{CuCl}_5]^{3-}$ , adopts both structures in the solid phase, the preference depending on the identity of the cation.

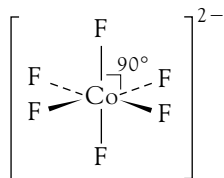
The most common number of simple ligands is six, and almost all of these complexes adopt the octahedral arrangement. This configuration is shown in



**FIGURE 19.2** (a) The tetrahedral tetrachloridocobaltate(II) ion and (b) the square planar tetrachloridoplatinate(II) ion.



**FIGURE 19.3** The two stereochemical arrangements of the pentachloridocuprate(II) ion: (a) trigonal bipyramid and (b) square-based pyramid.



**FIGURE 19.4** The octahedral hexafluoridocobaltate(IV) ion.

Figure 19.4 for the hexafluoridocobaltate(IV) ion,  $[\text{CoF}_6]^{2-}$ . Cobalt compounds usually have cobalt oxidation states of +2 and +3; thus, as we discussed in Chapter 17, Section 17.2, it is fluoride that has to be used to attain the unusual higher oxidation state of +4.

## Ligands

As mentioned earlier, the atoms, molecules, or ions attached to the metal ion are called ligands. For most ligands, such as water or chloride ion, each occupies one coordination site. These species are known as *monodentate* ligands (from the Greek word meaning “one-toothed”).

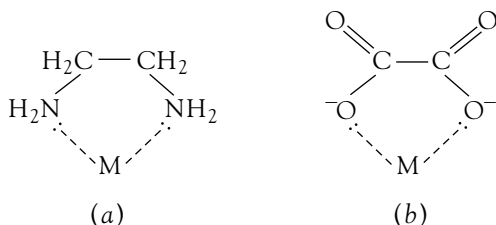
There are several molecules and ions that take up two bonding sites; common examples are the 1,2-diaminoethane molecule,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (commonly called *ethylenediamine* and abbreviated “en”), and the oxalate ion,  $^-\text{O}_2\text{CCO}_2^-$ . Such groups are called *bidentate* ligands (Figure 19.5).

More complex ligands can be synthesized and will bond to three, four, five, and even six coordination sites. These species are called *tridentate*, *tetradentate*, *pentadentate*, and *hexadentate* ligands, respectively. The best-known hexadentate ligand is the ethylenediaminetetraacetate ion,  $^{2-}(\text{OOC})_2\text{NCH}_2\text{CH}_2\text{N}(\text{COO})^{2-}$ , abbreviated to  $(\text{edta})^{4-}$  (Figure 19.6). All ligands that form more than one attachment to a metal ion are called *chelating* ligands (from the Greek *chelos*, meaning “clawlike”).

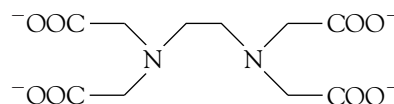
## Ligands and Oxidation States of Transition Metals

Another feature common to transition metals is their wide range of oxidation states. The preferred oxidation state is very dependent on the nature of the ligand; that is, various types of ligands stabilize low, normal, or high oxidation states.

- Ligands that tend to stabilize low-oxidation states.** The two common ligands that particularly favor metals in low-oxidation states are the carbon monoxide molecule and the isoelectronic cyanide ion. For example, iron has an oxidation state of 0 in  $[\text{Fe}(\text{CO})_5]$ .
- Ligands that tend to stabilize “normal” oxidation states.** Most common ligands, such as water, ammonia, and halide ions, fall into this category. For



**FIGURE 19.5** (a) The 1,2-diaminoethane molecule,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , and (b) the oxalate ion,  $^-\text{O}_2\text{CCO}_2^-$ . The atoms that coordinate to the metal have dashed lines to the metal ion, M, showing how the bonding will occur.



**FIGURE 19.6** The structure of ethylenediaminetetraacetate ion.

example, iron exhibits its common oxidation states of +2 and +3 with water:  $[\text{Fe}(\text{OH}_2)_6]^{2+}$  and  $[\text{Fe}(\text{OH}_2)_6]^{3+}$ . There are many cyanide complexes in normal-oxidation states as well. This is not unexpected, for the ion is a pseudo-halide ion (as discussed in Chapter 17, Section 17.12) and hence is capable of behaving like a halide ion.

**3. Ligands that tend to stabilize high-oxidation states.** Like nonmetals, transition metals only adopt high-oxidation states when complexed with fluoride and oxide ions. We have already mentioned the hexafluoridocobaltate(IV) ion,  $[\text{CoF}_6]^{2-}$ , as one example. In the tetraoxido ferrate(VI) ion,  $[\text{FeO}_4]^{2-}$ , the oxide ions stabilize the abnormal +6 oxidation state of iron.

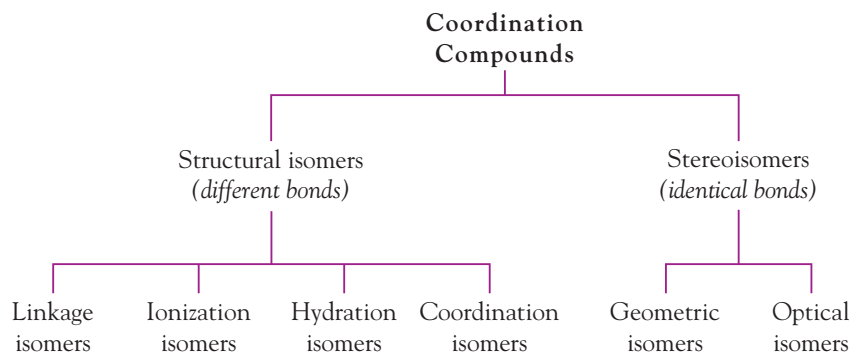
## 19.4 Isomerism in Transition Metal Complexes

In the early history of coordination chemistry, the existence of pairs of compounds with the same formula yet different properties proved to be very perplexing to inorganic chemists. Alfred Werner was among the first to realize that the different properties represented different structural arrangements (isomers). Isomers can be categorized as *structural isomers* and *stereoisomers*. For stereoisomers, the bonds to the metal ion are identical, whereas the bonds of structural isomers are different. These categories can be further subdivided, as shown in Figure 19.7.

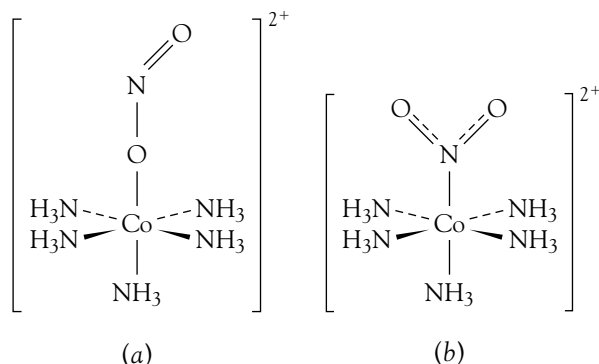
### Structural Isomerism

Structural isomerism has four common types: *linkage isomerism*, *ionization isomerism*, *hydration isomerism*, and *coordination isomerism*. Ionization and hydration isomerism are sometimes categorized together as *coordination-sphere isomerism* because, in both cases, it is the identity of the ligands that differs.

**1. Linkage isomerism.** Some ligands can form bonds through more than one atom. For example, the thiocyanate ion,  $\text{NCS}^-$ , can bond through either the nitrogen or the sulfur. This particular ambidentate ligand is a borderline base (see Chapter 7, Section 7.7) since the choice of ligating atom depends in part on the hard-soft acid nature of the metal ion. A classic example of linkage



**FIGURE 19.7** Classification of isomers.



**FIGURE 19.8** The two linkage isomers of the pentamminecobalt(III) nitrite complex: (a) the nitrito form, (b) the nitro form.

isomerism involves the nitrite ion, which can form bonds through the nitrogen atom,  $\text{—NO}_2$ , referred to as *nitro*, or through one of the oxygen atoms,  $\text{—ONO}$ , referred to as *nitrito*. A pentamminecobalt(III) complex,  $\text{Co}(\text{NH}_3)_5\text{Cl}_2(\text{NO}_2)$ , conveniently illustrates this isomerism since the two isomers have different colors. One of these, the red form, contains the  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$  ion, in which one of the oxygen atoms of the nitrite ion is bonded to the cobalt(III) ion (Figure 19.8a). The other isomer, the yellow form, contains the  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$  ion, in which the nitrogen atom is bonded to the cobalt(III) ion (Figure 19.8b).

**2. Ionization isomerism.** Ionization isomers give different ions when dissolved in solution. Again, there is a classic example:  $\text{Co}(\text{NH}_3)_5\text{Br}(\text{SO}_4)$ . If barium ion is added to a solution of the red-violet form, a white precipitate of barium sulfate forms. Addition of silver ion has no effect. Hence, the complex ion must have the formula  $[\text{CoBr}(\text{NH}_3)_5]^{2+}$ , with an ionic sulfate ion. A solution of the red form, however, does not give a precipitate with barium ion; instead, a cream-colored precipitate is formed with silver ion. Hence, this complex ion must have the structure of  $[\text{CoSO}_4(\text{NH}_3)_5]^+$ , with an ionic bromide ion.

**3. Hydration isomerism.** Hydration isomerism is very similar to ionization isomerism in that the identity of the ligand species is different for the two isomers. In this case, rather than different types of ions, it is the proportion of coordinated water molecules that differs between isomers. The three structural isomers of formula  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  provide the best example. In the violet form, the six water molecules are coordinated; hence, the formula for this compound is more correctly written as  $[\text{Cr}(\text{OH}_2)_6]^{3+}(\text{Cl}^-)_3$ . As evidence, all three chloride ions are precipitated from solution by silver ion. In the light green form, one of the chloride ions is not precipitated by silver ion; hence, the complex is assigned the structure  $[\text{CrCl}(\text{OH}_2)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ . Finally, only one chloride ion can be precipitated by silver ion from a solution of the dark green form; hence, this compound must have the structure  $[\text{CrCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ .

**4. Coordination isomerism.** *Coordination isomerism* occurs when both the cation and the anion are complex ions. The ligands interchange between the cation and anion, leading to different coordinated ligands. For example,  $[\text{Cr}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{CN})_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{CN})_6]^{3-}$  are coordination isomers.

## Stereoisomerism

The two types of inorganic stereoisomers, *geometric isomers* and *optical isomers*, are parallel to those found in organic chemistry except that in inorganic chemistry, optical isomerism is most common for a metal ion in an octahedral environment rather than for the tetrahedral environment of organic carbon compounds.

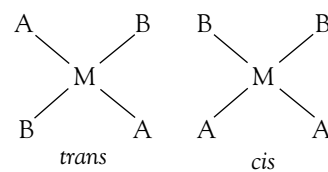
**1. Geometric isomerism.** Inorganic geometric isomers are analogous to organic geometric isomers that contain carbon-carbon double bonds. Geometric isomers must have two different ligands, A and B, attached to the same metal, M. For square planar compounds, geometric isomerism occurs in compounds of the form  $\text{MA}_2\text{B}_2$ , such as  $[\text{PtCl}_2(\text{NH}_3)_2]$ . The term *cis* is used for the isomer in which ligands of one kind are neighbors, and *trans* is used to identify the isomer in which ligands of one kind are opposite each other (Figure 19.9). Geometric isomers also exist for square planar complexes of the form  $\text{MA}_2\text{BC}$ , where *cis* refers to ligands A being neighbors and *trans* to ligands A being opposite each other (Figure 19.10).

There are two formulas of octahedral compounds having only two kinds of ligands for which geometric isomers are possible. Compounds with the formula  $\text{MA}_4\text{B}_2$  can have the two B ligands on opposite sides or as neighbors. Hence, these, too, are known as *trans* and *cis* isomers (Figure 19.10).

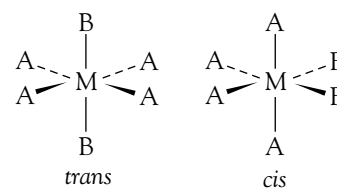
Octahedral compounds with the formula  $\text{MA}_3\text{B}_3$  also can have geometric isomers (Figure 19.11). If the A set of ligands occupies three sites of the corners of a triangular face of the octahedron,  $90^\circ$  apart from each other, and the B set, the opposing triangular face, then the prefix *fac*- (for *facial*) is used. However, if the three A ligands occupy the three sites in the horizontal plane and the B set, three sites in the vertical plane, then the geometry is described by the prefix *mer*- (for *meridional*) because like ligands span a meridian.

**2. Optical isomerism.** Again, inorganic optical isomerism is analogous to that of organic chemistry. Optical isomers are pairs of compounds in which one isomer is a nonsuperimposable mirror image of the other. One of the characteristics of optical isomers is that they rotate the plane of polarized light, one isomer rotating the light in one direction and the other isomer in the opposite direction. Compounds that exist as optical isomers are called *chiral compounds*.

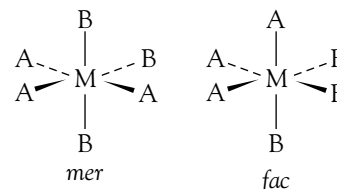
This form of isomerism is found most commonly when a metal is surrounded by three bidentate ligands; 1,2-diaminoethane,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (abbreviation en), mentioned earlier, is one such ligand. Hence, the complex ion



**FIGURE 19.9** The geometric isomers of a square planar  $\text{MA}_2\text{B}_2$  arrangement.

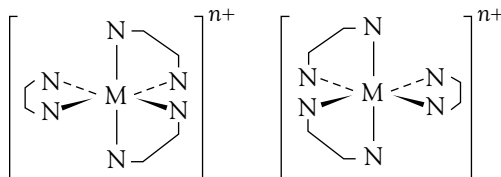


**FIGURE 19.10** The geometric isomers of an octahedral  $\text{MA}_4\text{B}_2$  arrangement.



**FIGURE 19.11** The geometric isomers of an octahedral  $\text{MA}_3\text{B}_3$  arrangement.

**FIGURE 19.12** The two optical isomers of the  $[M(en)_3]^{n+}$  ion. The linked nitrogen atoms represent the 1,2-diaminoethane bidentate ligands.



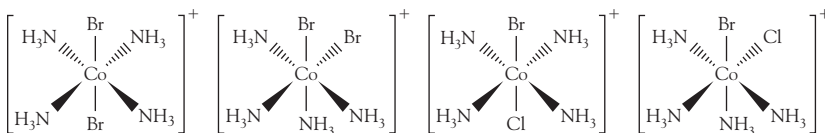
would have the formula  $[M(en)_3]^{n+}$ , where  $n+$  is the charge of the transition metal ion. The two optical isomers of this complex ion are shown in Figure 19.12, where the 1,2-diaminoethane molecules are depicted schematically as pairs of linked nitrogen atoms.

### WORKED EXAMPLE 19.2

Identify all possible isomers of  $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$ .

#### Answer

The maximum normal coordination number of cobalt(III) is six. Ammonia is a much stronger ligand than the halide ions, so these will occupy four of the ligand sites. There are two alternatives: two sites occupied by the bromide ions and the chloride as a free anion, or one chloride ion and one bromide ion as ligands and the other bromide ion free. Thus, two ionization isomers are possible:  $[\text{CoBr}_2(\text{NH}_3)_4]\text{Cl}$  and  $[\text{CoBrCl}(\text{NH}_3)_4]\text{Br}$ . For each of these isomers there are two geometric isomers; the halide ligands can be arranged *cis* or *trans*. ■



## 19.5 Naming Transition Metal Complexes

Because of the multiplicity of transition metal complexes, the simple system of inorganic nomenclature proved unworkable. As a result, special rules for naming transition metal complexes were devised.

1. Nonionic species are written as one word; ionic species are written as two words with the cation first.
2. Ligands are always placed in alphabetical order. (In formulas the ligands are listed in alphabetical order. Be aware that this may differ from the order in the name.)
3. The ligands are written as prefixes of the metal name. Neutral ligands are given the same name as the parent molecule, whereas the names of negative ligands are given the ending *-o* instead of *-e*. Thus, sulfate becomes sulfato and nitrite becomes nitrito. Anions with *-ide* endings have them completely replaced by *-o*. Hence, chloride ion becomes chlorido; iodide, iodido; cyanide, cyanido;

and hydroxide, hydroxido. There are three special names: coordinated water is commonly named aqua; ammonia, ammine; and carbon monoxide, carbonyl.

4. The central metal atom is identified by name, which is followed by the formal oxidation number in Roman numerals in parentheses, such as (IV) for a +4 state and (−II) for a −2 state. If the complex is an anion, the ending *-ate* adds to the metal name or replaces any *-ium*, *-en*, or *-ese* ending. Thus, we have cobaltate and nickelate, but chromate and tungstate (not chromiumate or tungstenate). For a few metals, the anion name is derived from the old Latin name of the element: ferrate (iron), argentate (silver), cuprate (copper), and aurate (gold).
5. For multiple ligands, the prefixes *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-* are used for 2, 3, 4, 5, and 6, respectively.
6. For multiple ligands already containing numerical prefixes (such as 1,2-diaminoethane), the prefixes used are *bis-*, *tris-*, and *tetrakis-* for 2, 3, and 4. This is not a rigid rule. Many chemists use these prefixes for all polysyllabic ligands.

### WORKED EXAMPLE 19.3

Provide the systematic name for  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ .

#### Answer

Because this compound has separate ions, the name will consist of (at least) two words (rule 1). There are two negative chloride ions outside of the complex, so the complex itself must have the formula  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ . The ammonia ligands are neutral; thus, the platinum must have an oxidation state of +2. As a result, we start with the stem name platinum(II) (rule 2). The ligand is ammonia, which has the name ammine (rule 3). But there are four ammonia ligands, so the prefix is added to give tetraammine (rule 5). Finally, the chloride anions must be included. They are free, uncoordinated chloride ions, so they are called chloride, not chlorido. We do not identify the number of chloride ions because the oxidation state of the metal ion enables us to deduce it. Hence, the full name is tetraammineplatinum(II) chloride. ■

### WORKED EXAMPLE 19.4

Provide the systematic name for  $[\text{PtCl}_2(\text{NH}_3)_2]$ .

#### Answer

This is a nonionic species, so it will have a one-word name (rule 1). Again, to balance the two chloride ions, the platinum is in the +2 oxidation state, so we start with platinum(II) (rule 2). The ligands are named ammine for ammonia and chlorido for chloride (rule 3). Alphabetically, ammine comes before chlorido (rule 4); thus, we have the prefix diamminedichlorido (rule 5). The whole name is diamminedichloridoplatinum(II). As mentioned earlier, this particular compound is square planar and exists as two geometric isomers. We refer to these isomers as *cis*-diamminedichloridoplatinum(II) and *trans*-diamminedichloridoplatinum(II). ■



**WORKED EXAMPLE 19.5**

Provide the systematic name for  $\text{K}_2[\text{PtCl}_4]$ .

**Answer**

Again, two words are needed (rule 1), but in this case, the platinum is in the anion,  $[\text{PtCl}_4]^{2-}$ . The metal is in the +2 oxidation state, so the anionic name will be platinate(II) (rule 2). There are four chloride ligands, giving the prefix tetrachlorido (rules 3 and 5), and the separate potassium cations. The complete name is potassium tetrachloridoplatinate(II). ■

**WORKED EXAMPLE 19.6**

Give the systematic name for  $[\text{Co}(\text{en})_3]\text{Cl}_3$ .

**Answer**

The complex ion is  $[\text{Co}(\text{en})_3]^{3+}$ . Because (en),  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , is a neutral ligand, the cobalt must be in a +3 oxidation state. The metal, then, will be cobalt(III). The full name of the ligand is 1,2-diaminoethane and contains a numerical prefix, so we use the alternate prefix set (rule 6) to give tris(1,2-diaminoethane)—parentheses are used to separate the ligand name from the other parts of the name. Finally, we add the chloride anions. The full name is tris(1,2-diaminoethane)cobalt(III) chloride. ■

## 19.6 An Overview of Bonding Theories of Transition Metal Compounds

For many decades, chemists and physicists struggled with possible explanations to account for the large number of transition metal compounds. Such explanations had to account for the variety of colors, the wide range of stereochemistries, and the magnetic properties.

### The Contrasting Theories

One of the first approaches was to regard the bonding as that between a Lewis acid (the metal ion) and Lewis bases (the ligands). This model produced the 18-electron rule or the effective atomic number (EAN) rule. The EAN rule works when the metal is in a low-oxidation state, but it does not work for most compounds, nor does it explain the color or paramagnetism of many transition metal compounds. It is useful in the context of organometallic compounds; thus, we will defer discussion of this bonding model to Chapter 23, Section 23.2.

Following from this, chemist Linus Pauling proposed the valence-bond approach (see later), in which he assumed that the bonding of transition metals is similar to that of typical covalent bonding of main group elements, assigning different modes of hybridization to the metal ion depending on the known geometry of the compound. This proposal did account for the different

stereochemistries and formulas, but it, too, failed to account for colors and unpaired electrons. We briefly outline this approach in the following subsection, although it is not widely used.

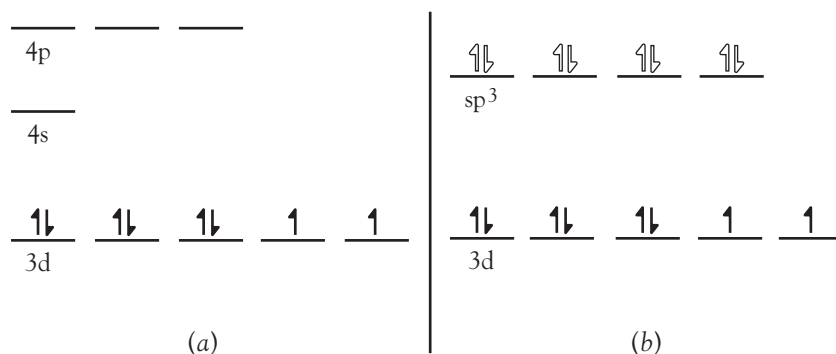
Two physicists, Hans Bethe and Johannes Van Vleck, approached the problem from a completely different direction. They assumed that the interaction between a metal ion and its ligands was totally electrostatic in nature. Known as *crystal field theory* (CFT) (see Section 19.7), it has been remarkably—amazingly—successful in accounting for the properties of transition metal complexes. Through this and the following chapter, most of our explanations of the behavior of transition metal complexes will be based on CFT. Nevertheless, it is clear that there is a component of covalent bonding between ligand and metal. This modified form of crystal field theory, adding covalent character, is known as *ligand field theory* (see Section 19.10).

The more complex approach is *molecular orbital* (MO) theory. In MO theory, bonding is considered as being covalent in nature, with the electrons shared throughout. This most sophisticated approach is not necessary for the discussion of conventional transition metal complexes.

### Valence-Bond Theory for Transition Metal Complexes

In Chapter 3, Section 3.5, we introduced valence-bond theory (VBT) in the context of the main group elements, together with the concept of orbital hybridization. Valence bond theory and orbital hybridization can also be used to explain some aspects of bonding in transition metal complexes. Using valence bond theory, we consider the interaction between the metal ion and its ligands to be that of a Lewis acid with Lewis bases, but in this case, the donated ligand electron pairs are considered to occupy the empty higher orbitals of the metal ion. This arrangement is shown for the tetrahedral tetrachloridonickelate(II) ion,  $[\text{NiCl}_4]^{2-}$ , in Figure 19.13. The free nickel(II) ion has an electron configuration of  $[\text{Ar}]3d^8$  with two unpaired electrons. According to the theory, the 4s and 4p orbitals of the nickel hybridize to form four  $sp^3$  hybrid orbitals, and these are occupied by an electron pair from each chloride ion (the Lewis bases).

This representation accounts for the two unpaired electrons in the complex ion and the tetrahedral shape expected for  $sp^3$  hybridization. However, we can only construct the VBT orbital diagram after the crystal structure has been determination and magnetic measurements recorded so that we know the



**FIGURE 19.13** (a) The electron distribution of the free nickel(II) ion. (b) According to VBT, the hybridization and occupancy of the higher-energy orbitals by electron pairs (open half-headed arrows) of the chloride ligands.

shape and number of unpaired electrons. For chemists, a theory should be predictive, if possible, and the valence-bond approach is not. For example, the hexaquaairon(II) ion,  $[\text{Fe}(\text{OH}_2)_6]^{2+}$ , has four unpaired electrons, whereas the hexacyanidoferrate(II) ion,  $[\text{Fe}(\text{CN})_6]^{4-}$ , has no unpaired electrons. Valence bond theory cannot predict or explain this.

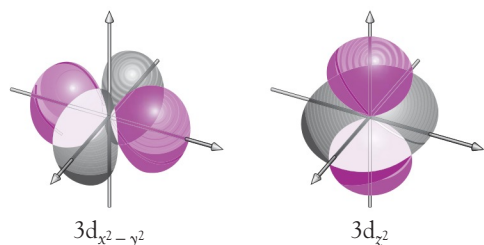
Valence bond theory also has some conceptual flaws. In particular, it does not explain why the electron pairs occupy higher orbitals, even though there are vacancies in the 3d orbitals. For some Period 4 transition metal complexes, the ligand electron pairs have to be assigned to 4d orbitals as well as to 4s and 4p orbitals, even though there is room in the 3d orbitals. In addition, the approach fails to account for the color of the transition metal complexes, one of the most obvious features of these compounds. For these reasons, the valence bond theory has become little more than a historical footnote.

## 19.7 Crystal Field Theory

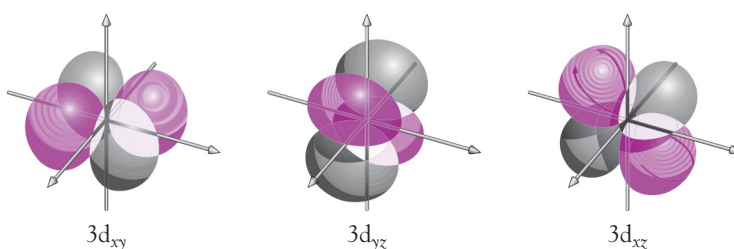
Crystal field theory assumes that the transition metal ion is free and gaseous, that the ligands behave like point charges, and that there are no interactions between metal d orbitals and ligand orbitals. The theory also depends on the probability model of the d orbitals, that there are two d orbitals whose lobes are oriented along the Cartesian axes  $d_{x^2-y^2}$  and  $d_{z^2}$  (Figure 19.14) and three d orbitals whose lobes are oriented between the Cartesian axes,  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  (Figure 19.15).

We can consider complex formation as a series of events:

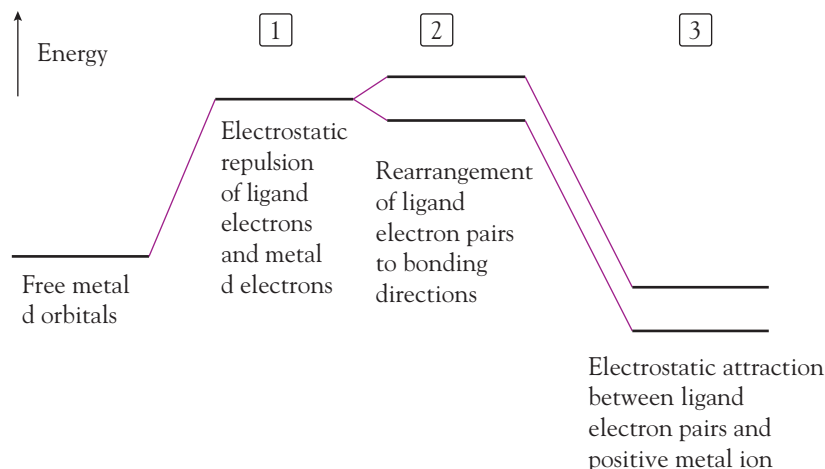
1. The initial approach of the ligand electrons forms a spherical shell around the metal ion. Repulsion between the ligand electrons and the metal ion electrons will cause an increase in energy of the metal ion d orbitals.
2. The ligand electrons rearrange so that they are distributed in pairs along the actual bonding directions (such as octahedral or tetrahedral). The mean metal d orbital energies will stay the same, but the orbitals oriented along the bonding directions will increase in energy, and those between the bonding directions will decrease in energy. This loss in d orbital degeneracy will be the focus of the crystal field theory discussion.



**FIGURE 19.14** Representations of the shapes of the  $3d_{x^2-y^2}$  and  $3d_{z^2}$  orbitals.



**FIGURE 19.15** Representations of the shapes of the  $3d_{xy}$ ,  $3d_{xz}$ , and  $3d_{yz}$  orbitals.



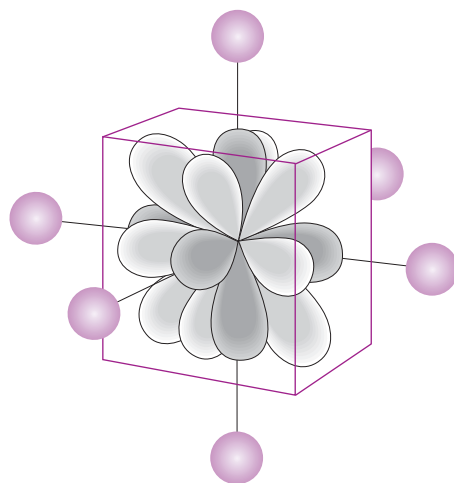
**FIGURE 19.16** The hypothetical steps in complex ion formation according to CFT.

3. Up to this point, complex formation would not be favored, because there has been a net increase in energy as a result of the ligand electron–metal electron repulsion (step 1). Furthermore, the decrease in the number of free species means that complex formation will generally result in a decrease in entropy. However, there will be an attraction between the ligand electrons and the positively charged metal ion that will result in a net decrease in energy. It is this third step that provides the driving force for complex formation.

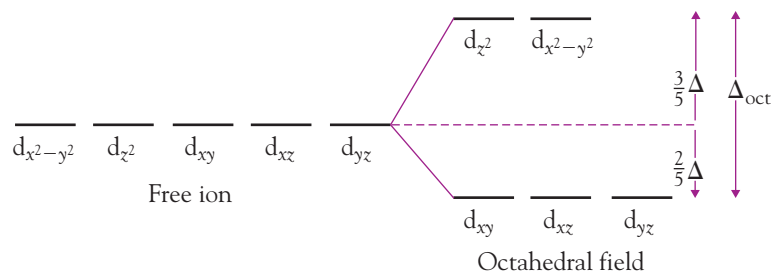
These three hypothetical steps are summarized in Figure 19.16.

### Octahedral Complexes

Although it is the third step that provides the energy for complex formation, it is the second step, the loss of degeneracy of the d orbitals, that is crucial for the explanation of the color and magnetic properties of transition metal complexes. Examining the octahedral situation first, we see that the six ligands are located along the Cartesian axes (Figure 19.17).



**FIGURE 19.17** The orientation of six ligands with respect to the metal d orbitals. [Adapted from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (New York: HarperCollins, 1993), p. 397.]

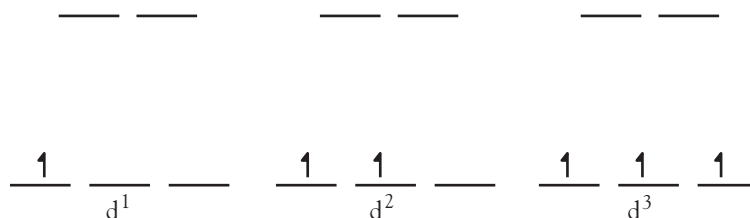


**FIGURE 19.18** The splitting of the d-orbital energies that occurs when the metal ion is surrounded by an octahedral array of ligands.

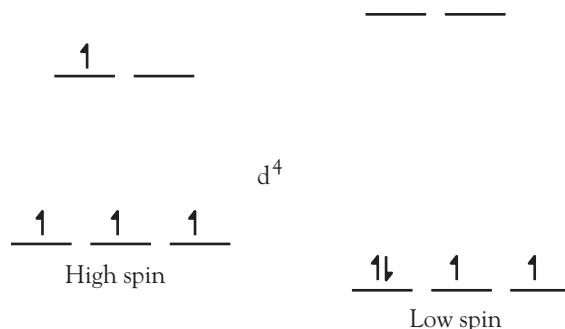
As a result of these negative charges along the Cartesian axes, the energies of the orbitals aligned along these axes, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals, will be higher than those of the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals. This splitting of the d orbitals into two sets is represented in Figure 19.18. The energy difference between the two sets of d orbitals in the octahedral field is given the symbol  $\Delta_{\text{oct}}$ . The sum of the orbital energies equals the degenerate energy (sometimes called the *baricenter*). Thus, the energy of the two higher-energy orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) is  $+\frac{3}{5}\Delta_{\text{oct}}$ , and the energy of the three lower-energy orbitals ( $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ ) is  $-\frac{2}{5}\Delta_{\text{oct}}$  below the mean.

If we construct energy diagrams for the different numbers of d electrons, we see that for the  $d^1$ ,  $d^2$ , and  $d^3$  configurations, the electrons will all fit into the lower-energy set (Figure 19.19). This net energy decrease is known as the crystal field stabilization energy (CFSE). The CFSE for the  $d^3$  configuration is  $3(-\frac{2}{5}\Delta_{\text{oct}})$  or  $-1.2\Delta_{\text{oct}}$ .

For the  $d^4$  configuration, there are two possibilities: the fourth d electron can either pair up with an electron in the lower-energy level or it can occupy the upper-energy level, depending on which situation is more energetically favorable. If the octahedral crystal field splitting,  $\Delta_{\text{oct}}$ , is smaller than the pairing energy, then the fourth electron will occupy the higher orbital. If the pairing energy is less than the crystal field splitting, then it is energetically preferred for the fourth electron to occupy the lower orbital. The two situations are shown in Figure 19.20. The result having the greater number of unpaired electrons is called the *high-spin* (or weak field) situation, and that having the lesser number of unpaired electrons is called the *low-spin* (or strong field) situation.



**FIGURE 19.19** The d-orbital filling for the  $d^1$ ,  $d^2$ , and  $d^3$  configurations.



**FIGURE 19.20** The two possible spin situations for the d<sup>4</sup> configuration.

**TABLE 19.2** The d electron configurations and corresponding number of unpaired electrons for an octahedral stereochemistry

Configuration	Number of unpaired electrons	Common examples
d <sup>1</sup>	1	Ti <sup>3+</sup>
d <sup>2</sup>	2	V <sup>3+</sup>
d <sup>3</sup>	3	Cr <sup>3+</sup>
d <sup>4</sup>	4 (h.s.), 2 (l.s.)	Mn <sup>3+</sup>
d <sup>5</sup>	5 (h.s.), 1 (l.s.)	Mn <sup>2+</sup> , Fe <sup>3+</sup>
d <sup>6</sup>	4 (h.s.), 0 (l.s.)	Fe <sup>2+</sup> , Co <sup>3+</sup>
d <sup>7</sup>	3 (h.s.), 1 (l.s.)	Co <sup>2+</sup>
d <sup>8</sup>	2	Ni <sup>2+</sup>
d <sup>9</sup>	1	Cu <sup>2+</sup>

Two possible spin conditions exist for each of the d<sup>4</sup>, d<sup>5</sup>, d<sup>6</sup>, and d<sup>7</sup> electron configurations in an octahedral environment. The number of possible unpaired electrons corresponding to each d electron configuration is shown in Table 19.2, where h.s. and l.s. indicate high spin and low spin, respectively.

### WORKED EXAMPLE 19.7

Calculate the CFSE for the two configurations shown in Figure 19.20.

#### Answer

The CFSE for the high spin d<sup>4</sup> configuration is  $3(-\frac{2}{5}\Delta_{\text{oct}}) + (\frac{3}{5}\Delta_{\text{oct}}) = -\frac{3}{5}\Delta$  or  $-0.6\Delta_{\text{oct}}$ .

The CFSE for the low spin d<sup>4</sup> configuration is  $4(-\frac{2}{5}\Delta_{\text{oct}}) = -\frac{8}{5}\Delta$  or  $-1.6\Delta_{\text{oct}}$ . ■

### Factors Affecting the Crystal Field Splitting

The energy-level splitting depends on four factors:

1. **The identity of the metal.** The crystal field splitting,  $\Delta$ , is about 50 percent greater for the second transition series compared to the first, whereas the

third series is about 25 percent greater than the second. There is a small increase in the crystal field splitting along each series.

**2. The oxidation state of the metal.** Generally, the higher the oxidation state of the metal, the greater the crystal field splitting. Thus, most cobalt(II) complexes are high spin as a result of the small crystal field splitting, whereas almost all cobalt(III) complexes are low spin as a result of the much larger splitting by the 3+ ion.

**3. The number of the ligands.** The crystal field splitting is greater for a larger number of ligands. For example,  $\Delta_{\text{oct}}$ , the splitting for six ligands in an octahedral environment, is much greater than  $\Delta_{\text{tet}}$ , the splitting for four ligands in a tetrahedral environment.

**4. The nature of the ligands.** The common ligands can be ordered on the basis of the effect that they have on the crystal field splitting. This ordered listing is called the *spectrochemical series*. The general guidelines for ordering the ligands is halides < oxygen donors < nitrogen donors < carbon donors. Among the common ligands, the splitting is largest with carbonyl and cyanide and smallest with iodide. The ordering for most metals is



Thus, for a particular metal ion, it is the ligand that determines the value of the crystal field splitting. Consider the  $d^6$  iron(II) ion. According to CFT, there are the two spin possibilities: high spin (weak field) with four unpaired electrons and low spin (strong field) with all electrons paired. We find that the hexaquaairon(II) ion,  $[\text{Fe}(\text{OH}_2)_6]^{2+}$ , possesses four unpaired electrons. The water ligands, being low in the spectrochemical series, produce a small  $\Delta_{\text{oct}}$ ; hence, the electrons adopt a high-spin configuration. Conversely, the hexacyanidoferrate(II) ion,  $[\text{Fe}(\text{CN})_6]^{4-}$ , is found to be diamagnetic (zero unpaired electrons). Cyanide is high in the spectrochemical series and produces a large  $\Delta_{\text{oct}}$ ; hence, the electrons adopt a low-spin configuration.

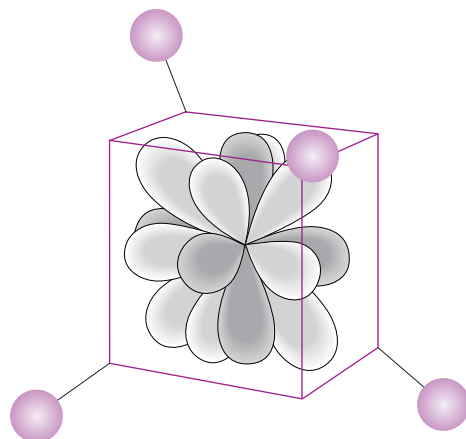
### WORKED EXAMPLE 19.8

Identify which one in each of the following pairs of complexes will have the larger value of  $\Delta_{\text{oct}}$ : (a)  $[\text{Fe}(\text{OH}_2)_6]^{2+}$  or  $[\text{Fe}(\text{OH}_2)_6]^{3+}$ ; (b)  $[\text{Cr}(\text{OH}_2)_6]^{3+}$  or  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ .

#### Answer

(a) The ligands are the same in each complex so we are comparing Fe(II) with Fe(III) oxidation states. The latter will have a larger value of  $\Delta_{\text{oct}}$  as it has a higher oxidation state.

(b) Both complexes are Cr(III) species but have different ligands. As  $\text{NH}_3$  is further to the right in the spectrochemical series,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  will have the larger value of  $\Delta_{\text{oct}}$ . ■



**FIGURE 19.21** The orientation of four ligands with respect to the metal d orbitals. [Adapted from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (New York: HarperCollins, 1993), p. 402.]

### Tetrahedral Complexes

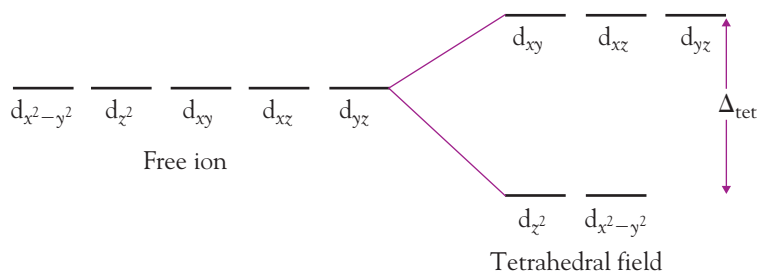
The second most common stereochemistry is tetrahedral. Figure 19.21 shows the tetrahedral arrangement of four ligands around the metal ion.

In this case, it is the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals that are more in line with the approaching ligands than the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. As a result, it is the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals that are lower in energy, and the tetrahedral energy diagram is inverted relative to the octahedral diagram (Figure 19.22).

With only four ligands instead of six and the ligands not quite pointing directly at the three d orbitals, the crystal field splitting is much less than that in the octahedral case; in fact, as we mentioned previously, it is about four-ninths of  $\Delta_{\text{oct}}$ . As a result of the small orbital splitting, the tetrahedral complexes are almost all high spin. Tetrahedral geometries are most commonly found for halide complexes, such as the tetrachloridocobaltate(II) ion,  $[\text{CoCl}_4]^{2-}$ , and for the oxyanions, such as the tetraoxidomolybdate(VI) ion,  $[\text{MoO}_4]^{2-}$  (commonly called *molybdate*).

### Square Planar Complexes

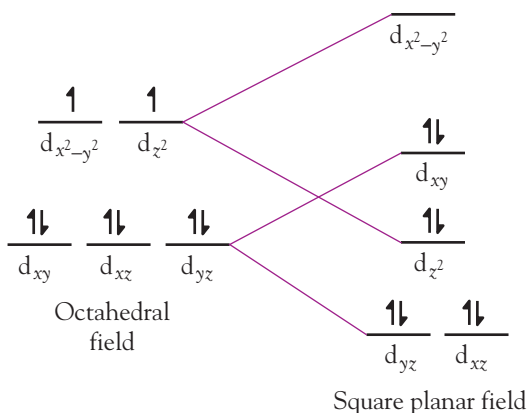
For the Period 4 transition metals, it is only nickel that tends to form square planar complexes, such as the tetracyanonickelate(II) ion,  $[\text{Ni}(\text{CN})_4]^{2-}$ .



**FIGURE 19.22** The splitting of the d-orbital energies that occurs when the metal ion is surrounded by a tetrahedral array of ligands.



**FIGURE 19.23** The  $d^8$ -orbital-energy diagram for the square planar environment, as derived from the octahedral diagram.



These complexes are diamagnetic. We can develop a crystal field diagram to see why this is so, even though both octahedral and tetrahedral geometries result in two unpaired electrons for the  $d^8$  configuration.

If we start from the octahedral field and withdraw the ligands from the  $z$ -axis, the  $d_{z^2}$  orbital will no longer feel the electrostatic repulsion from the axial ligands; hence, it will drop substantially in energy. The other two orbitals with  $z$ -axis components, the  $d_{xz}$  and  $d_{yz}$ , will also undergo a decrease in energy. Conversely, with the withdrawal of the axial ligands, there will be a greater electrostatic attraction on the ligands in the plane, and these will become closer to the metal ion. As a result, the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals will increase substantially in energy (Figure 19.23). Because the nickel(II) complex with cyanide is diamagnetic, the splitting of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals must be greater than the pairing energy for this combination.

## 19.8 Successes of Crystal Field Theory

A good chemical theory is one that can account for many aspects of physical and chemical behaviors. By this standard, crystal field theory is remarkably successful because it can be used to explain most of the properties that are unique to transition metal ions. Here we will look at a selection of them.

### Magnetic Properties

Any theory of transition metal ions has to account for the paramagnetism of many of the compounds. The degree of paramagnetism is dependent on the identity of the metal, its oxidation state, its stereochemistry, and the nature of the ligand. Crystal field theory explains the paramagnetism very well in terms of the splitting of the  $d$ -orbital energies, at least for the Period 4 transition metals. For example, we have just seen how crystal field theory can explain the diamagnetism of the square planar nickel(II) ion, which contrasts with the paramagnetism of the tetrahedral and octahedral geometries. The theoretical degree of paramagnetism is given by the *magnetic moment* of a compound. This can be calculated using the simple formula  $\mu = \sqrt{n(n+2)}$ , where  $n$  is the

number of unpaired electrons. The units of magnetic moment are Bohr magnetons,  $\mu_{\text{BM}}$ . Therefore,  $[\text{Ti}(\text{OH}_2)_6]^{3+}$  has 1 unpaired electron and has a magnetic moment of  $1.73 \mu_{\text{BM}}$ .

### WORKED EXAMPLE 19.9

The experimental magnetic moment of the complex  $[\text{Mn}(\text{NCS})_6]^{4-}$  is found to be  $6.06 \mu_{\text{BM}}$ . Determine whether it is a low-spin or high-spin complex.

#### Answer

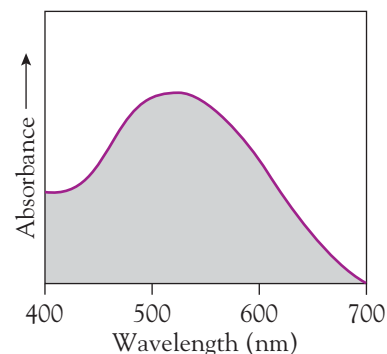
This complex contains Mn(II), which has five d electrons. A low-spin configuration would give one unpaired electron and as  $\mu = \sqrt{n(n+2)}$  the magnetic moment would be  $1.73 \mu_{\text{BM}}$ . The high-spin configuration would give five unpaired electrons and a magnetic moment of  $5.91 \mu_{\text{BM}}$ . Therefore, the complex must be high spin. ■

### Colors of Transition Metal Complexes

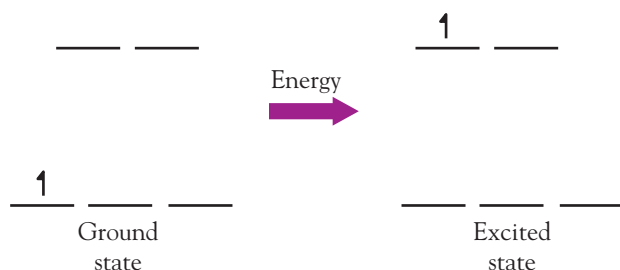
The most striking feature of transition metal complexes is the range of colors that they exhibit. These colors are the result of absorptions in the visible region of the electromagnetic spectrum. For example, Figure 19.24 shows the visible absorption spectrum of the purple hexaaquatitanium(III) ion,  $[\text{Ti}(\text{OH}_2)_6]^{3+}$ . This ion absorbs light in the green part of the spectrum, transmitting blue and red light to give the blended purple color.

The titanium(III) ion has a  $d^1$  electron configuration, and with six water molecules as ligands, we can consider the ion to be in an octahedral field. The resulting d-orbital splitting is shown on the left-hand side of Figure 19.25. An absorption of electromagnetic energy causes the electron to shift to the upper d-orbital set, as shown on the right-hand side of Figure 19.25. The electron subsequently returns to the ground state, and the energy is released as thermal motion rather than as electromagnetic radiation. The absorption maximum is at about 520 nm, which represents an energy difference between the upper and lower d-orbital sets of about  $230 \text{ kJ}\cdot\text{mol}^{-1}$ . This energy difference represents the value of  $\Delta$ , the crystal field splitting.

As is apparent from Figure 19.24, the electronic absorption bands are broad. These bands are broad because the electron transition time is much shorter



**FIGURE 19.24** The visible absorption spectrum of the hexaaquatitanium(III) ion.



**FIGURE 19.25** The electron transition corresponding to the visible absorption of the titanium(III) ion.

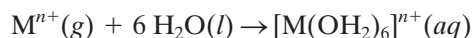
than the vibrations occurring within the molecule. When the ligands are farther away from the metal than the mean bond length, the field is weaker and the splitting is less; hence, the transition energy is smaller than the “normal” value. Conversely, when the ligands are closer to the metal, the field is stronger, the splitting is greater, and the transition energy is larger than the normal value. We can confirm this explanation by cooling the complex to close to absolute zero, thereby reducing the molecular vibrations. When we do, as predicted, the bands in the visible absorption spectrum become much narrower.

The hexachloridotitanate(III) ion,  $[\text{TiCl}_6]^{3-}$ , has an orange color as a result of an absorption centered at 770 nm. This value corresponds to a crystal field splitting of about  $160 \text{ kJ}\cdot\text{mol}^{-1}$ . The lower value reflects the weakness of the chloride ion as a ligand relative to the water molecule; that is, chloride is lower than water in the spectrochemical series.

For most branches of chemistry, we measure energy differences in kilojoules per mole, but transition metal chemists usually report crystal field splittings in a frequency unit called *wave numbers*. This is simply the reciprocal of the wavelength expressed as centimeters; thus, the units of wave numbers are  $\text{cm}^{-1}$ , called *reciprocal centimeters*. For example, the crystal field splitting for the hexaaquatitanium(III) ion is usually cited as  $19\,200 \text{ cm}^{-1}$  rather than as  $230 \text{ kJ}\cdot\text{mol}^{-1}$ . We will discuss the visible absorptions of other electron configurations later.

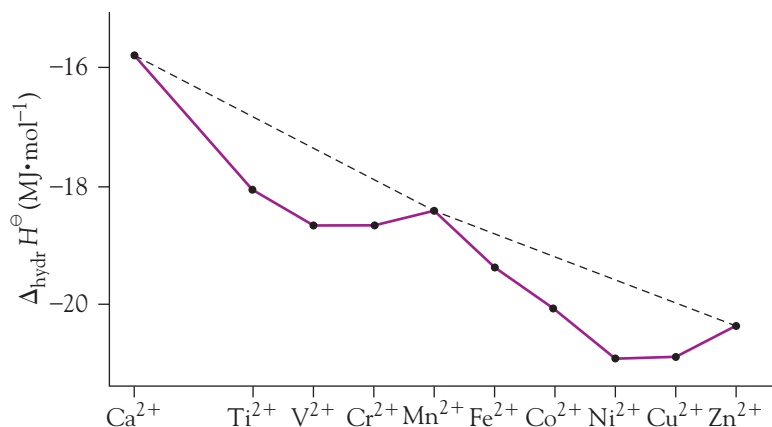
### Hydration Enthalpies

Another of the parameters that can be explained by crystal field theory is the enthalpy of hydration of transition metal ions. This is the energy released when gaseous ions are hydrated, a topic discussed in Chapter 6, Section 6.4:



As the effective nuclear charge of metal ions increases across a period, we expect the electrostatic interaction between the water molecules and the metal ions to increase regularly along the transition metal series. In fact, we find deviations from a linear relationship (Figure 19.26).

**FIGURE 19.26** Experimental hydration enthalpies of the di-positive ions of the Period 4 transition metals.



**TABLE 19.3** Crystal field stabilization energies (CFSE) for the dipositive, high-spin ions of various Period 4 metals

Ion	Configuration	CFSE
Ca <sup>2+</sup>	d <sup>0</sup>	−0.0 Δ <sub>oct</sub>
—	d <sup>1</sup>	−0.4 Δ <sub>oct</sub>
Ti <sup>2+</sup>	d <sup>2</sup>	−0.8 Δ <sub>oct</sub>
V <sup>2+</sup>	d <sup>3</sup>	−1.2 Δ <sub>oct</sub>
Cr <sup>2+</sup>	d <sup>4</sup>	−0.6 Δ <sub>oct</sub>
Mn <sup>2+</sup>	d <sup>5</sup>	−0.0 Δ <sub>oct</sub>
Fe <sup>2+</sup>	d <sup>6</sup>	−0.4 Δ <sub>oct</sub>
Co <sup>2+</sup>	d <sup>7</sup>	−0.8 Δ <sub>oct</sub>
Ni <sup>2+</sup>	d <sup>8</sup>	−1.2 Δ <sub>oct</sub>
Cu <sup>2+</sup>	d <sup>9</sup>	−0.6 Δ <sub>oct</sub>
Zn <sup>2+</sup>	d <sup>10</sup>	−0.0 Δ <sub>oct</sub>

To explain this observation, we assume that the greater hydration enthalpy is the result of the crystal field stabilization energy, which can be calculated in terms of Δ<sub>oct</sub>, the crystal field splitting. Recall that for an octahedral field, the d<sub>xy</sub>, d<sub>xz</sub>, and d<sub>yz</sub> orbitals are lowered in energy by  $\frac{2}{5}\Delta_{\text{oct}}$  and the d<sub>x<sup>2</sup>−y<sup>2</sup></sub> and d<sub>z<sup>2</sup></sub> orbitals are raised in energy by  $\frac{3}{5}\Delta_{\text{oct}}$ . Thus, for a particular electron configuration, it is possible to calculate the net contribution of the crystal field to the hydration enthalpy. Figure 19.27 illustrates the situation for the d<sup>4</sup> high-spin ion. This ion would have a net stabilization energy of

$$- [3(\frac{2}{5}\Delta_{\text{oct}})] + [1(\frac{3}{5}\Delta_{\text{oct}})] = -0.6\Delta_{\text{oct}}$$

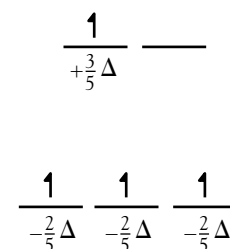
The complete set of crystal field stabilization energies is listed in Table 19.3.

These values correspond remarkably well with the deviations of the hydration enthalpies. Of particular note, it is only the d<sup>0</sup>, d<sup>5</sup> (high spin), and d<sup>10</sup> ions that fit the expected near-linear relationship, and these all have zero crystal field stabilization energy.

## Spinel Structures

Yet another triumph of crystal field theory is the explanation for the transition metal ion arrangements in the spinel structures that we first met in Chapter 5, Section 5.7. The spinel is a mixed oxide, usually of general formula (M<sup>2+</sup>)(M<sup>3+</sup>)<sub>2</sub>(O<sup>2−</sup>)<sub>4</sub>, with the metal ions occupying both octahedral and tetrahedral sites. In a normal spinel, all of the 2+ ions are in the tetrahedral sites and the 3+ ions are in the octahedral sites, whereas in an inverse spinel, the 2+ ions are in the octahedral sites and the 3+ ions fill the tetrahedral sites and the remaining octahedral sites.

The choice of normal spinel or inverse spinel for mixed transition metal oxides is determined usually (but not always) by which option will give the

**FIGURE 19.27** The crystal field stabilization energy for the d<sup>4</sup> high-spin electron configuration.

## The Earth and Crystal Structures

There is still much to be discovered about the structure of the planet that we inhabit. However, we do know that it consists of three regions: the crust, mantle, and core. The crust occupies the surface 30 to 70 km for continents and 5 to 15 km for oceanic crust. Then the mantle extends down to a depth of about 2900 km, where it meets the core. The core is predominantly iron, molten to a depth of about 5100 km and then solid at the center.

The mantle provides some interesting crystal-phase chemistry. Between about 100 and 400 km depth, the mantle consists of the mineral olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$ , where the composition varies since the two metal ions can both occupy the same lattice site in this simple silicate (see Chapter 9, Section 9.6). Below the olivine layer, it is a spinel structure, probably mainly  $\text{MgFe}_2\text{O}_4$ , that stretches down to the lower mantle. The lower mantle begins at a depth of about 670 km. This layer consists of the denser perovskite structure (see Chapter 16, Section 16.6),  $(\text{Mg,Fe})\text{SiO}_3$ .

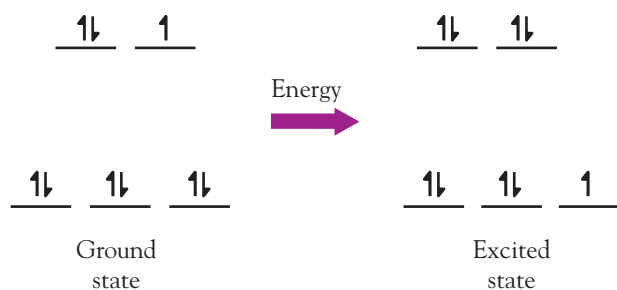
Scientists have become increasingly interested in the chemistry of the deep Earth and phenomena such as earthquakes. There are two types of earthquakes: shallow and deep. Deep earthquakes occur when dense spinel forms around the margins of descending streams of olivine. Shallow earthquakes seem more complex, but part of their origin may be from dehydration reactions. The surface rock, serpentine, is hydrated olivine. As a layer of serpentine is dragged down into the Earth at a trench boundary, the heat will cause the serpentine to dehydrate to olivine. The high-pressure water can act to force cracks open and also act as a lubricant. These are only hypotheses at present. Much more research needs to be done on the properties of spinels and perovskites under high pressure and the dehydration of minerals if we are to obtain a more detailed knowledge of our planet.

greater crystal field stabilization energy. This can be illustrated by a pair of oxides each of which contains ions of one metal in two different oxidation states:  $\text{Fe}_3\text{O}_4$ , containing  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and  $\text{Mn}_3\text{O}_4$ , containing  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ . The former adopts the inverse spinel structure:  $(\text{Fe}^{3+})_t(\text{Fe}^{2+}, \text{Fe}^{3+})_o(\text{O}^{2-})_4$ . All these ions are high spin, so the  $\text{Fe}^{3+}$  ion ( $d^5$ ) has a zero CFSE, but the  $\text{Fe}^{2+}$  ion ( $d^6$ ) has a nonzero CFSE. The crystal field splitting for the tetrahedral geometry is four-ninths that of the equivalent octahedral environment; thus the CFSE of an octahedrally coordinated ion will be greater than that of a tetrahedrally coordinated ion. This energy difference accounts for the octahedral site preference of the  $\text{Fe}^{2+}$  ion.

Unlike the mixed iron oxide, the mixed manganese oxide has the normal spinel structure:  $(\text{Mn}^{2+})_t(2\text{Mn}^{3+})_o(\text{O}^{2-})_4$ . In this case, it is the  $\text{Mn}^{2+}$  ion ( $d^5$ ) that has a zero CFSE and the  $\text{Mn}^{3+}$  ion ( $d^4$ ) that has a nonzero CFSE. Hence, it is the  $\text{Mn}^{3+}$  ion that preferentially occupies the octahedral sites.

## 19.9 More on Electronic Spectra

In the previous section, we saw that the single visible absorption of the titanium(III) ion can be explained in terms of a d-electron transition from the lower level to the upper level in the crystal field. We find that the visible spectra of  $d^1$ ,  $d^4$  (high spin),  $d^6$  (high spin), and  $d^9$  (Figure 19.28) can all be interpreted



**FIGURE 19.28** The electron transition for the  $d^9$  electron configuration.

in terms of a single transition. Here we will look at transitions of other electron configurations and revisit the  $d^1$  configuration in more detail.

### Spectra of $d^2$ , $d^3$ , $d^7$ , and $d^8$ Ions

For  $d^2$  ions, we might expect two absorption peaks, corresponding to the excitation of one or both of the electrons. However, a total of three fairly strong absorptions are observed. To explain this, we have to consider interelectronic repulsions. For example, in the ground state, a  $d^2$  ion, such as the hexaaquavanadium(III) ion, has two electrons with parallel spins in any two of the three lower-energy orbitals:  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ . When one electron is excited, the resulting combination can have different energies, depending on whether the two electrons are occupying overlapping orbitals and therefore repelling each other. For example, an excited configuration of  $(d_{xy})^1(d_{z^2})^1$  will be lower in energy because the two electrons occupy very different volumes of space, whereas the  $(d_{xy})^1(d_{x^2-y^2})^1$  configuration will be higher in energy because both electrons occupy space in the  $x$  and  $y$  planes.

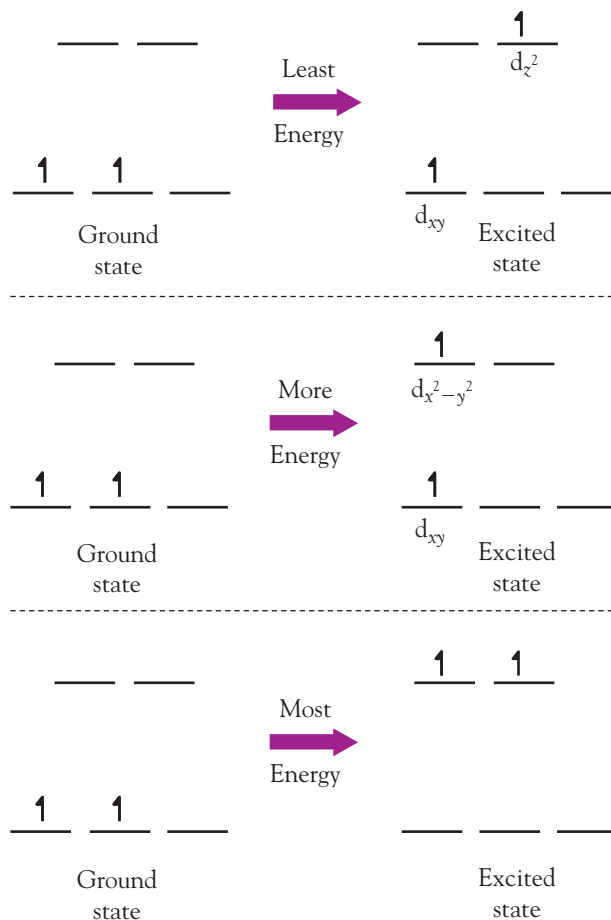
By calculation, it can be shown that the combinations  $(d_{xy})^1(d_{z^2})^1$ ,  $(d_{xz})^1(d_{x^2-y^2})^1$ , and  $(d_{yz})^1(d_{x^2-y^2})^1$  all have the same lower energy, and  $(d_{xy})^1(d_{x^2-y^2})^1$ ,  $(d_{xz})^1(d_{z^2})^1$ , and  $(d_{yz})^1(d_{z^2})^1$  all have the same higher energy. This accounts for two of the transitions, and the third transition corresponds to the excitation of both electrons into the upper levels to give the configuration  $(d_{x^2-y^2})^1(d_{z^2})^1$ . The spectra of  $d^2$ ,  $d^3$ ,  $d^7$  (high spin), and  $d^8$  electron configurations can all be interpreted in terms of three transitions. Three possibilities of the transitions for the  $d^2$  configuration are shown in Figure 19.29.

### Intensity of Electronic Spectra

The absorption spectra of octahedrally coordinated transition metal ions are comparatively weak; that is, the compounds usually have pale colors. The paleness of the  $d \rightarrow d$  electronic transitions is explained by the fact that the transitions are formally forbidden by the *Laporte selection rule*. The rule states that transitions do not occur when the molecule has a center of inversion (see Chapter 3, Section 3.13). Molecular vibrations remove some of this symmetry in octahedral complexes, resulting in broad transitions and pale colors. Tetrahedral complexes do not have a center of symmetry; thus, their colors are more intense.

Sometimes very weak absorptions also appear in the visible spectrum. These correspond to transitions in which an electron has reversed its spin, such

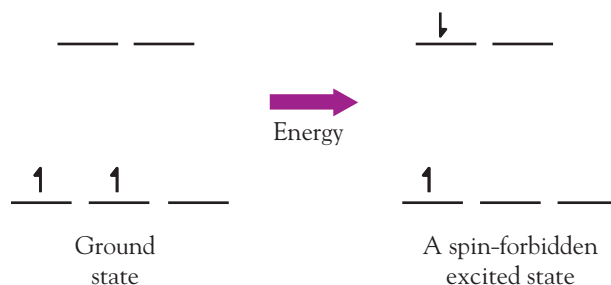
**FIGURE 19.29** Three possible electron transitions for the  $d^2$  electron configuration.



as those shown in Figure 19.30. Such transitions, which involve a change in spin state, are known as *spin-forbidden transitions*. These transitions are of low probability and so have very low intensity in the spectrum.

Some transition metal complexes are very intensely colored, such as purple tetraoxidomanganate(VII),  $[\text{MnO}_4]^-$  (permanganate), and yellow tetraoxidochromate(VI),  $[\text{CrO}_4]^{2-}$  (chromate). Both of these complexes have a  $d^0$  configuration, so the color cannot be due to d-d transitions. In fact, the intense colors of these complexes are due to transitions of p electrons on the oxygen into empty d orbitals on the metal. Such transitions are called

**FIGURE 19.30** A possible spin-forbidden transition for the  $d^2$  electron configuration.



**TABLE 19.4** Comparative intensities of electronic transitions

Transition type	Example	Comparative intensity
Spin forbidden Laporte forbidden	$[\text{Mn}(\text{OH}_2)_6]^{2+}$	1
Spin allowed (center of symmetry) Laporte forbidden	$[\text{Co}(\text{OH}_2)_6]^{2+}$	$10^1$
Spin allowed (no center of symmetry) Laporte allowed	$[\text{CoCl}_4]^{2-}$	$5 \times 10^2$
Spin allowed Laporte allowed (charge transfer)	$[\text{MnO}_4]^-$	$10^4$

*charge transfer transitions.* The comparative intensities of electronic transitions are shown in Table 19.4. A more detailed study of transition metal ion spectra is the domain of theoretical inorganic chemistry.

### Spectrum of the $d^5$ High-Spin Ion

The remaining high-spin case,  $d^5$ , is unique in that each orbital contains a single electron, all with parallel spins (Figure 19.31). As a result, the only possible transitions are spin forbidden. Examples of  $d^5$  complexes are the hexaaquamanganese(II) ion and the hexaaquairon(III) ion, both of which have very pale colors (see Chapter 20, Sections 20.5 and 20.6).

### Jahn-Teller Distortion

In Figure 19.24, we showed the visible absorption spectrum for the  $d^1 \text{Ti}^{3+}$  ion. As mentioned in the previous section, such spectra are always broad. However, for  $d^1$ ,  $d^4$  (high spin),  $d^7$  low spin, and  $d^9$ , the band is particularly broad. In fact, if the sample is cooled to liquid nitrogen temperatures to decrease thermal vibrations, it can be seen the peak is not a single peak at all. That is, there is more than one transition and hence more than two energy levels.

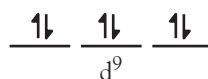
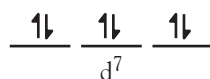
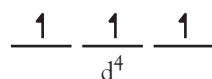
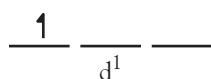
The observation of multiple bands could be explained by the Jahn-Teller distortion. This effect only arises when one of the orbital sets is asymmetrically filled. These configurations are shown in Figure 19.32.

With the orbitals asymmetrically filled, as the six ligands approach the cation along the  $x$ -,  $y$  and  $z$ -axes, the extent of the electron-electron repulsion



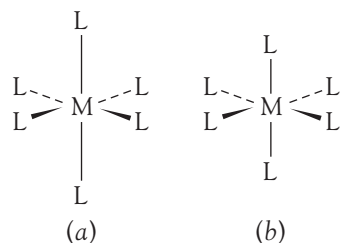
High spin

**FIGURE 19.31** The high-spin  $d^5$  configuration can only have spin-forbidden transitions.

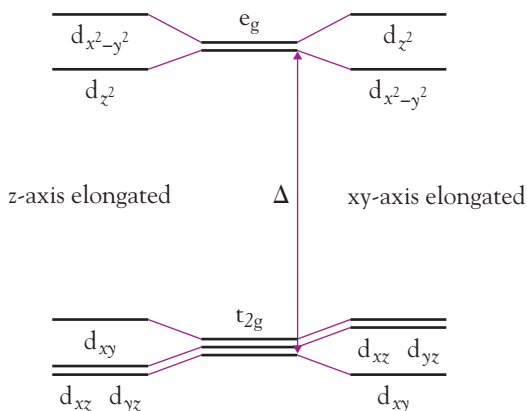


**FIGURE 19.32** Arrangements of electrons that give rise to Jahn-Teller distortion.





**FIGURE 19.33** Jahn-Teller distortion in the (a) axial and (b) equatorial directions.



**FIGURE 19.34** Splitting of the  $e_g$  and  $t_{2g}$  energy levels corresponding to Jahn-Teller distortion in the (a) axial and (b) equatorial directions.

they experience will be different along those axes. Additional repulsion along the  $z$ -axis results in the axial ligands being more distant from the metal ion than the equatorial ligands (Figure 19.33a). Conversely, additional repulsion along the  $x$ - and  $y$ -axes results in equatorial ligands being more distant from the metal ion than the axial ligands (Figure 19.33b).

With the  $e_g$  and  $t_{2g}$  sets no longer degenerate, the energy levels will split, as is shown in Figure 19.34. The direction of splitting will depend upon whether the lengthened bonds are in the axial or equatorial directions.

### WORKED EXAMPLE 19.10

Predict whether the  $[\text{Cr}(\text{OH}_2)]^{2+}$  ion exhibits Jahn-Teller distortion.

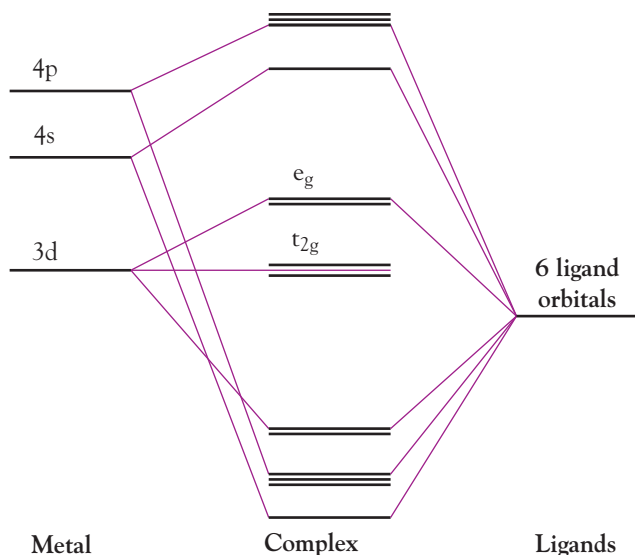
#### Answer

$\text{Cr}(\text{II})$  has a  $d^4$  configuration and the  $\text{H}_2\text{O}$  ligands, being low in the spectrochemical series, would result in a high-spin complex. Therefore, the complex should be distorted. ■

## 19.10 Ligand Field Theory

One failure of crystal field theory is that it cannot explain the spectrochemical series. CFT is a conceptually simple model that treats the ligands as point charges and ignores overlap between orbitals on the ligands with orbitals on the metal. Ligand field theory uses a molecular orbital treatment of the complex that considers the interactions between the ligands and the metal. We then focus on the orbitals on the central metal atom in the same way as we do in CFT.

First, we must consider the orbitals involved in forming  $\sigma$  bonds between the ligands and the metal in an octahedral complex, one on each ligand and the five  $d$ , three  $p$ , and one  $s$  orbital on the metal. These orbitals overlap to form 15 molecular orbitals. The molecular orbital diagram is shown in Figure 19.35. It is not necessary to concern ourselves with the labeling of the molecular

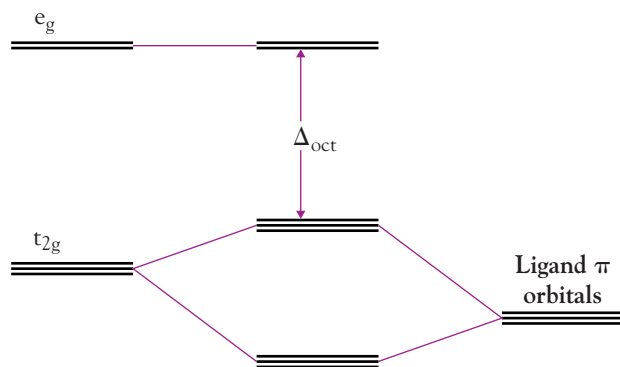


**FIGURE 19.35** Molecular-orbital-energy-level diagram of a typical octahedral complex.

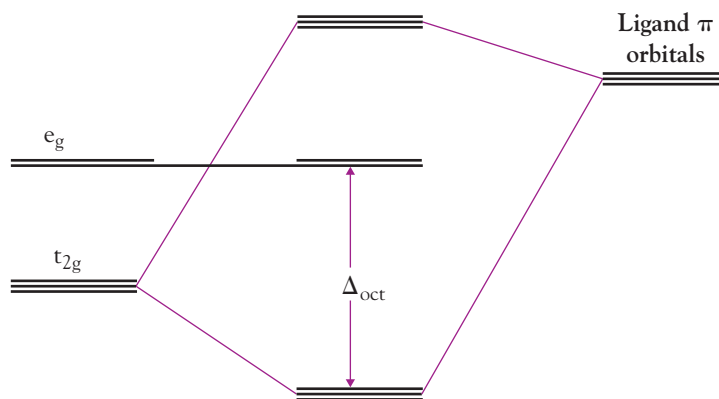
orbitals, but it is important to notice the orbitals labeled  $t_{2g}$  and  $e_g$  in the center of the diagram—the same as those we used in CFT. The 12 electrons donated by the ligands fill up the six lowest-energy molecular orbitals. This means that the electrons provided by the metal fill up the  $t_{2g}$  and  $e_g$  orbitals, just as they did in CFT. The  $t_{2g}$  and  $e_g$  orbitals are separated by the energy  $\Delta_{\text{oct}}$ .

The success of ligand field theory is that it enables us to consider how  $\pi$  bonding between the ligands and the metal affects the magnitude of  $\Delta_{\text{oct}}$ . Some ligands donate or accept electrons through a  $\pi$  bond. This interaction takes place between orbitals on the ligand of  $\pi$  symmetry and the  $t_{2g}$  orbitals on the metal. If the ligand is able to donate electron density to the metal, the ligands must have filled orbitals, and these will have lower energy than the  $t_{2g}$  orbitals on the metal. The ligand orbital will interact with the  $t_{2g}$  orbital, and this leads to a decrease in the value of  $\Delta_{\text{oct}}$ , as shown in Figure 19.36. A decrease in the value of  $\Delta_{\text{oct}}$  would result in a tendency to form high-spin complexes. In fact,  $\pi$ -donor ligands such as halides do give high-spin complexes.

Ligands that are able to accept electrons through a  $\pi$  bond must have empty orbitals, and these will have higher energy than the metal orbitals. Consequently, the interaction between the ligand and the metal orbitals results in a



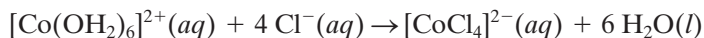
**FIGURE 19.36** The effect of a  $\pi$ -donor ligand on  $\Delta_{\text{oct}}$ .

**FIGURE 19.37** The effect of a  $\pi$ -acceptor ligand on  $\Delta_{\text{oct}}$ .

larger value of  $\Delta_{\text{oct}}$ , as shown in Figure 19.37, and there will be a tendency to form low-spin complexes.  $\pi$ -Acceptor ligands such as the carbonyl ligand do form low-spin complexes as predicted by the large value of  $\Delta_{\text{oct}}$ .

## 19.11 Thermodynamic versus Kinetic Factors

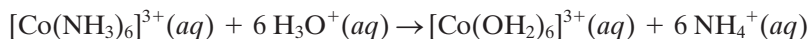
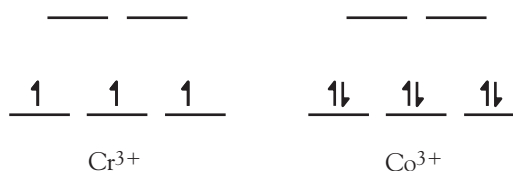
For a reaction to proceed, there must be a decrease in free energy. However, we must always keep kinetic factors in mind. Most solution reactions of transition metal ions proceed rapidly. For example, addition of a large excess of chloride ion to the pink hexaaquacobalt(II) ion,  $[\text{Co}(\text{OH}_2)_6]^{2+}$ , gives the dark blue color of the tetrachloridocobaltate(II) ion,  $[\text{CoCl}_4]^{2-}$ , almost instantaneously:



This reaction is thermodynamically favored and also has a low-activation energy. Complexes that react quickly (for example, within 1 minute) are said to be *labile*. The common dipositive Period 4 transition metal ions form labile complexes. For labile complexes, it is impossible to physically separate isomers.

The two common Period 4 transition metal ions that form kinetically *inert* complexes are chromium(III) and cobalt(III). The former has a  $d^3$  electron configuration and the latter, a low-spin  $d^6$  configuration (Figure 19.38). It is the stability of the half-filled and the filled lower set of d orbitals that precludes any low-energy pathway of reaction.

To illustrate the reaction of an inert complex, concentrated acid added to the hexaamminecobalt(III) ion should cause a ligand replacement according to free energy calculations. However, such a reaction occurs so slowly that several days must elapse before any color change is noticeable:

**FIGURE 19.38** Inert complexes are formed by metal ions with the  $d^3$  and low-spin  $d^6$  electron configurations.

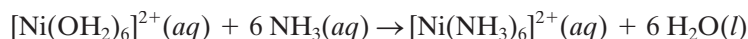
For this reason, to synthesize specific cobalt(III) or chromium(III) complexes, we usually find a pathway that involves synthesizing the complex of the respective labile 2+ ion and then oxidizing it to the inert 3+ ion. Isomers of inert complexes, including optical isomers, can be crystallized separately.

## 19.12 Synthesis of Coordination Compounds

There are many different routes of synthesizing coordination compounds, the two most common being ligand replacement and oxidation-reduction.

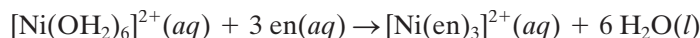
### Ligand Replacement Reactions

Many transition metal complexes are synthesized in aqueous solution by displacement of the water ligands. For example, we can produce the hexaamminenickel(II) ion by adding an excess of aqueous ammonia to a solution of the hexaaquanickel(II) ion:



Ammonia, which is higher than water in the spectrochemical series, readily replaces the water ligands. In other words, the nickel-ammonia bond is stronger than the nickel-water bond, and the process is exothermic. As there are seven ions and molecules on each side, any entropy change in the reaction must be quite small. Hence, the reaction must be enthalpy driven.

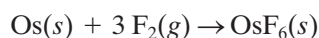
With a chelating ligand, the equilibrium is driven strongly to the right by entropy factors as well. The formation of the tris(1,2-diaminoethane)nickel(II) ion from the hexaaquanickel(II) ion is a good example:



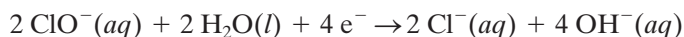
In this reaction, there is a similar enthalpy increase to that with ammonia, but there is also a major entropy increase because the total number of ions and molecules has increased from four to seven. It is the entropy factor that results in such strong complex formation by chelating ligands, behavior that is known as the *chelate effect*.

### Oxidation-Reduction Reactions

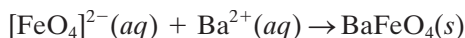
Redox reactions are particularly important as a means of synthesizing compounds in “abnormal” oxidation states. High-oxidation-state fluorides can be synthesized by simple combination reactions, for example:



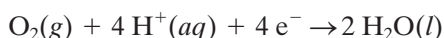
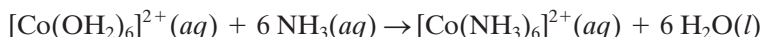
Other high-oxidation-state compounds and polyatomic ions can be produced using oxidizing agents. For example, the red-purple ferrate(VI) ion,  $\text{FeO}_4^{2-}$ , can be prepared using the hypochlorite ion in basic solution:



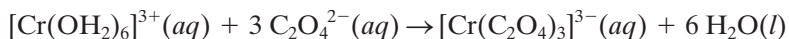
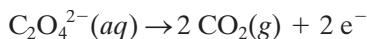
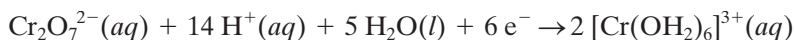
The ion can then be precipitated as the barium salt:



As described in the previous section, because cobalt(III) complexes are kinetically inert, substitution reactions for cobalt(III) complexes are usually impractical. Cobalt(II) is the dominant oxidation state, and the hexaaquacobalt(II) ion can be used as a reagent to produce a range of cobalt(III) complexes. For example, we can synthesize the hexaamminecobalt(III) ion by the air oxidation of the hexaamminecobalt(II) complex. (As we will see in Chapter 20, Section 20.9, replacement of water by ammonia ligands changes the necessary redox potential substantially.)



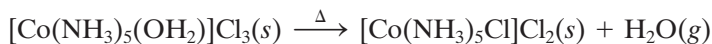
One method of preparing chromium(III) complexes is by reduction of the dichromate ion. In the following example, an oxalic acid–oxalate ion mixture is used as both the reducing agent and the ligand:



The large anion can then be crystallized as the potassium salt,  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ .

### Partial Decomposition Reactions

In a few cases, the identity of the coordinating ligands can be changed by gentle heating and vaporization of the more volatile ligand. An example in cobalt(III) chemistry is:



and an example from chromium(III) chemistry is:

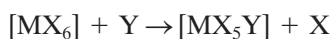


## 19.13 Reaction Mechanisms

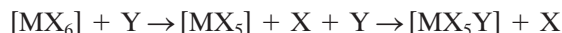
In this section, we look at the reaction mechanisms of two types of reactions of transition metal complexes; substitution reactions and redox processes.

### Substitution Reactions

In substitution reactions, a coordinated ligand is substituted by an uncoordinated ligand. The general reaction for octahedral complexes is:

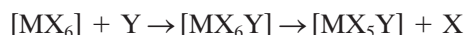


The reaction can take place via several possible mechanisms. The mechanism is described as *dissociative*, D, if the M—X bond is broken before the entering ligand Y attaches to the central metal atom. The coordination number is reduced from six to five in the *transition state*:



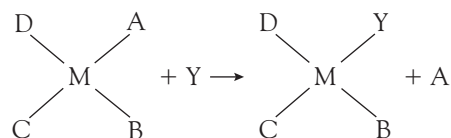
The rates of dissociative reactions are affected by the strength of the M—X bond but unaffected by the nature of the entering ligand Y. The rate is also affected by the steric bulkiness of the ligands with bulky ligands favoring a less crowded five-coordinate intermediate.

In the *associative* mechanism, A, the entering group attaches to M before any weakening of the M—X bond occurs. The coordination number of M is increased by one in the transition state.

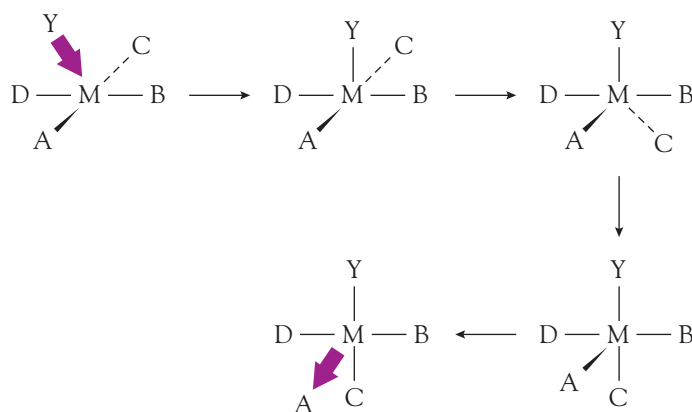


The *interchange* mechanism, I, lies in between these extremes as it involves the simultaneous weakening of the M—X bond and attachment of Y. If the weakening of the M—X bond makes a bigger contribution to the transition state then the mechanism is  $\text{I}_\text{d}$ . If making the M—Y bond makes a bigger contribution it is labeled  $\text{I}_\text{a}$ . I is used when the contributions are equal.

For square planar complexes, the space available above the plane means that these invariably react via an associative mechanism. The reaction,

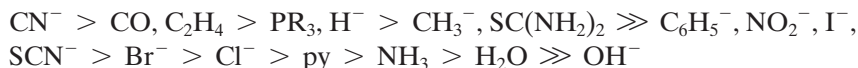


is stereospecific. If ligands C and A are *cis*-related in the reactant and so are C and Y in the product. If ligands C and A are *trans*-related in the reactant then so are C and Y in the product. The reaction mechanism is believed to be that shown in Figure 19.39:



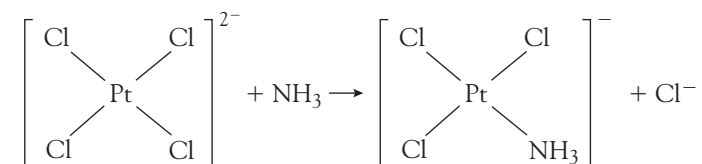
**FIGURE 19.39** The proposed mechanism for substitution in a square planar complex.

Which ligands are substituted in a square planar complex is determined by the *trans* effect, which is defined as the effect of a ligand on the rate of substitution of the ligand *trans* to it. Ligands can be placed in order of their ability of a ligand to activate the *trans*-ligand:

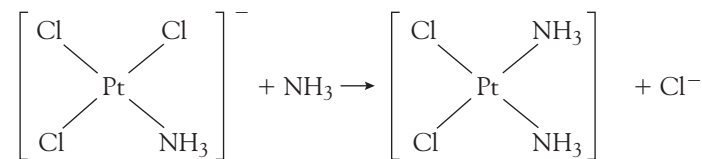


The ligands which are high in the series are either good  $\sigma$ -donors, such as  $\text{H}^-$ , or  $\pi$ -acceptors, such as CO.

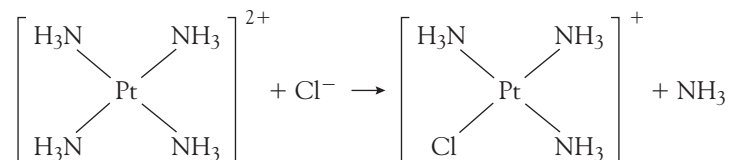
The *trans* effect series is very useful in the design of synthetic routes. For example, the stereospecific synthesis of the chemotherapy agent *cis*- $\text{PtCl}_2(\text{NH}_3)_2$  can be achieved by using  $[\text{PtCl}_4]^{2-}$  as the starting material. When ammonia is added, one of the  $\text{Cl}^-$  ligands is replaced.



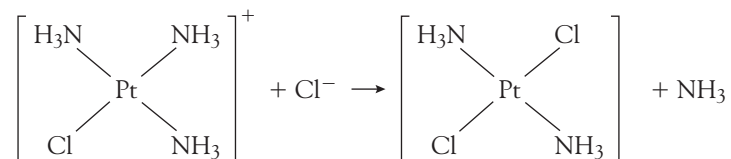
Addition of a second equivalent of ammonia substitutes a  $\text{Cl}^-$  located *trans* to a chloride faster than a  $\text{Cl}^-$  *trans* to the  $\text{NH}_3$ , as  $\text{Cl}^-$  is higher in the *trans*-effect series.



To make the *trans* isomer,  $[\text{Pt}(\text{NH}_3)]^{2+}$  is used as the starting material. Addition of  $\text{Cl}^-$  leads to substitution of an ammonia.



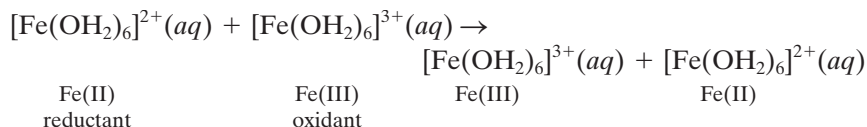
When a second equivalent of  $\text{Cl}^-$  is added, it substitutes the  $\text{NH}_3$  located *trans* to the chloride rather than one *trans* to an ammonia in accordance with the *trans*-effect series,



## Redox Reactions

Redox reactions are very important in inorganic and bioinorganic chemistry. The shuttling of electrons between transition metal cations is at the center of a wide variety of vital biological processes. Redox reactions involving transition metal complexes generally occur very rapidly. This is why thermodynamics (using  $E^0$  values) is so useful in predicting the outcome of reactions.

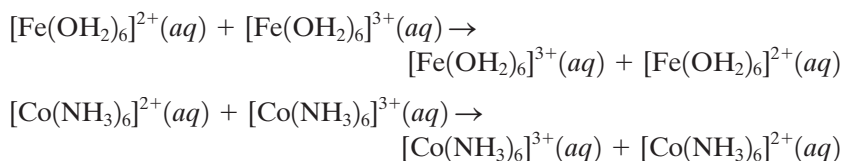
Redox processes appear to occur by two mechanisms. In an *outer sphere* reaction such as:



The two complexes diffuse together in solution to form an outer sphere complex, an electron is transferred from reductant to oxidant and then the complexes diffuse apart. The ligands coordinated to the metals remain attached throughout the reaction and electron transfer is very fast. This would lead to products that have bond lengths that are too long or too short for the new oxidation state of the metal unless the geometries are distorted. In fact there is an activation step in which the Fe—OH<sub>2</sub> bonds in both oxidant and reductant are distorted so that they are all the same length and they then relax to ideal bond lengths after electron transfer. The rates of these outer sphere reactions are fastest for reactions where the differences in bond lengths between the two oxidation states is small.

### WORKED EXAMPLE 19.11

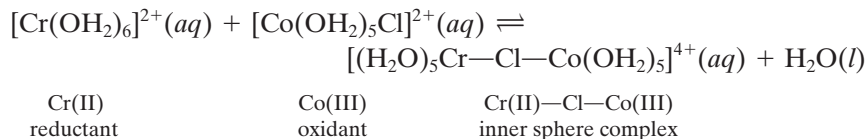
Which of the following two outer-sphere reactions is likely to have the fastest reaction rate given the following ionic radii:  $r\text{Fe}^{2+} = 92$  pm,  $r\text{Fe}^{3+} = 78$  pm,  $r\text{Co}^{2+} = 88$  pm,  $r\text{Co}^{3+} = 68$  pm.



### Answer

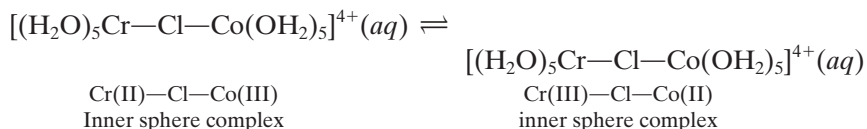
The difference between the bond lengths for the iron reaction is  $(92 - 78)$  pm = 14 pm, whereas that for the cobalt reaction is  $(88 - 68)$  pm = 20 pm. Therefore, we would expect the iron reaction to have the faster reaction rate. ■

In the *inner sphere* mechanism, a bridged complex between oxidant and reductant is formed before electron transfer occurs:

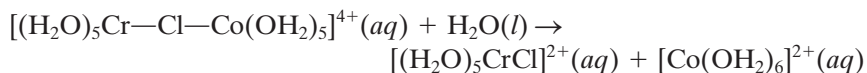




This reaction is a ligand substitution reaction of a water on the Cr(II). The electron is then transferred from the reductant to the oxidant via the bridging group:



The bridged complex breaks apart:



There are several conditions for the formation of the inner sphere complex:

1. One of the reactants must be labile so that substitution is rapid (in the example above,  $\text{Cr}^{2+}$  is a labile ion).
2. The oxidant must possess a ligand that is capable of bridging (that is, it must have a free lone pair of electrons like  $\text{Cl}^-$  above).
3. The reactants must not be so bulky that the inner sphere complex is very sterically crowded.

## 19.14 Coordination Complexes and the Hard-Soft Acid-Base (HSAB) Concept

Just as the HSAB concept can help us predict main group reactions (as we saw in Chapter 7, Section 7.7), so it can help us understand the ligand preferences of transition metals in different oxidation states. Table 19.5 shows the qualitative divisions into hard/borderline/soft acids of some of the first row transition elements.

Ligand atoms can be similarly classified into hard/borderline/soft. These ligand-atom categories generally apply, irrespective of the other atoms of the ligand. For example, all nitrogen-donor ligands of the form  $\text{NR}_3$  are hard bases, where R is an alkyl group such as methyl or hydrogen. Conversely, all carbon-donor ligands, such as carbon monoxide and cyanide, are soft bases (Figure 19.40). Chloride ion is regarded as a hard base, but not as hard as fluoride or an oxygen-donor ligand. Hence, chloride is depicted in Figure 19.40 as half-white and half-mauve.

The HSAB concept accounts for the fact that high-oxidation states of metal ions (hard acids) are found with fluoride or oxide ligands (hard bases). It is the

C	N	O	F
	P	S	Cl
	As	Se	Br
		Te	I

**FIGURE 19.40** Classification of the HSAB ligand atoms into hard (white), borderline (light mauve), and soft (dark mauve).

**TABLE 19.5** Some common first row transition metal ions categorized according to the HSAB concept

Hard	Borderline	Soft
$\text{Ti}^{4+}$ , $\text{V}^{4+}$ , $\text{Cr}^{3+}$ , $\text{Cr}^{6+}$ $\text{Mn}^{2+}$ , $\text{Mn}^{4+}$ , $\text{Mn}^{7+}$ , $\text{Fe}^{3+}$ , $\text{Co}^{3+}$	$\text{Fe}^{2+}$ , $\text{Co}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Cu}^{2+}$	$\text{Cu}^+$ All metals with 0 or negative oxidation states

low-oxidation states (soft acids) that are stabilized by such ligands as the carbon-bonded carbonyl (a soft base). To provide a specific example, copper(II) fluoride is known, whereas copper(I) fluoride is not; conversely, copper(I) iodide is known, whereas copper(II) iodide is not. We can use this principle to help us synthesize transition metal compounds in which the metal ions have abnormal oxidation states. For example, iron is usually found in +2 and +3 oxidation states. We can prepare a compound of the hard-acid iron(VI) using the hard-base oxide ion to give the tetraoxido ferrate(VI) ion,  $[\text{FeO}_4]^{2-}$  (as described in the previous section). Similarly, we can prepare a compound of soft-acid iron(0) using the soft-base carbonyl molecule to give pentacarbonyliron(0),  $[\text{Fe}(\text{CO})_5]$ .

### Chemical Symbiosis

The HSAB concept is also relevant to reactions of transition metal complexes. In particular, there is a general tendency for a complex ion to prefer ligand atoms of the same type. Thus, a complex with some hard-base ligands will prefer to add another hard-base ligand. Similarly, a complex with soft-base ligands will prefer to add another soft-base ligand. This preference for ligands of the same HSAB type is known as *chemical symbiosis*.

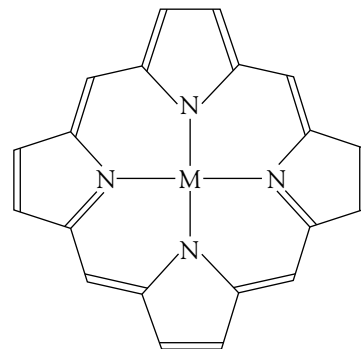
Cobalt(III) chemistry is particularly useful for the illustration of symbiosis. For example, the complex  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  is much more stable in aqueous solution than  $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$ . This can be explained in HSAB terms by considering that Co(III) is “hardened” by the presence of five hard-base ammonia ligands. Thus, the soft-base iodide ion is comparatively easily replaced by water (a hard-base ligand) to form  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ . On the other hand,  $[\text{Co}(\text{CN})_5\text{I}]^{3-}$  is more stable in water than  $[\text{Co}(\text{CN})_5\text{F}]^{3-}$ . Chemists contend that the five soft-base cyanide ions “soften” the cobalt(III) complex, resulting in a preference for the soft-base iodide at the sixth coordination site rather than the hard-base water molecule.

### Linkage Isomerism and the HSAB Concept

A particularly interesting example of the application of the HSAB concept to transition metal complexes involves linkage isomerism. The thiocyanate ion,  $\text{NCS}^-$ , can bond either through the nitrogen atom, in which case it acts as a borderline base, or through the sulfur atom, in which case it behaves as a soft base. We find that in the pentamminethiocyanatocobalt(III) ion,  $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ , it is bonded through nitrogen, as we would expect, since the other ligands are hard bases, while in the pentacyanidothiocyanatocobalt(III) ion,  $[\text{Co}(\text{CN})_5(\text{SCN})]^{3-}$ , coordination is through the sulfur, as is consistent with the other ligands, cyanides, being soft bases.

## 19.15 Biological Aspects

The chelate effect is important in biological complexes. One tetradentate ligand is of particular importance to biological systems—the porphyrin ring. The basic structure of this complex is shown in Figure 19.41. It is an organic molecule in which alternating double bonds hold the structure in a rigid plane with four nitrogen atoms oriented toward the center. The space in the center is the right size for many metal ions.



**FIGURE 19.41** The core of metalloporphyrin complexes.

In biological systems, the porphyrin ring carries different substituents on the edge of the molecule, but the core—a metal ion surrounded by four nitrogen atoms—is consistent throughout the biological world. Plant life depends on the chlorophylls, which contain magnesium-porphyrin units, for the process of photosynthesis. Animal life depends on several metal porphyrin systems such as the hemoglobin molecule, used for oxygen transport, which contains four iron-porphyrin units. Thus, the porphyrin metal complexes are among the most important in the living world.

## KEY IDEAS

- A wide range of oxidation states is a characteristic of transition metal ions compared to the single (or, in a few cases, two) oxidation state(s) found for ions of main group metals.
- A variety of geometrical shapes are adopted by transition metal complexes.
- Transition metal complexes exhibit several types of isomerism.
- Among the bonding theories for transition metal complexes, CFT is one of the most useful.
- CFT can be used to explain many of the properties of transition metal complexes.
- The HSAB concept can be applied to the formulas and reaction types of transition metal complexes.

## EXERCISES

**19.1** Define the following terms: (a) transition metal; (b) ligand; (c) crystal field splitting.

**19.2** Define the following terms: (a) coordination number; (b) chelate; (c) chelate effect.

**19.3** Nickel forms two tetracyanido complexes,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{4-}$ . Explain why you might expect complexes with nickel in both normal (+2) and low (0) oxidation states.

**19.4** Suggest why the fluoride in which chromium has its highest oxidation state is  $\text{CrF}_6$ , whereas the highest oxidation state chromium assumes in a chloride is  $\text{CrCl}_4$ .

**19.5** In addition to the two geometric isomers of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , there is a third isomer. It has the same empirical formula and square planar geometry, but it is electrically conducting in solution. Write the structure of the compound.

**19.6** Identify the probable type of isomerism for (a)  $\text{Co}(\text{en})_3\text{Cl}_3$ ; (b)  $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ .

**19.7** Draw the geometric and optical isomers for the  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  ion.

**19.8** Provide systematic names for each of the following compounds: (a)  $[\text{Fe}(\text{CO})_5]$ ; (b)  $\text{K}_3[\text{CoF}_6]$ ; (c)  $[\text{Fe}(\text{OH}_2)_6]\text{Cl}_2$ ; (d)  $[\text{CoCl}(\text{NH}_3)_5]\text{SO}_4$ .

**19.9** Provide systematic names for each of the following compounds: (a)  $(\text{NH}_4)_2[\text{CuCl}_4]$ ; (b)  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]\text{Br}_3$ ; (c)  $\text{K}_3[\text{Cr}(\text{CO})_4]$ ; (d)  $\text{K}_2[\text{NiF}_6]$ ; (e)  $[\text{Cu}(\text{NH}_3)_4](\text{ClO}_4)_2$ .

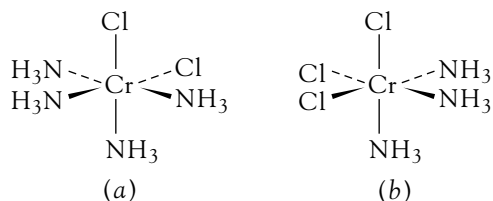
**19.10** Deduce the formula of each of the following transition metal complexes:

- hexaamminechromium(III) bromide
- aquabis(1,2-diaminoethane)thiocyanatocobalt(III) nitrate
- potassium tetracyanidonickelate(II)
- tris(1,2-diaminoethane)cobalt(III) iodide

**19.11** Deduce the formula of each of the following transition metal complexes:

- hexaaquamanganese(II) nitrate
- palladium(II) hexafluoropalladate(IV)
- tetraaquadichloridochromium(III) chloride dihydrate
- potassium octacyanidomolybdenate(V)

**19.12** Write the names of the following geometric isomers:



**19.13** Construct energy-level diagrams for both high- and low-spin situations for the  $d^6$  electron configuration in (a) an octahedral field; (b) a tetrahedral field.

**19.14** Which one of the iron(III) complexes, hexacyanidoferrate(III) ion or tetrachloridoferrate(III), is likely to be high spin and which low spin? Give your reasons (two in each case).

**19.15** The crystal field splittings,  $\Delta$ , are listed in the following table for three ammine complexes of cobalt. Explain the differences in values.

Complex	$\Delta(\text{cm}^{-1})$
$[\text{Co}(\text{NH}_3)_6]^{3+}$	22 900
$[\text{Co}(\text{NH}_3)_6]^{2+}$	10 200
$[\text{Co}(\text{NH}_3)_4]^{2+}$	5 900

**19.16** The crystal field splitting,  $\Delta$ , are listed in the following table for four complexes of chromium. Explain the differences in values.

Complex	$\Delta(\text{cm}^{-1})$
$[\text{CrF}_6]^{3-}$	15 000
$[\text{Cr}(\text{OH}_2)_6]^{3+}$	17 400
$[\text{CrF}_6]^{2-}$	22 000
$[\text{Cr}(\text{CN})_6]^{3-}$	26 600

**19.17** For which member of the following pairs of complex ions would  $\Delta_{\text{oct}}$  be greater? Explain your reasoning.

- (a)  $[\text{MnF}_6]^{2-}$  and  $[\text{ReF}_6]^{2-}$   
 (b)  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$

**19.18** Construct a table of d electron configurations and corresponding number of unpaired electrons for a tetrahedral stereochemistry (similar to Table 19.2).

**19.19** Construct a table of crystal field stabilization energies for the dipositive high-spin ions of the Period 4 transition metals in a tetrahedral field in terms of  $\Delta_{\text{tet}}$  (similar to Table 19.3).

**19.20** Predict whether (a)  $[\text{Fe}(\text{OH}_2)]^{2+}$  or (b)  $[\text{Co}(\text{CN})_6]^{4-}$  would Jahn Teller distorted.

**19.21** Would you predict that  $\text{NiFe}_2\text{O}_4$  would adopt a normal spinel or an inverse spinel structure? Explain your reasoning.

**19.22** Would you predict that  $\text{NiCr}_2\text{O}_4$  would adopt a normal spinel or an inverse spinel structure? Explain your reasoning.

**19.23** Ortho-phenanthroline,  $\text{C}_8\text{H}_6\text{N}_2$ , is a bidentate ligand, commonly abbreviated as phen. Explain why  $[\text{Fe}(\text{phen})_3]^{2+}$  is diamagnetic while  $[\text{Fe}(\text{phen})_2(\text{OH}_2)_2]^{2+}$  is paramagnetic.

**19.24** The ligand  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ , commonly known as *det*, is a tridentate ligand, coordinating to metal ions through all three nitrogen atoms. Write a balanced chemical equation for the reaction of this ligand with the hexaaquanickel(II) ion and suggest why the formation of this complex would be strongly favored.

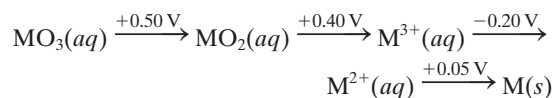
## BEYOND THE BASICS

**19.25** Copper(II) normally forms a complex anion of formula  $[\text{CuCl}_4]^{2-}$  with cations such as cesium. However, the cation  $[\text{Co}(\text{NH}_3)_6]^{3+}$  can be used to precipitate an anion of formula  $[\text{CuCl}_5]^{3-}$ . Suggest two reasons why this cation stabilizes the formation of the  $[\text{CuCl}_5]^{3-}$  anion. Also, give the correct name for the complete compound formed.

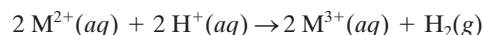
**19.26** Iron(III) chloride reacts with triphenylphosphine,  $\text{PPh}_3$ , to form the complex  $[\text{FeCl}_3(\text{PPh}_3)_2]$ . However, with the ligand tricyclohexylphosphine,  $\text{PCh}_3$ , the compound  $[\text{FeCl}_3(\text{PCh}_3)]$  is formed. Suggest a reason for the difference.

**19.27** A complex of nickel,  $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ , is paramagnetic, whereas the palladium analog,  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ , is diamagnetic. How many isomers would you predict for each compound? Give your reasoning.

**19.28** With the availability of many oxidation states, Latimer, Frost, and Pourbaix diagrams are of considerable importance in the study of transition metal chemistry, as we will see in Chapter 20. For the imaginary transition metal M, the Latimer diagram is as follows:



- (a) Identify any species prone to disproportionation, and write the corresponding chemical equation.  
 (b) Calculate the pH at which the reaction:



becomes spontaneous. Assume standard conditions except for  $[\text{H}^+(\text{aq})]$ .

**19.29** Which of the following ions will have the greater stability:  $[\text{AuF}_2]^-$  or  $[\text{AuI}_2]^-$ ? Give your reasoning.

**19.30** Nickel forms an anion  $[\text{NiSe}_4]^{2-}$  that is square planar, while the analogous zinc anion,  $[\text{ZnSe}_4]^{2-}$ , is tetrahedral. Suggest an explanation for the different structures.

**19.31** Many canned or bottled food products, such as commercial mayonnaise, salad dressings, and kidney beans, contain the hexadentate ligand ethylenediaminetetraacetate,  $^{2-}(\text{OOC})_2\text{NCH}_2\text{CH}_2\text{N}(\text{COO})_2^{2-}$ , abbreviated  $\text{edta}^{4-}$ , or a related compound. Suggest a reason for this.

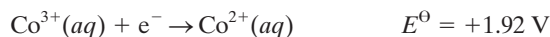
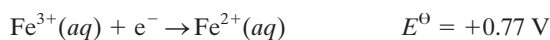
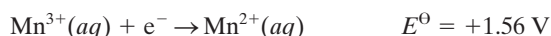
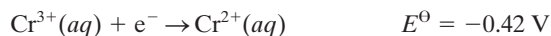
**19.32** Three hydrates of chromium(III) chloride are known: form A is a hexahydrate; form B, a pentahydrate; and form C, a tetrahydrate. Addition of excess silver ion solution to a solution of 1 mole of each form results in the precipitation of the following number of moles of silver chloride: from A 3; from B 2; from C 1. Using this information, deduce the actual structure of each hydrate and write the corresponding name.

**19.33** Should silver be designated a transition metal if its common oxidation state is +1? Discuss.

**19.34** The complex  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  is yellow-orange, while  $[\text{Co}(\text{OH}_2)_3\text{F}_3]$  is blue. Suggest an explanation for the difference in color.

**19.35** Suggest synthetic routes to *cis* and *trans*- $[\text{PtCl}_2(\text{NH}_3)(\text{PPh}_3)]$  using  $\text{PPh}_3$ ,  $\text{NH}_3$  and  $[\text{PtCl}_4]^{2-}$ .

**19.36** The +3 to +2 reduction potentials for some first row transition metals are as follows:



Suggest why the manganese reduction potential is higher than might be expected while the value for the iron reduction is lower than might be expected.

**19.37** Hydration enthalpies and values of  $\Delta_{\text{oct}}$  for some metal ions are given in the table below.

Ion	$\Delta_{\text{hyd}}H^\ominus/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{oct}}/\text{cm}^{-1}$
$\text{Ca}^{2+}$	2478	0
$\text{V}^{2+}$	2789	12 600
$\text{Cr}^{2+}$	2806	13 900
$\text{Mn}^{2+}$	2747	7800
$\text{Fe}^{2+}$	2856	10 400
$\text{Co}^{2+}$	2927	9300
$\text{Ni}^{2+}$	3007	8300
$\text{Cu}^{2+}$	3011	1260
$\text{Zn}^{2+}$	2969	0

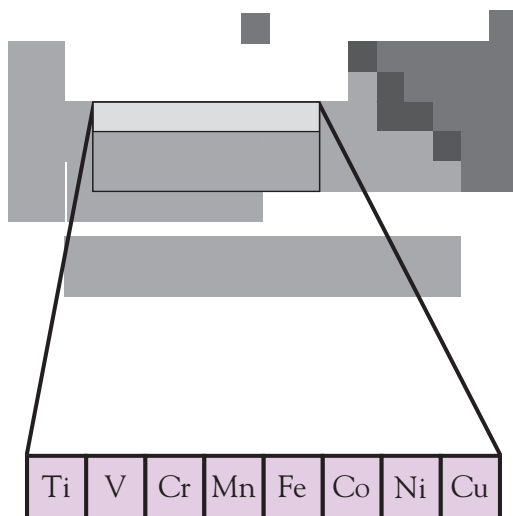
Calculate the number of d electrons for each metal ion and plot the hydration enthalpies against the number of d electrons. Calculate the high-spin crystal field stabilization energy in  $\text{cm}^{-1}$  and convert these values to  $\text{kJ}\cdot\text{mol}^{-1}$ . Use this value to correct the enthalpies of hydration for crystal field effects. Plot the enthalpies of hydration in the absence of crystal field effects.

## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# PROPERTIES OF THE 3d TRANSITION METALS

## CHAPTER 20



The 3d transition metals form a series in themselves and their chemistry is significantly different from that of the 4d and 5d series of transition metals. In particular, many complexes of 3d metal ions are high spin, while those of the heavier transition metals are almost always low spin. Also, the 3d metals are the transition metals which we most often encounter in our lives, such as iron and copper. Thus, this chapter will cover the patterns, trends, and interesting compounds of the 3d series. The properties and reactions will be linked to the principles of transition metal chemistry which were introduced in Chapter 19.

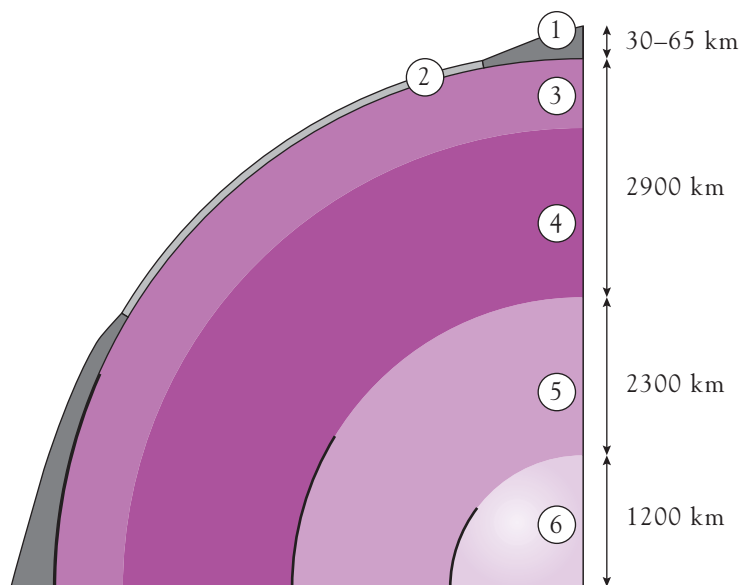
### Context: Iron Is at the Core of Everything

We live on an enormous sphere of iron. Most of the core of planet Earth consists of this one element; the highest atomic number element that is formed exothermically by nuclear fusion (Chapter 2, Section 2.2), together with about 20% nickel and small proportions of gold, platinum, and other metals. When the Earth initially formed, it is believed to have been a mixture of metals and silicates. Through collisions and the heat of radioactive decays, the temperature rose to over 1500 K, producing an emulsion, with one component being an iron-nickel alloy and the other mineral silicates. Iron being a dense metal (see Section 20.6), the

25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 20.1** Overview of the 3d Transition Metals
- 20.2** Group 4: Titanium
- 20.3** The Vanadium-Chromium-Manganese Triad
- 20.4** Group 5: Vanadium
- 20.5** Group 6: Chromium
- 20.6** Group 7: Manganese
- 20.7** The Iron-Cobalt-Nickel-Copper Tetrad
- 20.8** Group 8: Iron
- 20.9** Group 9: Cobalt
- 20.10** Group 10: Nickel
- 20.11** Group 11: Copper
- 20.12** Biological Aspects
- 20.13** Element Reaction Flowcharts

Schematic view of the interior of Earth: (1) continental crust; (2) oceanic crust; (3) upper mantle; (4) lower mantle; (5) outer core; (6) inner core.



metallic globules sank toward the center of the molten planet, leaving the silicates floating above. The core has two components (see the figure above)—the inner core (6) and the outer core (5).

The inner core is a solid sphere with a radius of about 1200 km and an average temperature of about 5400°C. It is the extreme pressure which keeps the inner core solid. The outer core is about 2300 km thick, and it is liquid, the temperature being higher and the pressure slightly less. Iron and nickel are both ferromagnetic metals (Section 20.7). The eddy currents in the outer core produce the Earth's magnetic field. It is the magnetic field which protects us from the intense bombardment of particles from the Sun (the solar wind). Without the protection of the magnetic field, life would be impossible and, in fact, the wind would have blown away most of our atmosphere long ago.

## 20.1 Overview of the 3d Transition Metals

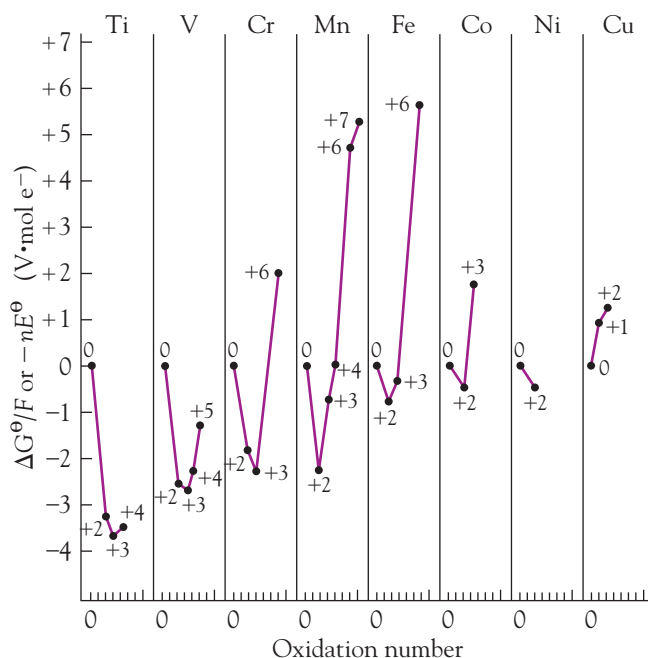
All the transition metals are hard (except copper), dense, and have high melting points. There are patterns in the oxidation states of the 3d transition metals, which are illustrated in the formulas of the common oxides (Table 20.1).

The first four members of the period are found in oxidation states up to and including their group number. From iron through to copper, the stable oxidation states are much lower and decrease. Manganese, iron, and cobalt each form oxides in which one-third of the metal ions are in the +2 state and the other two-thirds in the +3 state; thus, they are more correctly written as  $(M^{2+})(M^{3+})_2(O^{2-})_4$ . Unlike the main group metals, transition metals exhibit almost every possible oxidation number; for example, there are various compounds of manganese in which manganese has every oxidation number from +7 to -1.

**TABLE 20.1** The oxides of the 3d transition metals

Ox. No.	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper
+1								Cu <sub>2</sub> O
+2	TiO	VO		MnO	FeO	CoO	NiO	CuO
+2 & 3				Mn <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	Co <sub>3</sub> O <sub>4</sub>		
+3	Ti <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>			
+4	TiO <sub>2</sub>	VO <sub>2</sub>	CrO <sub>2</sub>	MnO <sub>2</sub>			NiO <sub>2</sub>	
+5		V <sub>2</sub> O <sub>5</sub>						
+6			CrO <sub>3</sub>					
+7				Mn <sub>2</sub> O <sub>7</sub>				

Figure 20.1 summarizes the Frost diagrams for these elements. Titanium metal (oxidation state 0) is strongly reducing, but the elements become less so along the row. Copper is unique in that the metal itself is the most thermodynamically stable oxidation state. Traversing the row, the highest oxidation state becomes less favored, and by chromium, it has become highly oxidizing. The most thermodynamically stable oxidation number is +3 for titanium, vanadium, and chromium, whereas +2 is favored by the other elements. Copper is unique in having a stable +1 oxidation number, but as is apparent from Figure 20.1, it is prone to disproportionation to the +2 and 0 oxidation states.

**FIGURE 20.1** Frost diagrams for the 3d transition metals under acid conditions.

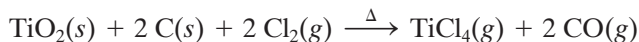


## 20.2 Group 4: Titanium

Titanium, a hard, silvery white metal, is the least dense ( $4.5 \text{ g}\cdot\text{cm}^{-3}$ ) of the transition metals. This combination of high strength and low density makes it a preferred metal for military aircraft and nuclear submarines, where cost is less important than performance. The metal has more mundane applications in high-performance bicycle frames and golf clubs.

### Extraction of Titanium

Although titanium is the ninth most abundant element in the Earth's crust, the pure metal is difficult to obtain from the most common titanium ore,  $\text{TiO}_2$ , rutile. Reduction of titanium(IV) oxide,  $\text{TiO}_2$ , with carbon produces the metal carbide rather than the metal. The only practical route (the *Kroll process*) involves the initial conversion of the titanium(IV) oxide to titanium(IV) chloride by heating the oxide with carbon and dichlorine:



The titanium(IV) chloride is then reduced by a more reactive metal. Magnesium is usually preferred on the basis of lower cost and also of ease of separating the titanium metal from the other metal chloride and from excess metal reactant:

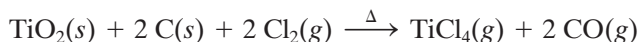


The spongy mass of titanium metal is porous, and the magnesium chloride and excess magnesium metal can be dissolved out by using dilute acid. The titanium metal granules are then fabricated into whatever shape is required.

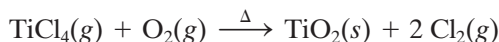
### Titanium(IV) Oxide

Although the production of titanium metal is vital for the defense industry, the enormous quantities of titanium ores mined each year are destined for a more innocuous purpose—as a white pigment which is used in products as diverse as paint, paper, and toothpaste. Of the 5 million tonnes of titanium ore produced each year, Canada provides about one-third and Australia provides about one-fourth of the element. Although the element is found as the dioxide (rutile), it is too impure to be used directly.

The purification process of titanium(IV) oxide involves the conversion of rutile to the chloride, as in the metal synthesis:



The chloride is then reacted with dioxygen at about  $1200^\circ\text{C}$  to give pure white titanium(IV) oxide while the chlorine is recycled:



Prior to the use of titanium(IV) oxide in paints, the common white pigment was “white lead,”  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ . Apart from its toxicity, it discolored in industrial city atmospheres to give black lead(II) sulfide. Titanium(IV) oxide, which is

stable to discoloration in polluted air, has now replaced white lead completely. Not only is titanium(IV) oxide of very low toxicity, it has the highest refractive index of any white or colorless inorganic substance—even higher than diamond. As a result of this high light-scattering ability, it covers and hides previous paint layers more effectively. In addition to its use in white paint, it is also added to colored paints to make the colors paler and mask previous colors better.

### 20.3 The Vanadium-Chromium-Manganese Triad

Although the chemistry of titanium is dominated by the highly insoluble titanium(IV) oxide, the chemistry of the next three members of the 3d transition metals—vanadium, chromium, and manganese—is quite different. These three transition metals form a distinct subsection (the *V-Cr-Mn triad*) in that they readily form oxoanions such as vanadate,  $\text{VO}_4^{3-}$ ; chromate,  $\text{CrO}_4^{2-}$ ; and permanganate,  $\text{MnO}_4^-$ . These species are tetrahedral ions that exist both in solution and in solid ionic compounds. The predominance diagram under highly oxidizing conditions is shown in Table 20.2.

It is for these three metals in their highest oxidation states for which we find the most parallels with their main group analogs. That is, as discussed in Chapter 9, Section 9.4, there are considerable similarities between the (*n*) elements and the corresponding (*n* + 10) elements. For example, the vanadate ion behaves as the conjugate base of the very weak acid  $\text{H}_3\text{VO}_4$ , analogous to phosphoric acid,  $\text{H}_3\text{PO}_4$ , and the two corresponding intermediate acid anions are known:  $[\text{HVO}_4]^{2-}$  and  $[\text{H}_2\text{VO}_4]^-$ . Vanadium also forms the solid-state oxyanion  $[\text{VO}_3]^-$ , which, like  $[\text{PO}_3]^-$ , consists of long chains of  $\text{VO}_4$  tetrahedra, two of the corner oxygen atoms being shared with the neighboring tetrahedra.

Chromium parallels sulfur in that the chromate ion is the conjugate base of the strong acid chromic acid (analogous to sulfuric acid). Thus, little hydrolysis occurs when chromates are dissolved in water. Similarly, among the many parallels between the chemistry of manganese and chlorine, permanganate resembles perchlorate in being the conjugate base of a very strong oxidizing acid.

Of course, in chemistry, patterns are not as clearly defined as we humans would like. Thus, manganese also has similarities to the later members of the 3d series in that the thermodynamically most stable oxidation state is +2 (see Figure 20.1). More specifically, as shown in Table 20.1, manganese forms a stable oxide with mixed oxidation states,  $\text{Mn}_3\text{O}_4$ , parallel to those of iron and cobalt.

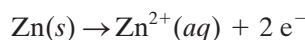
**TABLE 20.2** The pH dependence of species for vanadium, chromium, and iron under highly oxidizing conditions

	Very acidic	Acidic	Basic	Very basic
Vanadium	$\text{VO}_2^+(aq)$	$\text{H}_2\text{VO}_4^-(aq)$	$\text{HVO}_4^{2-}(aq)$	$\text{VO}_4^{3-}(aq)$
Chromium	$\text{H}_2\text{CrO}_4(aq)$	$\text{HCrO}_4^-(aq)$	$\text{CrO}_4^{2-}(aq)$	
Manganese	$\text{MnO}_4^-(aq)$			

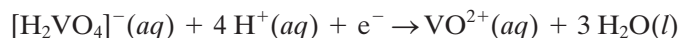
## 20.4 Group 5: Vanadium

Vanadium is used for vanadium steels, a particularly hard alloy employed for knife blades and various workshop tools. The simple redox chemistry of vanadium is particularly interesting to inorganic chemists because vanadium readily exists in four different oxidation states: +5, +4, +3, and +2, corresponding to the  $d^0$ ,  $d^1$ ,  $d^2$ , and  $d^3$  electron configurations. With an oxidation number of +5 for vanadium, the colorless vanadate ion,  $[\text{VO}_4]^{3-}$ , exists in very basic solution; under neutral conditions, conjugate acids such as the pale yellow dihydrogen vanadate ion,  $[\text{H}_2\text{VO}_4]^-$ , are formed.

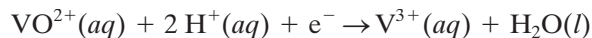
A reducing agent, such as zinc metal in acid solution, can be used to reduce the vanadium(V) to give the characteristically colored ions of vanadium in lower oxidation states:



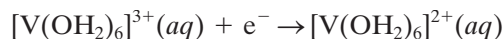
Initial reduction of the dihydrogen vanadate ion by zinc metal in acid solution (or by a weak reducing agent, such as sulfur dioxide) gives the deep blue vanadyl ion,  $\text{VO}^{2+}$  (with +4 oxidation number). For simplicity, the ion is commonly written as  $\text{VO}^{2+}$ , but, in fact, the ion is  $[\text{VO}(\text{OH}_2)_5]^{2+}$  because five water molecules occupy the other coordination sites:



As reduction continues, the bright blue color of the vanadyl ion is replaced by that of the green hexaaquavanadium(III) ion,  $[\text{V}(\text{OH}_2)_6]^{3+}$  (or  $\text{V}^{3+}(\text{aq})$ , for simplicity):



Provided air is excluded, further reduction results in the formation of the lavender hexaaquavanadium(II) ion,  $[\text{V}(\text{OH}_2)_6]^{2+}$ :

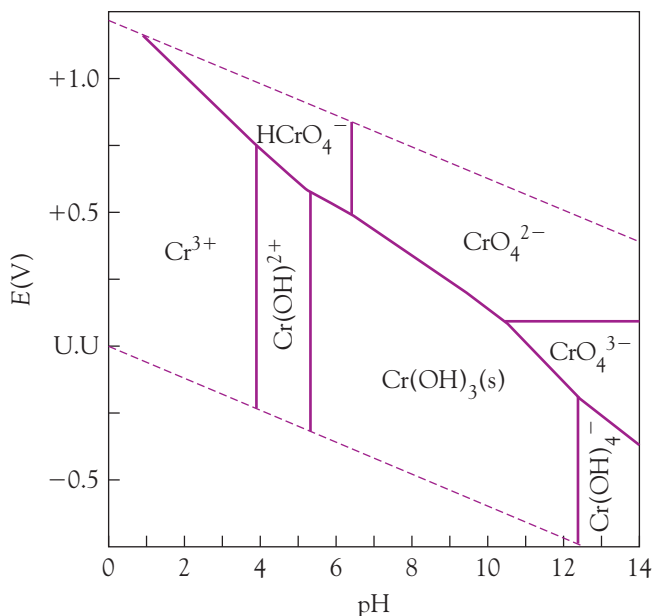


As soon as this solution is exposed to air, the vanadium(II) ion re-oxidizes first to the vanadium(III) ion and eventually to the vanadyl ion.

## 20.5 Group 6: Chromium

Chromium metal provides a shiny protective coating for iron and steel surfaces. Chromium metal is not inert in itself; instead, it has a very thin, tough, transparent oxide coating that confers the protection. The element is found mainly as the ore chromite,  $\text{FeCr}_2\text{O}_4$ ; 96 percent of the world's reserves are found in southern Africa. Although referred to as chromite, the structure is more accurately called iron(II) chromium(III) oxide,  $(\text{Fe}^{2+})(\text{Cr}^{3+})_2(\text{O}^{2-})_4$ . Less common is crocoite,  $\text{PbCrO}_4$ , lead(II) chromate.

As the Frost diagram in Figure 20.1 shows, chromium(III) is the most thermodynamically stable oxidation state, with chromium(VI) being highly oxidizing. The Pourbaix diagram for a  $1 \text{ mmol} \cdot \text{L}^{-1}$  chromium is shown in



**FIGURE 20.2** Pourbaix diagram for chromium species at  $1 \text{ mmol} \cdot \text{L}^{-1}$  showing their dependence on pH and  $E$ .

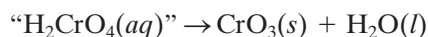
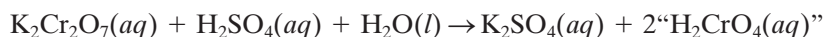
Figure 20.2, and it can be seen that the chromate and hydrogen chromate ions are only thermodynamically preferred under oxidizing conditions. Under highly basic conditions, the dark green chromate(V) ion,  $[\text{CrO}_4]^{3-}$ , can be formed. This oxidation state is involved in the reduction of chromium(VI) to chromium(III) under basic conditions and by bacteria.

### Chromium Oxides

For titanium, the only oxide of significance is titanium(IV) oxide,  $\text{TiO}_2$ , and for vanadium, vanadium(V) oxide,  $\text{V}_2\text{O}_5$ , both of which are high-melting-point ionic solids. Chromium has two oxides of importance, chromium(VI) oxide,  $\text{CrO}_3$ , and chromium(III) oxide,  $\text{Cr}_2\text{O}_3$ .

Chromium(VI) oxide is a red crystalline solid. With a low melting point and a high solubility in water, the bonding is best described as small-molecule covalent. It is an acidic oxide, as are most metal oxides in which the metal has a very high oxidation number, dissolving in water to form “chromic acid,” which is in fact a mixture of species. The strongly oxidizing (and acidic) nature of the solution results in its occasional use as a final resort for cleaning laboratory glassware. However, the hazard of the solution itself (it is carcinogenic and very acidic) and the potential danger from exothermic redox reactions with glassware contaminants make it a very unwise choice.

Preparation of this oxide can be accomplished by adding concentrated sulfuric acid to a cold concentrated solution of potassium dichromate. The synthesis can be viewed as an initial formation of chromic acid followed by a decomposition to the acidic oxide and water:



**TABLE 20.3** A comparison of the properties of chromium(VI) oxide and chromium(III) oxide

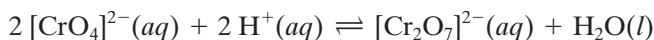
Oxide	Appearance	Melting point (°C)	Aqueous solubility	Acid-base properties	Bonding classification
CrO <sub>3</sub>	Red crystals	190	Soluble	Acidic	Small-molecule covalent
Cr <sub>2</sub> O <sub>3</sub>	Green powder	2450	Insoluble	Amphoteric	Ionic

The green, powdery compound, chromium(III) oxide, Cr<sub>2</sub>O<sub>3</sub>, is a high-melting-point, water-insoluble amphoteric oxide, as might be expected from the lower oxidation number of the metal. The properties of the two oxides are compared in Table 20.3.

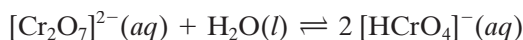
Just as lead(II) chromate (chrome yellow) is an important yellow pigment, so chromium(III) oxide is a common green pigment. It is chromium(III) oxide that has, since 1862, provided the pigment for the green U.S. currency (“greenbacks”). Because the pigment is a mineral rather than an organic dye, the green will not fade, nor is it affected by acids, bases, or either oxidizing or reducing agents.

### Chromates and Dichromates

Kinetically slow decomposition enables chromium(VI) ions to exist under conditions outside of the boundaries shown on the Pourbaix diagram. The most important of these are the chromates and dichromates. The yellow chromate ion, [CrO<sub>4</sub>]<sup>2−</sup>, can only exist in solution under neutral or alkaline conditions, and the orange dichromate ion, [Cr<sub>2</sub>O<sub>7</sub>]<sup>2−</sup>, only under acid conditions because of the equilibrium:

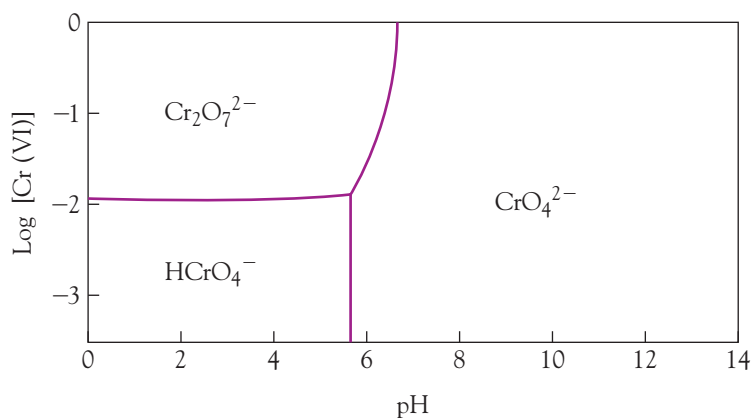


In dilute acidic solution, as Figure 20.3 shows, the dichromate hydrolyzes to form the hydrogen chromate ion, [HCrO<sub>4</sub>]<sup>−</sup>:



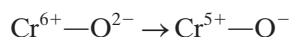
The Group 1 chromates are soluble, while those of Group 2 are insoluble. In fact, the solubility products of the Group 2 chromates are very close to those of

**FIGURE 20.3** Predominance diagram for chromium(VI) species showing their dependence on pH and chromium concentration.



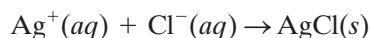
the equivalent sulfates (further evidence of the  $(n)$  and  $(n + 10)$  group linkage). However, transition metal chromates are insoluble (such as copper(II) chromate), whereas the analogous sulfates are soluble (such as copper(II) sulfate). If the cation is colorless, then the compound is usually yellow, such as lead(II) chromate,  $\text{PbCrO}_4$ . The insolubility of lead(II) chromate and its high refractive index (hence high opacity) have resulted in its use for yellow highway markings.

In both the chromate and the dichromate ions, chromium has an oxidation state of +6; hence, the metal has a  $d^0$  electron configuration. Without d electrons, we might expect these and all  $d^0$  configurations to be colorless. This is obviously not the case. The color comes from an electron transition from the ligand to the metal; a process known as *charge transfer* (see Chapter 19, Section 19.9). That is, an electron is excited from a filled ligand p orbital through a  $\pi$  interaction into the empty metal ion d orbitals. We can depict the process simply as:

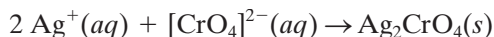


Such transitions require considerable energy; hence, the absorption is usually centered in the ultraviolet part of the spectrum, with just the edge of the absorption in the visible region. Charge transfer is particularly evident when the metal is in high-oxidation states, such as chromates and dichromates.

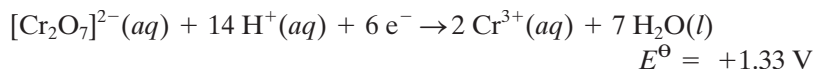
Silver(I) chromate,  $\text{Ag}_2\text{CrO}_4$ , has a brick red color, unlike any other metal ion apart from thallium(I) (see Chapter 9, Section 9.6). The color of the chromate makes it a useful compound in the analysis of silver ion. One route is a precipitation titration (the *Mohr method*), in which silver ion is added to chloride ion to give a white precipitate of silver chloride:



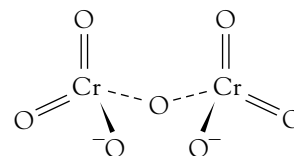
In the presence of chromate ion (usually about  $0.01 \text{ mol} \cdot \text{L}^{-1}$ ), the brick red, slightly more soluble silver chromate will form as soon as the chloride ion is completely consumed, the color change indicating that the equivalence point has been reached (actually, slightly exceeded):



The dichromate ion has a structure involving a bridging oxygen atom (Figure 20.4). This ion is a strong oxidizing agent, although the carcinogenic nature of the chromium(VI) ion means that it should be treated with respect, particularly the powdered solid, which can be absorbed through the lungs. The orange dichromate ion is a good oxidizing agent and is reduced to the green hexaaquachromium(III) ion,  $[\text{Cr}(\text{OH}_2)_6]^{3+}$ , in the redox reaction



The oxidation of organic compounds with dichromate ion is a common reaction in organic chemistry. Sodium dichromate is preferred because it has a higher solubility than potassium dichromate. This reaction is used in breath analyzers for the detection of excessive alcohol intake. The ethanol in the breath is bubbled through an acidic solution of dichromate, the color change



**FIGURE 20.4** The shape of the dichromate ion,  $[\text{Cr}_2\text{O}_7]^{2-}$ .

The toxicity of chromium(VI) is the central theme of the movie *Erin Brockovich*.



being detected quantitatively. In the reaction, the ethanol is oxidized to ethanoic (acetic) acid:



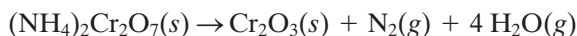
For quantitative analysis, sodium dichromate cannot be used as a primary standard because of its deliquescence. However, potassium dichromate is an ideal primary standard because it does not hydrate. Also, the potassium compound can be obtained in high purity by recrystallization as its solubility in water increases rapidly with increasing temperature. One application is the determination of iron(II) ion concentrations in an acidic solution. In this titrimetric procedure, the dichromate is reduced to chromium(III) ion and the iron(II) ion is oxidized to iron(III) ion:



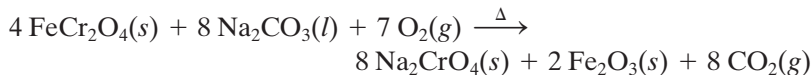
The characteristic color change of orange to green as the dichromate is reduced to the chromium(III) ion is not sensitive enough; thus, an indicator, barium diphenylamine sulfonate, has to be used. This indicator is less readily oxidized than iron(II) ions, but it is oxidized to give a blue color when all the iron(II) ions have been converted to the iron(III) state. Because free iron(III) ions affect the indicator and thus give rise to an inaccurate endpoint, some phosphoric acid is added before starting the titration. This reagent gives a stable iron(III) phosphate complex.



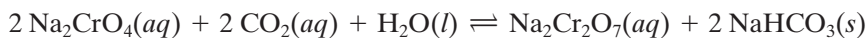
Ammonium dichromate,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , is often used in “volcano” demonstrations. If a red-hot wire or a lit match is touched to a pile of ammonium dichromate, exothermic decomposition is initiated, emitting sparks and water vapor in a spectacular way. However, this is not a safe demonstration because a dust containing carcinogenic chromium(VI) compounds is usually released. The reaction is nonstoichiometric, producing chromium(III) oxide, water vapor, nitrogen gas, and some ammonia gas. It is commonly represented as:



The industrial production of dichromate provides some interesting chemistry. The starting material is chromite,  $\text{FeCr}_2\text{O}_4$ . The powdered ore is heated to about  $1000^\circ\text{C}$  with sodium carbonate in air, thereby causing the chromium(III) to be oxidized to chromium(VI):



Addition of water dissolves the sodium chromate, a process called *leaching*; it leaves the insoluble iron(III) oxide. To obtain sodium dichromate, the Le Châtelier principle is applied. The following equilibrium lies to the left under normal conditions, but under high pressures of carbon dioxide (obtained from the previous reaction), the yield of sodium dichromate is high:

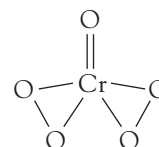
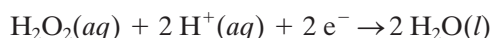


In fact, the aqueous carbon dioxide is really employed as a low-cost way of decreasing the pH to favor the dichromate ion in the chromate-dichromate



equilibrium. It can be seen that the mole ratio of carbon dioxide to chromate produced in the previous step is exactly the same as that employed in this step. The slightly soluble sodium hydrogen carbonate has to be filtered off under pressure to prevent the equilibrium from shifting to the left. The sodium hydrogen carbonate is then reacted with an equimolar proportion of sodium hydroxide to obtain the sodium carbonate that can be reused in the first step. Thus, the ore and sodium hydroxide are the only bulk chemicals used in the process.

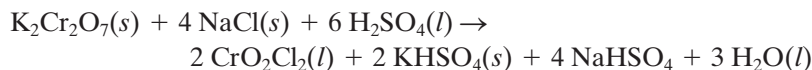
A common test for dichromate is the addition of hydrogen peroxide. The peroxo species extracts into ethoxyethane (diethyl ether) to give a characteristic intense blue color, believed to contain the  $\text{CrO}_5$  molecule, which actually contains one doubly bonded oxygen atom and two chelating peroxo units,  $\text{CrO}(\text{O}_2)_2$ , chromium(VI) oxide peroxide (Figure 20.5):



**FIGURE 20.5** The shape of the  $\text{CrO}_5$  molecule.

### Chromyl Chloride

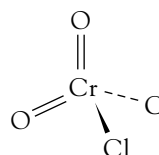
Chromyl chloride, a red, oily liquid of formula  $\text{CrO}_2\text{Cl}_2$ , has a tetrahedral arrangement around the central chromium atom, with appreciable double bond character in the  $\text{Cr}-\text{O}$  bonds (Figure 20.6). The compound is of interest only as a definitive means of identifying chloride ion if a halide ion is known to be present. When concentrated sulfuric acid is added to a mixture of solid orange potassium dichromate and an ionic chloride, such as white sodium chloride, the mixture turns dark as a result of the formation of chromyl chloride:



When heated gently and very cautiously, the chromyl chloride vaporizes to give a deep red, toxic gas. This gas can be collected and condensed as the pure dark red covalent liquid. If this liquid is added to a basic solution, it immediately hydrolyzes to the yellow chromate ion:



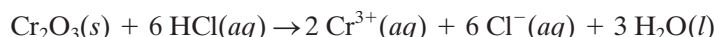
Because bromides and iodides do not form analogous chromyl compounds, this test is specific for chloride ions.



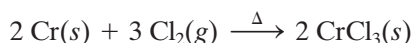
**FIGURE 20.6** The shape of the chromyl chloride molecule,  $\text{CrO}_2\text{Cl}_2$ .

### Chromium(III) Chloride

Chromium(III) chloride can be prepared by reacting chromium(III) oxide with hydrochloric acid and then evaporating the solution until deep green  $[\text{Cr}(\text{OH})_4\text{Cl}_2]^+(\text{Cl}^-) \cdot 2\text{H}_2\text{O}$  crystallizes:



Anhydrous chromium(III) chloride,  $\text{CrCl}_3$ , is a reddish violet solid obtained when chlorine is passed over strongly heated chromium metal:





**WORKED EXAMPLE 20.1**

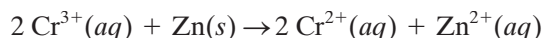
There are three hydration isomers of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ : dark green  $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ , light green,  $[\text{Cr}(\text{OH}_2)_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  and violet,  $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$ . How could you distinguish between the three isomers?

**Answer**

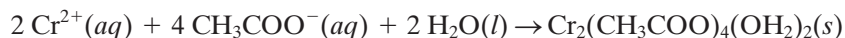
The three isomers will release varying amounts for free chloride ions when dissolved in water. Their solutions will precipitate 1-, 2-, and 3-mole equivalents of silver chloride, respectively, on addition of silver nitrate solution. If  $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  and  $[\text{Cr}(\text{OH}_2)_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  are heated gently, they will lose 2- and 1-mole equivalents of water, respectively, which could be determined by the change in mass. ■

**Chromium(II) Acetate**

Although chromium(II) is an abnormally low-oxidation state for this element, there is one compound that is easy to synthesize—chromium(II) acetate. This insoluble red compound is prepared by reducing chromium(III) ion with zinc metal:

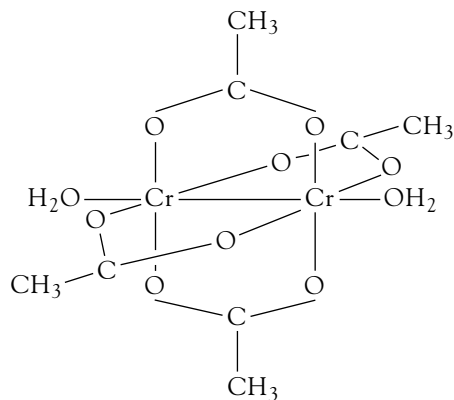


then adding acetate ion:



Acetates are generally soluble; in fact, they form the most soluble compounds except for nitrate. Thus, the insolubility of the compound is an indication that the product is not a simple compound. And indeed, it is not. The complex is a dimer with the four acetate ligands acting as  $-\text{O}-\text{C}-\text{O}-$  bridges between the two chromium(II) ions, which are directly linked by a chromium-chromium bond. The two water molecules occupy the sixth coordination sites on the ends of the molecule (Figure 20.7).

**FIGURE 20.7** The shape of the chromium(II) acetate dimer complex.



## 20.6 Group 7: Manganese

Manganese is the third most abundant transition metal after iron and titanium. Unlike chromium, it is found mainly as a silicate mineral, braunite,  $\text{Mn}_7\text{SiO}_{12}$ , containing both manganese(II) and manganese(III). The structure can be best understood by writing it in mineralogical form:  $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ . Manganese is important as an additive in specific types of steel.

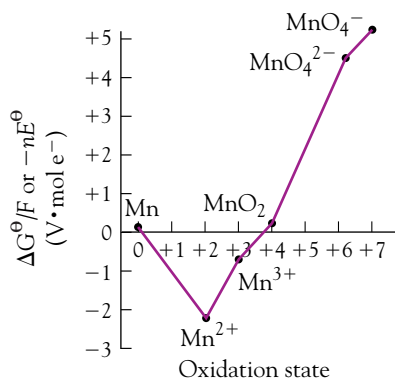
### Oxidation States of Manganese

Manganese readily forms compounds over a range of oxidation states that is wider than that of any other common metal. Figure 20.8 shows the relative stabilities for the oxidation states of manganese in acid solution.

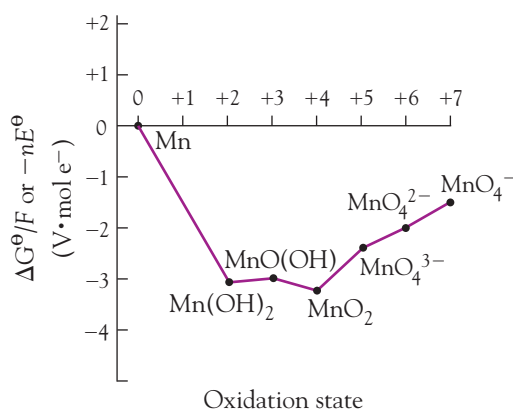
From this diagram, we can see that the permanganate ion,  $[\text{MnO}_4]^-$ , also called *tetraoxidomanganate(VII)*, is very strongly oxidizing in acid solution. The deep green manganate ion,  $[\text{MnO}_4]^{2-}$ , known also as *tetraoxidomanganate(VI)*, is strongly oxidizing as well, but it disproportionates readily to the permanganate ion and manganese(IV) oxide. Manganese(IV) oxide is oxidizing with respect to the most stable manganese species, the manganese(II) ion. In acid solution, the manganese(III) ion disproportionates. Finally, the metal itself is reducing. However, in basic solution, we find a different situation, as can be seen in Figure 20.9.

The differences between acidic and basic conditions can be summarized as follows:

1. For a particular oxidation state, many of the compounds are unique. Manganese, like most metals, at high pH forms insoluble hydroxides (and oxide hydroxides) in which the metal has low oxidation states.
2. The higher oxidation states are not strongly oxidizing, as they are in acid solution. This difference can be explained simply in terms of reductions that involve hydrogen ion concentration, for these reactions will be strongly pH dependent. In the Frost diagram for acid solution, the concentration of



**FIGURE 20.8** Frost (oxidation state) diagram for manganese in acidic solution.



**FIGURE 20.9** Frost (oxidation state) diagram for manganese in basic solution.

hydrogen ion is  $1 \text{ mol} \cdot \text{L}^{-1}$ ; in the diagram for basic solution, the hydrogen ion concentration is  $10^{-14} \text{ mol} \cdot \text{L}^{-1}$  (that is,  $1 \text{ mol} \cdot \text{L}^{-1}$  concentration of hydroxide ion). Using the Nernst equation, we can show that this change in ion concentration will have a major effect on the standard reduction potential.

3. Oxidation states that are very unstable in acid can exist in basic solution (and vice versa). Thus, the deep green manganate ion  $[\text{MnO}_4]^{2-}$  (more correctly, the tetraoxidomanganate(VI) ion) and the bright blue manganite ion,  $[\text{MnO}_4]^{3-}$  (more correctly, the tetraoxidomanganate(V) ion), can be formed in basic solution.

4. In basic solution, the most thermodynamically stable species is manganese(IV) oxide, although the manganese(III) oxide hydroxide,  $\text{MnO}(\text{OH})$ , and manganese(II) hydroxide also are both moderately stable. In fact, above pH 14, manganese(III) oxide hydroxide is thermodynamically more stable than manganese(II) hydroxide.

## Manganese Oxides

Manganese has the widest range of oxides of all the 3d transition metals, including  $\text{Mn}_2\text{O}_7$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{MnO}$ . These range in properties from the acidic manganese(VII) oxide,  $\text{Mn}_2\text{O}_7$ , to the basic manganese(II) oxide,  $\text{MnO}$ . The three of particular interest are manganese(VII) oxide,  $\text{Mn}_2\text{O}_7$ ; manganese(IV) oxide,  $\text{MnO}_2$ ; and manganese(II) manganese(III) oxide,  $\text{Mn}_3\text{O}_4$ .

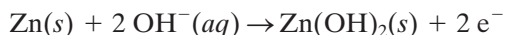
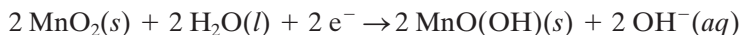
Manganese(VII) oxide is a greenish brown liquid at room temperature. Like chromium(VI) oxide, it is strongly oxidizing and its bonding is best described as small-molecule covalent. The oxide decomposes explosively to the more stable manganese(IV) oxide:



Manganese(IV) oxide is a gray-black insoluble solid and is considered to have an essentially ionic structure. It is the only common compound of manganese in the +4 oxidation state. (In Chapter 9, Section 9.5, we noted the parallel between manganese(IV) oxide and chlorine dioxide.) The compound is a strong oxidizing agent: it releases chlorine from concentrated hydrochloric acid and is, at the same time, reduced to manganese(II) chloride:



This oxide is a key component of the common alkaline battery. The cell consists of a zinc case (the anode) with a central rod as cathode. This rod consists of a compressed mixture of graphite (a good electrical conductor) and manganese(IV) oxide. The electrolyte is a potassium hydroxide solution. In the cell reaction, the manganese(IV) oxide is reduced to the manganese(III) oxide hydroxide  $\text{MnO}(\text{OH})$ , while the zinc is oxidized to zinc hydroxide:



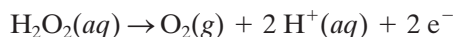
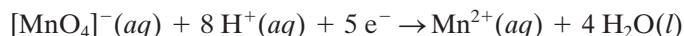
In the overall process, 2 moles of hydroxide ion are consumed at the anode and 2 moles of hydroxide ion are produced at the cathode. As a result of the constancy of hydroxide ion concentration, the cell potential remains constant, a useful advantage over the old “dry cell,” in which the deliverable voltage drops over the lifetime of the battery.

Manganese(II) manganese(III) oxide,  $\text{Mn}_3\text{O}_4$ , is a red-brown solid of interest because of its formula. In the crystal, there are both  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  ions; thus, the structure is best represented as  $(\text{Mn}^{2+})(\text{Mn}^{3+})_2(\text{O}^{2-})_4$ . We previously mentioned these two oxides,  $\text{Mn}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ , in the context of the spinel structures (see Chapter 5, Section 5.7). Crystal field theory can be used to account for the fact that the manganese compound adopts the spinel structure, while the iron compound adopts the inverse spinel packing.

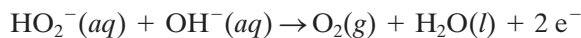
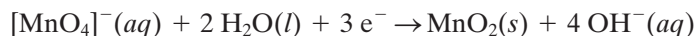
### Permanganates

Potassium permanganate,  $\text{KMnO}_4$ , a violet-black solid, is the best-known manganese compound, with a manganese oxidation number of +7. Like chromium(VI) compounds, the color in this  $d^0$  ion is derived from charge transfer electron transitions. Dissolving potassium permanganate in water gives a deep purple solution, characteristic of the permanganate ion.

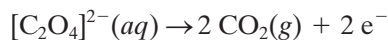
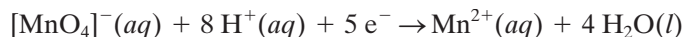
The permanganate ion is an extremely powerful oxidizing agent, and under acid conditions, it is reduced to the colorless manganese(II) ion. For example, with hydrogen peroxide, the two half-reactions are:



In base, brown solid manganese(IV) oxide is formed (oxidations in organic chemistry often employ permanganate in basic solution):



Potassium permanganate is an important reagent in redox titrations. Unlike potassium dichromate, it is not a suitable primary standard because its purity cannot be guaranteed. Samples of the substance contain some manganese(IV) oxide, and aqueous solutions slowly deposit brown manganese(IV) oxide on standing. Its precise concentration is determined by titration against a standard solution of oxalic acid. Potassium permanganate solution is run into the oxalic acid solution from a burette, and the purple color disappears as the (almost) colorless manganese(II) ions and carbon dioxide are formed. The permanganate acts as its own indicator, for the slightest excess of permanganate gives a pink tint to the solution:



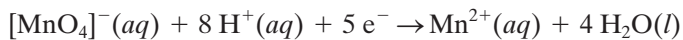
This particular reaction has a high activation energy. To provide a reasonable reaction rate, the oxalate solution is initially warmed. However, once some



VIDEO CLIP

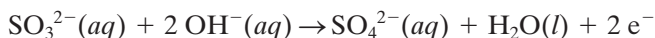
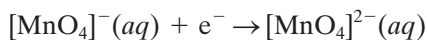
manganese(II) ion is produced, it acts as its own catalyst, and the reaction occurs more quickly as the titration proceeds.

A standardized solution of potassium permanganate can be used for the quantitative determination of iron in samples such as mineral ores or food-stuffs. The iron is converted to iron(II) ion, which is then titrated with standardized permanganate ion solution, again using the permanganate ion as reagent and indicator:



### The Manganate Ion

With a weak reducing agent, such as the sulfite ion, in basic solution, the permanganate ion is reduced to the green manganate (tetraoxidomanganate(VI)) ion:



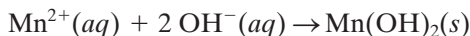
Like the isoelectronic tetraoxidochromate(V) ion,  $[\text{CrO}_4]^{3-}$  (see Section 20.5), the tetraoxidomanganate(VI) ion is only stable in the solid phase or in extremely basic conditions. For example, when potassium manganate is dissolved in water, it disproportionates, as predicted by the Frost diagram:



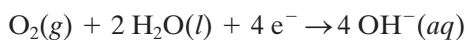
### Manganese(II) Compounds

Under acid conditions, the most thermodynamically stable oxidation number of manganese is +2. Manganese in this oxidation state exists as a very pale pink ion,  $[\text{Mn}(\text{OH}_2)_6]^{2+}$ , a species present in all the common salts of manganese, such as nitrate, chloride, and sulfate. The very pale color of this ion contrasts with the strong colors of most other transition metal ions. As was discussed in Chapter 19, Section 19.9, for high-spin  $d^5$  configurations, only low-probability spin-forbidden transitions are possible, resulting in near-white solids and close to colorless solutions.

When base is added to a solution containing manganese(II) ion, the white manganese(II) hydroxide is formed:



However, the manganese(III) state is favored under basic conditions, and the manganese(II) hydroxide oxidizes in the air to a brown hydrated manganese(III) oxide,  $\text{MnO}(\text{OH})$ :



One of the few oxidizing agents even more powerful than permanganate is the bismuthate ion,  $[\text{BiO}_3]^{-}$ . A test for manganese(II) ion is the addition of

## Mining the Seafloor

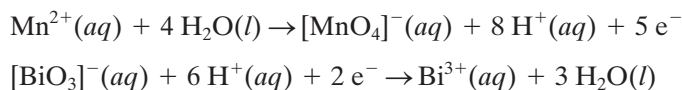
We usually think of minerals as coming from mines bored into Earth's crust, yet there is increasing interest in mining ore deposits from the seafloor. In 1873, the *Challenger* expedition to the Pacific Ocean first dredged up mineral nodules from the bottom of the sea. We now know that nodules are widespread over the ocean floors. Generally, manganese and iron each make up between 15 and 20 percent of the content of these nodules; smaller concentrations of titanium, nickel, copper, and cobalt are also present. However, the composition varies from site-to-site, with some nodule beds containing up to 35 percent manganese.

The question of how such nodules formed puzzled chemists for a long time. It was the Swedish chemist I. G. Sillén who proposed that the oceans be considered as a giant chemical reaction vessel. As the metal ions accumulate in the seas from land runoff and undersea volcanic vents, the products of their reactions with anions in the

seawater exceed the solubility product. The compounds then start to crystallize out very slowly over thousands and perhaps millions of years in the form of these nodules.

Because the nodules are such concentrated ores, there is much interest in using them for their metal content, particularly by the United States, which has to import much of the manganese, cobalt, and nickel it uses. A number of mining techniques are being developed to remove up to 200 tonnes of nodules per hour. However, there are two concerns: the first of which relates to the life on the seafloor—such large-scale excavations could have a major effect on bottom ecosystems. Furthermore, there is the question of ownership. Should the nodules be the property of whichever company and/or country can mine them first, or, being in international waters, should they be the collective property of the world? Both of these issues need to be discussed and solved in the very near future.

sodium bismuthate to a sample under cold, acidic conditions. The purple permanganate ion is produced, thereby indicating the presence of manganese:



### WORKED EXAMPLE 20.2

From the Frost diagrams, predict which manganese species will disproportionate in (a) acidic solution and (b) in basic solution.

#### Answer

A species that lies above a line connecting the two adjacent species will disproportionate into those species.

(a) In acidic solution,  $\text{MnO}_4^{2-}$  will disproportionate into  $\text{MnO}_4^{-}$  and  $\text{MnO}_2$ , while  $\text{Mn}^{3+}$  will disproportionate into  $\text{MnO}_2$  and  $\text{Mn}^{2+}$ .

(b) In basic solution,  $\text{MnO}_4^{3-}$  will disproportionate into  $\text{MnO}_4^{2-}$  and  $\text{MnO}_2$ , while  $\text{MnO}(\text{OH})$  will disproportionate into  $\text{MnO}_2$  and  $\text{Mn}(\text{OH})_2$ . ■

## 20.7 The Iron-Cobalt-Nickel-Copper Tetrad

Whereas vanadium, chromium, and manganese all have stable oxoanions of  $d^0$  configuration, the aqueous chemistry of the next four 3d transition metals, the *Fe-Co-Ni-Cu tetrad*, is dominated by their chemistry in the +2 oxidation

**TABLE 20.4** The pH dependence of +2 oxidation-state species for iron, cobalt, nickel, and copper

	Very acidic	Acidic	Basic	Very basic
Iron	$\text{Fe}^{2+}(aq)$		$\text{Fe}(\text{OH})_2(s)$	
Cobalt	$\text{Co}^{2+}(aq)$		$\text{Co}(\text{OH})_2(s)$	$\text{Co}(\text{OH})_4^{2-}(aq)$
Nickel	$\text{Ni}^{2+}(aq)$		$\text{Ni}(\text{OH})_2(s)$	
Copper	$\text{Cu}^{2+}(aq)$		$\text{Cu}(\text{OH})_2(s)$	$\text{Cu}(\text{OH})_4^{2-}(aq)$

state. The first three members of the tetrad are the most similar; have similarities in their chemistry; for example, the metals are all ferromagnetic. Each of the +2 tetrad metal ions form hexaaqua ions,  $[\text{M}(\text{OH}_2)_6]^{2+}$ , which in basic solution precipitate out as gelatinous hydroxides (see Table 20.4). Under very basic conditions, the tetrahydroxido-complex is formed for cobalt(II) and copper(II) ions.

In addition to the +2 oxidation state, the +3 oxidation state is common for iron, less common for cobalt, and very rare for nickel and copper.

## 20.8 Group 8: Iron

Iron is the most important material in our civilization. It does not hold this place because it is the “best” metal; after all, it corrodes much more easily than many other metals. Its overwhelming dominance in our society comes from a variety of factors:

1. Iron is the second most abundant metal in the Earth’s crust, and concentrated deposits of iron ore are found in many localities, thus making it easy to mine.
2. The common ore can be easily and cheaply processed thermochemically to obtain the metal.
3. The metal is malleable and ductile, whereas many other metals are relatively brittle.
4. The melting point ( $1535^\circ\text{C}$ ) is low enough that the liquid phase can be handled without great difficulty.
5. By the addition of small quantities of other elements, alloys that have exactly the required combinations of strength, hardness, or ductility for very specific uses can be formed.

The relatively easy oxidation of iron is a major disadvantage—consider all the rusting automobiles, bridges, and other iron and steel structures, appliances, tools, and toys. At the same time, it does mean that our discarded metal objects will crumble to rust rather than remain an environmental blight forever.

## Iron Oxides

There are three common oxides of iron: iron(II) oxide,  $\text{FeO}$ ; iron(III) oxide,  $\text{Fe}_2\text{O}_3$ ; and iron(II) iron(III) oxide,  $\text{Fe}_3\text{O}_4$ . Black iron(II) oxide is actually a nonstoichiometric compound, always being slightly deficient in iron(II) ions, as discussed in Chapter 5, Section 5.8.

Iron(III) oxide, or hematite, is found in large underground deposits. The oldest beds of iron(III) oxide have been dated at about 2 billion years old. Because iron(III) oxide can only form in an oxidizing atmosphere, our current dioxygen-rich atmosphere must have commenced at that time. The appearance of dioxygen, in turn, indicates that photosynthesis (and life itself) became widespread about 2 billion years ago. The oxide can be made in the laboratory by heating the iron(III) oxide hydroxide, which can be generated by adding hydroxide ion to iron(III) ion. The product formed by this route,  $\alpha\text{-Fe}_2\text{O}_3$ , consists of a hexagonal close-packed array of oxide ions with the iron(III) ions in two-thirds of the octahedral holes. A different structural form,  $\gamma\text{-Fe}_2\text{O}_3$ , is produced by oxidizing iron(II) iron(III) oxide. In this form, the iron(III) oxide has a cubic close-packed array of oxide ions with the iron(III) ions distributed randomly among the tetrahedral and octahedral holes.

The third common oxide of iron contains iron in both the +2 and +3 oxidation states, and we have mentioned this compound,  $(\text{Fe}^{2+})(\text{Fe}^{3+})_2(\text{O}^{2-})_4$ , previously in the context of normal and inverse spinels (see Chapter 19, Section 19.8). This compound is found naturally as magnetite or lodestone, and a piece of this magnetic compound, suspended by a thread so that it would turn, was used as a primitive compass. Nature, as is often the case, beat us to that discovery. To enable them to navigate using the Earth's magnetic field, *magnetotactic* bacteria contain crystals of magnetite or, in sulfur-rich environments, the sulfur equivalent greigite,  $\text{Fe}_3\text{S}_4$ .

The iron oxides are in great demand as paint pigments. Historically, colors such as yellow ochre, Persian red, and umber (brown) were obtained from iron ore deposits containing certain particle sizes of iron oxides, often with consistent levels of specific impurities. Most yellow, red, and black paints are still made from iron oxides, but they are industrially synthesized to give precise compositions and particle sizes to ensure the production of consistent colors.

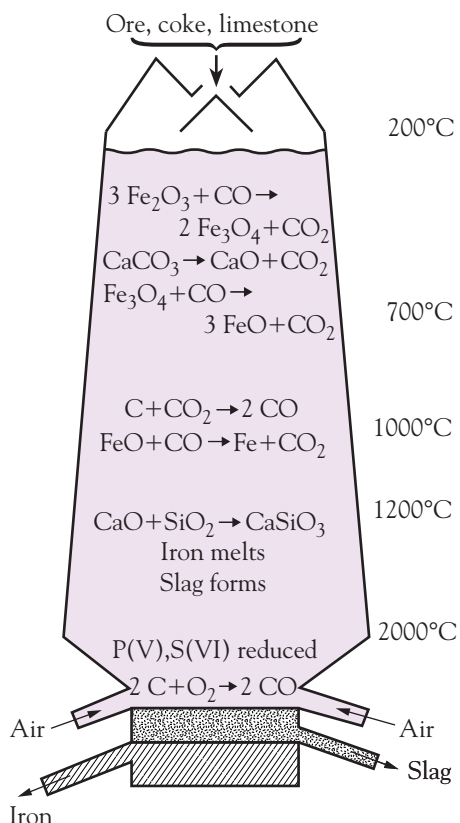
## Production of Iron

The most common sources of iron are the two oxides,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ , together with a hydrated iron(III) oxide hydroxide, best represented as  $\text{Fe}_2\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  (limonite). The conventional extraction of iron is carried out in a *blast furnace* (Figure 20.10), which can be between 25 and 60 m in height and up to 14 m in diameter.

The furnace itself is constructed of steel and has a lining of a heat- and corrosion-resistant material. Formerly, brick was used for the lining, but now it is made of highly specialized ceramic materials. In fact, half of the high-temperature ceramics used today are produced for iron and steel smelter linings. The main ceramic material used for the lining is aluminum oxide (commonly called

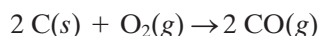


**FIGURE 20.10** A blast furnace. [D. Shriver and P. Atkins, *Inorganic Chemistry*, 3rd. ed. (New York: W. H. Freeman and Co., 1998), p. 182.]



*corundum*), although the lining of the lower parts of the furnace consists of ceramic oxides of formula  $\text{Al}_x\text{Cr}_{(2-x)}\text{O}_3$ . In these oxides, the chromium (III) ion has replaced some of the aluminum ions. These mixed-metal oxide ceramics are more chemical- and temperature-resistant than the pure oxide ceramics.

A mixture of iron ore, limestone, and coke in the correct proportions is fed into the top of the blast furnace through a cone and hopper arrangement to prevent escape of the gases. Air, preheated to 600°C by combustion of the exhaust gases, is injected into the lower part of the furnace. The gases move up the furnace, while the solids descend as the products are drawn off from the bottom. The heat is generated by the reaction of the dioxygen in the air with the carbon (coke):



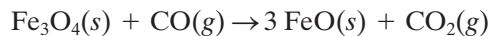
It is the hot carbon monoxide (initially at about 2000°C) that is the reducing agent for the iron ore.

At the top of the furnace, the temperature ranges from 200 to 700°C; a temperature sufficient to reduce iron(III) oxide to iron(II) iron(III) oxide,  $\text{Fe}_3\text{O}_4$ :

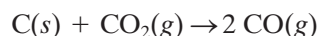
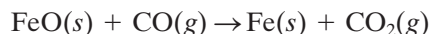


Farther down in the furnace, where the temperature is about 850°C, the iron(II) iron(III) oxide is reduced to iron(II) oxide, and the temperature is high enough

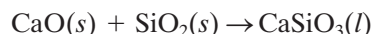
also to decompose the calcium carbonate (limestone) to calcium oxide and carbon dioxide:



As the mixture descends into the hotter regions (between 850 and 1200°C), the iron(II) oxide is reduced to iron metal and the carbon dioxide formed is re-reduced to carbon monoxide by the coke:

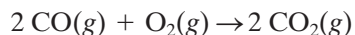


Lower still, at temperatures between 1200 and 1500°C, the iron melts and sinks to the bottom of the furnace, and the calcium oxide reacts with the silicon dioxide (and other impurities, such as phosphorus compounds) in the iron ore to give calcium silicate, commonly called *slag*. This is a high-temperature acid-base reaction between the basic metallic oxide, CaO, and the acidic nonmetal oxide, SiO<sub>2</sub>:



The blast furnace is provided with two tapholes that are plugged with clay, the lower one for the denser iron metal and the upper one for the less dense slag. These plugs are periodically removed, releasing a stream of molten iron through the lower taphole and liquid slag through the upper. Blast furnaces are run 24 hours a day, and depending on its size, a furnace can produce from 1000 to 10 000 tonnes of iron every 24 hours.

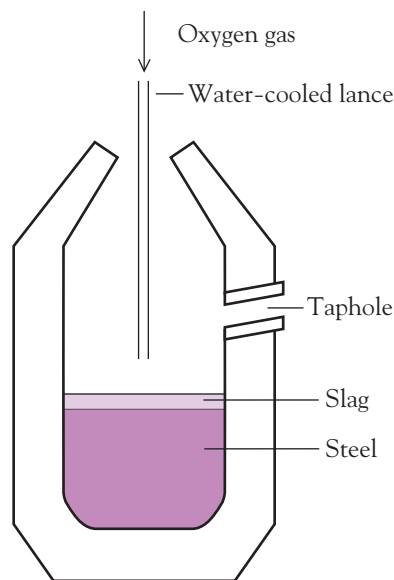
The molten metal is usually conveyed directly in the liquid form to steel-making plants. The slag can be either cooled to the solid phase, ground, and used in concrete manufacture or, while liquid, mixed with air and cooled into a “woolly” material that can be used for thermal insulation. The hot gases emerging from the top of the furnace contain appreciable amounts of carbon monoxide, and these are burned to preheat the air for the furnace:



The iron produced contains a wide range of impurities, such as silicon, sulfur, phosphorus, carbon, and oxygen. The carbon content, which can be as high as 4.5 percent, is a particular contributor to the brittleness of the material. Iron is rarely used in pure form; more commonly, carefully controlled levels of impurities are needed to provide exactly the properties required. One method for controlling content is the *basic oxygen process*. A schematic diagram of a typical furnace is shown in Figure 20.11.

Unlike the blast furnace, this process is not continuous. The converter is filled with about 60 tonnes of molten iron. A blast of oxygen diluted with carbon dioxide is blown through the converter. Oxygen is used instead of air because the nitrogen in air would react with the iron at these temperatures to form a brittle metal nitride. Oxygen reacts with the impurities and raises the temperature in the furnace to about 1900°C, and the diluent carbon dioxide

**FIGURE 20.11** A furnace used for the basic oxygen process.



prevents the temperature from increasing excessively. In addition, cold scrap metal is usually added to keep the temperature down.

In the basic oxygen process, carbon is oxidized to carbon monoxide, which burns at the top of the converter to carbon dioxide. The silicon, an impurity, is oxidized to silicon dioxide, which then reacts with the oxides of other elements to form a slag. The furnace also is lined with limestone (calcium carbonate), which reacts with acidic phosphorus-containing impurities. After several minutes, the flame at the top of the converter sinks, indicating that all the carbon has been removed. The slag is poured off, and any required trace elements are added to the molten iron.

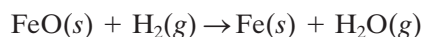
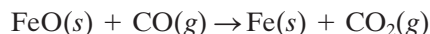
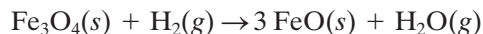
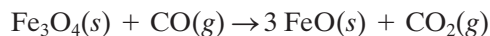
For normal steel, between 0.1 and 1.5 percent carbon is required. The carbon reacts with the iron to form iron carbide,  $\text{Fe}_3\text{C}$ , commonly called *cementite*. Cementite, as its name implies, forms small crystals between the crystals of iron. As a result, the ductility of the iron is reduced and the hardness increased. To remove trapped oxygen from the iron, argon is blown through the liquid metal. About  $3 \text{ m}^3$  of argon are used per tonne of iron. The properties of iron can be altered to suit our needs by adding controlled proportions of other elements. Examples of various iron alloys are given in Table 20.5.

**TABLE 20.5** Important alloys of iron

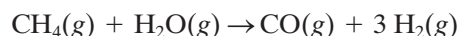
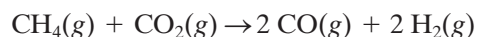
Name	Approximate composition	Properties and uses
Stainless steel	73% Fe, 18% Cr, 8% Ni	Corrosion resistant (tableware, cookware)
Tungsten steel	94% Fe, 5% W	Hard (high-speed cutting tools)
Manganese steel	86% Fe, 13% Mn	Tough (rock drill bits)
Permalloy	78% Ni, 21% Fe	Magnetic (electromagnets)

### Direct Reduction Iron (DRI)

An increasing proportion of iron is produced by direct reduction from the ore in the solid phase. For this method, high-purity iron ore must be used. Carbon monoxide and hydrogen, the reductants, are passed over heated iron ore. The iron(II) iron(III) oxide undergoes stepwise reduction:



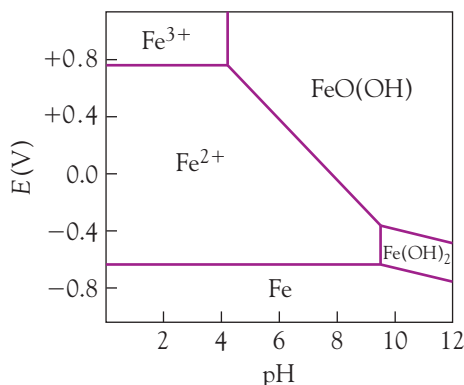
The reducing gases are obtained by re-forming methane with carbon dioxide and water. Thus, the economics of the process depend on the price of cheap natural gas. In fact, this process can use poor-quality methane; that is, methane deposits that contain high proportions of nonflammable gases. These deposits are unsuitable for most other commercial uses.



The advantage of DRI is that iron can be produced without the need for a massive expensive smelting operation; its primary disadvantage is that the product contains most element impurities from the natural ore. In developed countries, the major use of DRI is as a “sweetener,” or diluent, in steel recycling. Scrap steel often contains unacceptable levels of metals such as copper, nickel, chromium, and molybdenum. DRI is low in these metals; thus, mixing in a proportion of DRI results in an acceptable composition for electric arc steel manufacture. In developing countries, particularly, DRI provides an economical source of iron and steel.

### Chemistry of Iron

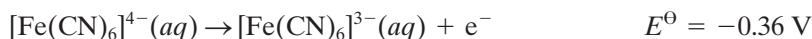
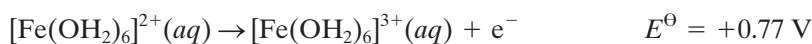
The Pourbaix diagram for iron is shown in Figure 20.12. For simplicity, the aqueous cations are simply shown as  $\text{Fe}^{3+}(aq)$  and  $\text{Fe}^{2+}(aq)$ , respectively, although, as we will see, there is a whole range of different hydrated iron(III)



**FIGURE 20.12** Simplified Pourbaix diagram for iron species.

ions that depend on the pH. The iron(III) ion is only thermodynamically preferred under oxidizing conditions (very positive  $E$ ) and low pH. The iron(III) oxide hydroxide (commonly called *rust*), however, predominates over much of the basic range. It is the iron(II) ion that is preferred over most of the  $E$  range and under acid conditions, whereas the iron(II) hydroxide,  $\text{Fe}(\text{OH})_2$ , is only stable at high pH and strongly reducing conditions (very negative  $E$ ).

The actual oxidation potential of iron(II) to iron(III) is very dependent on the ligands. For example, the hexacyanidoferrate(II) ion,  $[\text{Fe}(\text{CN})_6]^{4-}$ , is less hard to oxidize than the hexaaquairon(II) ion,  $[\text{Fe}(\text{OH}_2)_6]^{2+}$ :



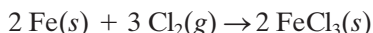
This might seem surprising, considering that cyanide ion generally stabilizes low-oxidation states, not high ones, and that, in fact, the iron-carbon bond is stronger in the iron(II) ion than in the iron(III) ion. But there is a thermodynamic aspect to the cyanide equilibrium: the aqueous  $[\text{Fe}(\text{CN})_6]^{4-}$  is of such high charge density that there is a strongly organized sphere of water molecules around it. Such an ion has a very negative entropy of hydration, but oxidation decreases the charge density, thereby reducing the organization of the hydration sphere and increasing the entropy. The oxidation, then, is entropy driven.

## Iron(VI) Compounds

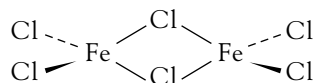
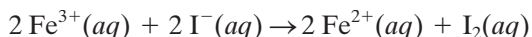
Beyond manganese, the 3d transition metals do not form compounds in which they have a  $d^0$  electron configuration. In fact, a compound with a metal in an oxidation state higher than +3 is very difficult to prepare, and such compounds are only stable in the solid phase. The tetraoxido ferrate(VI) ion,  $[\text{FeO}_4]^{2-}$ , in which the  $d^2$  iron has an oxidation number of +6, is one of these rare compounds. This purple tetrahedral ion can be prepared in highly basic oxidizing conditions and then stabilized by forming an insoluble ionic compound such as the red-purple solid barium tetraoxido ferrate(VI),  $\text{BaFeO}_4$ . (The method of synthesis was described in Chapter 19, Section 19.11.)

## Iron(III) Compounds

The iron(III) ion itself is small and sufficiently polarizing that its anhydrous compounds exhibit covalent character. For example, iron(III) chloride is a red-black, covalent solid with a network covalent structure. When heated to the gas phase, it exists as the dimeric species  $\text{Fe}_2\text{Cl}_6$ , shown in Figure 20.13. Iron(III) chloride can be made by heating iron in the presence of dichlorine:

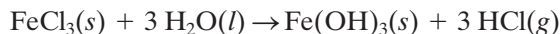


The bromide is similar to the chloride, but the iodide cannot be isolated because the iodide ion reduces iron(III) to iron(II):



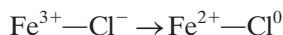
**FIGURE 20.13** The shape of the diiron hexachloride molecule,  $\text{Fe}_2\text{Cl}_6$ .

Anhydrous iron(III) chloride reacts exothermically with water, producing hydrogen chloride gas:

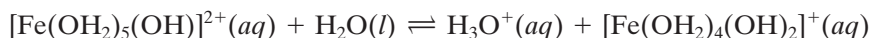


This reaction contrasts with that of the golden yellow, ionic, hydrated salt,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , which simply dissolves in water to give the hexahydrate ion in solution. The properties are similar to those of aluminum chloride, and there are many parallels between aluminum and iron(III), as discussed below.

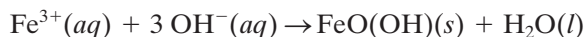
The hexaaquairon(III) ion,  $[\text{Fe}(\text{OH}_2)_6]^{3+}$ , is very pale purple, a color that can be seen in the solid iron(III) nitrate nonahydrate. Like the manganese(II) ion, the iron(III) ion is a high-spin  $d^5$  species. Lacking any spin-allowed electron transitions, its color is very pale relative to that of other transition metal ions. The yellow color of the chloride compound is due to the presence of ions such as  $[\text{Fe}(\text{OH}_2)_5\text{Cl}]^{2+}$  in which a charge transfer transition can occur:



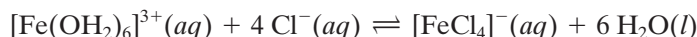
All the iron(III) salts dissolve in water to give an acidic solution, a characteristic of high-charge-density, hydrated cations. In such circumstances, the coordinated water molecules become sufficiently polarized that other water molecules can function as bases and abstract protons. The iron(III) ion behaves as follows:



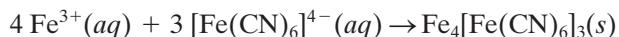
and so on. The equilibria are pH dependent; thus, addition of hydronium ion will give the almost colorless hexaaquairon(III) ion. Conversely, addition of hydroxide ion gives an increasingly yellow solution, followed by precipitation of a rust-colored gelatinous (jelly-like) precipitate of iron(III) oxide hydroxide,  $\text{FeO}(\text{OH})$ :



Although iron(III) species usually adopt an octahedral stereochemistry, the yellow tetrachloridoferrate(III) ion,  $[\text{FeCl}_4]^-$ , is tetrahedral. This ion is easily formed by adding concentrated hydrochloric acid to a solution of the hexaaquairon(III) ion:



A specific test for the presence of the iron(III) ion is the addition of a solution of hexacyanidoferrate(II) ion,  $[\text{Fe}(\text{CN})_6]^{4-}$ , to give a dark blue precipitate of iron(III) hexacyanidoferrate(II),  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ :

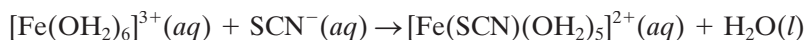


In this compound, commonly called *Prussian blue*, the crystal lattice contains alternating iron(III) and iron(II) ions. The intense blue of this compound led to its use in the nineteenth century as a dye for the uniforms of Prussian soldiers, hence the origin of the name. The compound is used in blue inks and



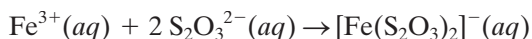
paints, and it is the blue pigment in traditional architectural and engineering blueprints.

The most sensitive test for the iron(III) ion is the addition of potassium thiocyanate solution. The appearance of the intense red color of the penta-aquathiocyanidoiron(III) ion,  $[\text{Fe}(\text{SCN})(\text{OH}_2)_5]^{2+}$ , indicates the presence of iron(III):

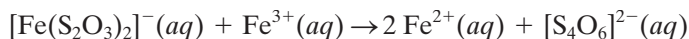


This test for iron(III) ion has to be used cautiously, for a solution of iron(II) ion usually contains enough iron(III) impurity to give some color.

A unique reaction of iron(III) ion is that with an ice-cold solution of thio-sulfate. Mixing these two nearly colorless solutions gives the dark violet bis(thiosulfato)ferrate(III) ion:



When the solution is warmed to room temperature, the iron(III) is reduced to iron(II) and the thiosulfate is oxidized to the tetrathionate ion,  $[\text{S}_4\text{O}_6]^{2-}$ :



### Iron(III) and Aluminum: A Case of Similarities between ( $n + 5$ ) and ( $n + 10$ ) Species

In Chapter 9, Section 9.4, it was shown that, in several ways, aluminum more closely resembled scandium in Group 3 than the members of Group 13. The chemistry of aluminum also has some properties that are like those of the iron(III) ion. Iron(III) and aluminum ions have the same charge and similar sizes (and hence similar charge densities), leading to several similarities. For example, in the vapor phase, both of these ions form covalent chlorides of the form  $\text{M}_2\text{Cl}_6$ . These (anhydrous) chlorides can be used as Friedel-Crafts catalysts in organic chemistry, where they function by the formation of the  $[\text{MCl}_4]^{-}$  ion. In addition, the  $[\text{M}(\text{OH}_2)_6]^{3+}$  ions of both metals are very strongly acidic, another result of their high charge densities.

There are, however, some significant differences. For example, the oxides have different properties: aluminum oxide,  $\text{Al}_2\text{O}_3$ , is an amphoteric oxide, whereas iron(III) oxide,  $\text{Fe}_2\text{O}_3$ , is a basic oxide. This difference is utilized in the separation of pure aluminum oxide from the iron-containing bauxite ore in the production of aluminum (see Chapter 13, Section 13.6). The amphoteric aluminum oxide reacts with hydroxide ion to give the soluble tetrahydroxoaluminate ion,  $[\text{Al}(\text{OH})_4]^{-}$ , whereas the basic iron(III) oxide remains in the solid phase:



### Ferrites

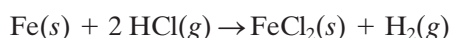
It is not just iron oxides that are important magnetic materials. There are several mixed-metal oxides, one metal being iron, that have valuable properties. These magnetoceramic materials are called *ferrites*. There are two classes of ferrites: “soft” ferrites and the “hard” ferrites. These terms do not refer to their physical hardness but to their magnetic properties.

The soft ferrites can be magnetized rapidly and efficiently by an electromagnet, but they lose their magnetism as soon as the current is discontinued. Such properties are essential for the record-erase heads in videotape and audiotape systems and computer drive heads. The compounds have the formula  $MFe_2O_4$ , where M is a di-positive metal ion such as  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ , or  $Mg^{2+}$  and the iron is in the form of  $Fe^{3+}$ . These compounds have spinel structures (see Chapter 5, Section 5.7).

The hard ferrites retain their magnetic properties constantly; that is, they are permanent magnets. These materials are used in DC motors, alternators, and other electrical devices. The general formula of these compounds is  $MFe_{12}O_{19}$ , where again the iron is  $Fe^{3+}$  and the two preferred di-positive metal ions are  $Ba^{2+}$  and  $Sr^{2+}$ . The hard ferrites adopt a more complex structure than the soft ferrites. The use of both ferrites is not particularly large in terms of mass, but in terms of value, annual world sales are several billion dollars.

### Iron(II) Compounds

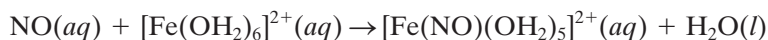
Anhydrous iron(II) chloride,  $FeCl_2$ , can be made by passing a stream of dry hydrogen chloride over the heated metal; the hydrogen produced acts as a reducing agent, preventing iron(III) chloride from being formed:



The pale green hexaaquairon(II) chloride,  $[Fe(OH_2)_6]Cl_2$ , can be prepared by reacting hydrochloric acid with iron metal. Both anhydrous and hydrated forms of iron(II) chloride are ionic.

All the common hydrated iron(II) salts contain the pale green  $[Fe(OH_2)_6]^{2+}$  ions, although partial oxidation to yellow or brown iron(III) compounds is quite common. In addition, crystals of the simple salts, such as iron(II) sulfate heptahydrate,  $FeSO_4 \cdot 7H_2O$ , tend to lose some of the water molecules (efflorescence). In the solid phase, the double salt, ammonium iron(II) sulfate hexahydrate,  $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ , more correctly written as  $(NH_4^+)_2[Fe(OH_2)_6]^{2+}(SO_4^{2-})_2$ , ammonium hexaaquairon(II) sulfate, shows the greatest lattice stability. Commonly known as *Mohr's salt*, it neither effloresces nor oxidizes when exposed to the atmosphere. For this reason, it is used as a standard for redox titrations, especially for determining the concentration of potassium permanganate solutions. The tris(1,2-diaminoethane)iron(II) sulfate,  $[Fe(en)_3]SO_4$ , is also used as a redox standard.

In the presence of nitrogen monoxide, one molecule of water is displaced from the hexaaquairon(II) ion and replaced by the nitrogen monoxide to give the pentaaquanitrosyliron(II) ion,  $[Fe(NO)(OH_2)_5]^{2+}$ :



This complex is dark brown, and the previous reaction is the basis of the "brown-ring" test for ionic nitrates (the nitrate having been reduced to nitrogen monoxide by a reducing agent).

Addition of hydroxide ion to iron(II) gives an initial precipitate of green, gelatinous iron(II) hydroxide:

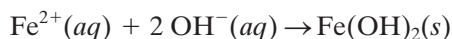
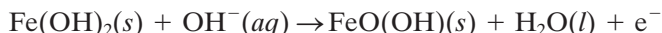




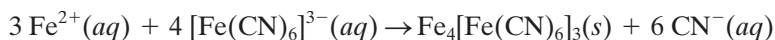
Table salt sometimes contains 0.01 percent sodium hexacyanidoferrate(II),  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ , to keep it from “caking,” so that it flows freely even in damp climates.



However, as Figure 20.12 shows, except for strongly reducing conditions (or the absence of air), hydrated iron(III) oxide is thermodynamically stable in basic solution over most of the potential range. Thus, the green color is replaced by the yellow-brown of the hydrated iron(III) oxide as the oxidation proceeds:



Just as iron(III) ion can be detected with the hexacyanidoferrate(II) ion,  $[\text{Fe}(\text{CN})_6]^{4-}$ , so can iron(II) ion be detected with the hexacyanidoferrate(III) ion,  $[\text{Fe}(\text{CN})_6]^{3-}$ , to give the same product of Prussian blue (formerly called *Turnbull's blue* when it was thought to be a different product):

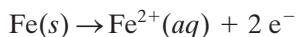


### The Rusting Process

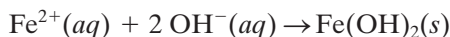
It is a common experiment in junior high science to show that the oxidation of iron (commonly called *rusting*) requires the presence of both dioxygen and water. By use of an indicator, it can also be shown that around parts of an iron surface, the pH rises. From these observations, the electrochemistry of the rusting process can be determined. This process is really a reflection of the Nernst equation, which states that potential is dependent on concentration—in this case, the concentration of dissolved dioxygen. At the point on the iron surface that has a higher concentration of dioxygen, the dioxygen is reduced to hydroxide ion:



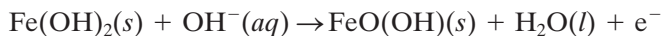
The bulk iron acts like a wire connected to a battery, conveying electrons from another point on the surface that has a lower oxygen concentration, a point at which the iron metal is oxidized to iron(II) ions:



These two ions diffuse through the solution, and where they meet, insoluble iron(II) hydroxide is formed:



Like hydrated manganese(III) oxide, the iron(III) oxide hydroxide (rust) is thermodynamically preferred to iron(II) hydroxide in basic solution:



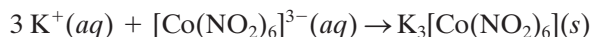
## 20.9 Group 9: Cobalt

Cobalt is a bluish white, hard metal, and, like iron, cobalt is a magnetic (ferromagnetic) material. The element is quite unreactive chemically. The most common oxidation numbers of cobalt are +2 and +3, with the former being the “normal” state for simple cobalt compounds. For cobalt, the +3 state is more oxidizing than the +3 state of iron.

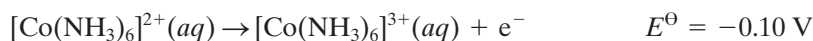
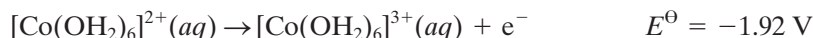
## Cobalt(III) Compounds

All cobalt(III) complexes contain octahedrally coordinated cobalt, and, like chromium(III), the low-spin complexes are very kinetically inert; meaning that we can separate different chiral isomers where they are feasible. Typical examples of cobalt(III) complexes are the hexaamminecobalt(III) ion,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , and the hexacyanidocobaltate(III) ion,  $[\text{Co}(\text{CN})_6]^{3-}$ .

An unusual complex ion is the hexanitritocobaltate(III) ion,  $[\text{Co}(\text{NO}_2)_6]^{3-}$ , which is usually synthesized as the sodium salt,  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ . As would be expected for an alkali metal salt, the compound is water soluble. However, the potassium salt is quite insoluble (as are the rubidium, cesium, and ammonium salts), the reason relating to relative ion sizes. The potassium ion is much closer in size to the polyatomic anion; hence, the balance of lattice energy and hydration energies favors a lower solubility for the compound. This is one of the few precipitation reactions that can be used for the potassium ion. We described this reaction in the context of similarities of the ammonium ion with the heavier alkali metals ions (see Chapter 11, Section 11.12).



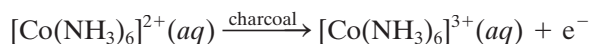
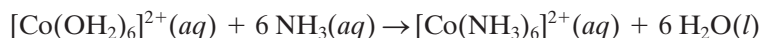
As noted for the iron ions, altering the ligands produces dramatic changes in  $E^\ominus$  values, which in turn affects the stabilities of the various oxidation states. For example, the oxidation of the hexaamminecobalt(II) ion is much more thermodynamically feasible than that of the hexaaquacobalt(II) ion:



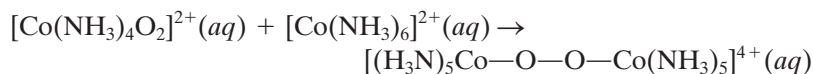
Coupling with the reduction of dioxygen:



enables  $[\text{Co}(\text{NH}_3)_6]^{2+}$  to be oxidized to  $[\text{Co}(\text{NH}_3)_6]^{3+}$  in aqueous solution. For example, with charcoal as a catalyst, the following overall reaction process occurs:

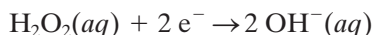


This reaction must proceed in a series of steps, for it is possible in the absence of a catalyst to isolate an intermediate from the reaction, a brown compound containing the  $[(\text{H}_3\text{N})_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{4+}$  ion. It is believed to form in a two-step process. Thus, it would seem that the dioxygen molecule attaches in a bidentate fashion to one cobalt(II) ion and then links two cobalt(II) complexes, oxidizing each cobalt(II) to cobalt(III), in the process being reduced to the peroxo unit,  $\text{O}_2^{2-}$ :

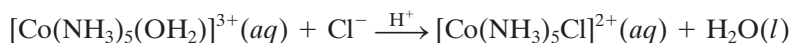
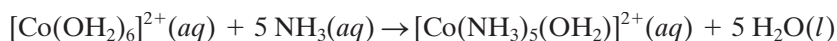


In a further series of steps, the peroxo unit is reduced to 2 moles of hydroxide ion and, for each molecule of dioxygen used, a total of 4 moles of the cobalt(II) complex is oxidized to the hexaamminecobalt(III) ion.

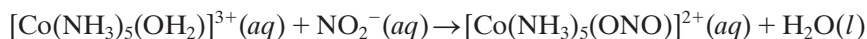
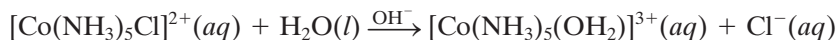
The product of oxidation is very sensitive to the precise conditions. For example, with hydrogen peroxide as the oxidizing agent:



It is possible to form the pentaammineaquacobalt(III) ion and then to use concentrated hydrochloric acid to perform a ligand replacement to give the pentaamminechloridocobalt(III) ion:



The monochloro species is a useful reagent for the synthesis of other mono-substituted cobalt(III) complexes. In particular, we can synthesize the nitrito and nitro-linkage isomers described in Chapter 19, Section 19.4:



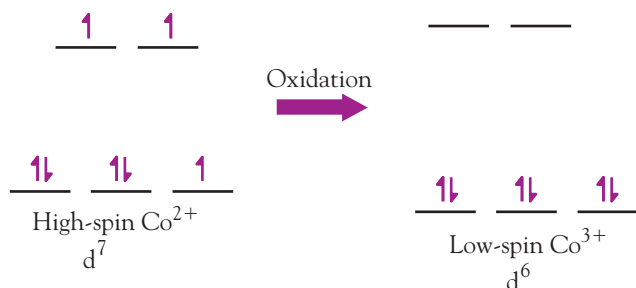
Using appropriate synthetic conditions, we can synthesize several permutations of cobalt(III) with ammonia and chloride ligands (Table 20.6). It is very easy to determine the formulas of these compounds. The number of ions can be identified from conductivity measurements, and the free chloride ion can be quantitatively precipitated with silver ion.

If 1,2-diaminoethane is employed as the ligand, cobalt(II) can be oxidized to the tris(1,2-diaminoethane)cobalt(III) ion and crystallized as the chloride,  $[\text{Co}(\text{en})_3]\text{Cl}_3$ . This compound, as we mentioned in Chapter 19, Section 19.4, can be separated into the two chiral isomers. By decreasing the ligand- to metal ion ratio, it is possible to synthesize *trans*-dichloridobis-(1,2-diaminoethane) cobalt(III) chloride,  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ . Dissolving in water and evaporating the solution causes the compound to isomerize to the *cis* form.

By comparing the electron configurations in an octahedral field, we can see why ligands causing a larger crystal field splitting would enable cobalt(II) to be

**TABLE 20.6** Complexes derived from cobalt(III) chloride and ammonia

Formula	Color
$[\text{Co}(\text{NH}_3)_6]^{3+}(\text{Cl}^-)_3$	Orange-yellow
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{Cl}^-)_2$	Purple
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+(\text{Cl}^-)$ ( <i>cis</i> )	Violet
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+(\text{Cl}^-)$ ( <i>trans</i> )	Green

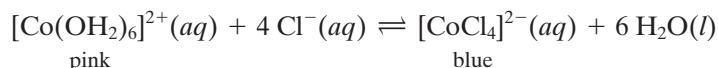


**FIGURE 20.14** Comparison of cobalt(II) and cobalt(III) crystal field stabilization energies.

readily oxidized. For cobalt(II), nearly all the complexes are high spin, whereas cobalt(III), with its higher charge, is almost always low spin. Thus, the oxidation results in a much greater crystal field stabilization energy (CFSE) (Figure 20.14). The higher the ligands in the spectrochemical series, the greater the  $\Delta_{\text{oct}}$  value and the greater the CFSE increase obtained by oxidation.

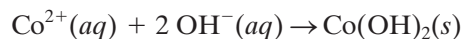
### Cobalt(II) Compounds

In solution, cobalt(II) salts are pink, the color being due to the presence of the hexaaquacobalt(II) ion,  $[\text{Co}(\text{OH}_2)_6]^{2+}$ . When a solution of a cobalt(II) salt is treated with concentrated hydrochloric acid, the color changes to deep blue. This color change is characteristic for the cobalt(II) ion. The blue color is the result of the formation of the tetrahedral tetrachloridocobaltate(II) ion,  $[\text{CoCl}_4]^{2-}$ :

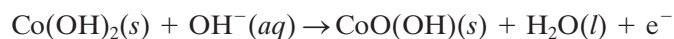


There is also a pink-to-blue transition when solid pink hexaaquacobalt(II) chloride is dehydrated. Paper impregnated with the blue form will turn pink on addition of water—a good test for water. Silica gel and calcium sulfate drying agents are often colored with cobalt(II) chloride. As long as the granules retain the blue color, they are an effective drying agent, with the appearance of pink indicating that the drying agent is water saturated and must be heated to expel the absorbed moisture.

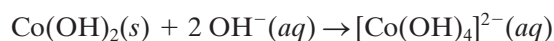
The addition of hydroxide ion to the aqueous cobalt(II) ion results in the formation of cobalt(II) hydroxide, which precipitates first in a blue form and then changes to a pink form on standing:



The cobalt(II) hydroxide is slowly oxidized by the dioxygen in the air to a cobalt(III) oxide hydroxide,  $\text{CoO}(\text{OH})$ :



Cobalt(II) hydroxide is amphoteric. When concentrated hydroxide ion is added to cobalt(II) hydroxide, a deep blue solution of the tetrahydroxido-cobaltate(II) ion,  $[\text{Co}(\text{OH})_4]^{2-}$ , is formed:

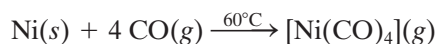


## 20.10 Group 10: Nickel

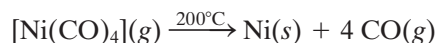
Nickel is a silvery white metal that is quite unreactive. In fact, nickel plating is sometimes used to protect iron. The only common oxidation number for nickel is +2. Most nickel complexes have an octahedral geometry, but some tetrahedral and square-planar complexes are known. Square-planar geometry is otherwise exceedingly rare for the compounds of 3d transition metals.

### Extraction of Nickel

Although the extraction of nickel from its compounds is complex, the isolation of pure nickel metal is of particular interest. To separate the nickel from the other metals, such as cobalt and iron, there are two alternatives. One is an electrolytic process whereby impure nickel is cast into anodes and, by using solutions of nickel sulfate and chloride as electrolytes, 99.9 percent pure nickel is deposited at the cathode. The other process utilizes a reversible chemical reaction known as the *Mond process*. In this reaction, nickel metal reacts at about 60°C with carbon monoxide gas to form a colorless gas, tetracarbonylnickel(0),  $[\text{Ni}(\text{CO})_4]$  (b.p. 43°C):



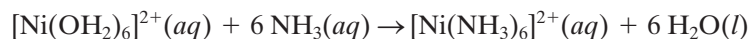
The highly toxic compound can be piped off, for nickel is the only metal to form a volatile carbonyl compound so easily. Heating the gas to 200°C shifts the equilibrium in the opposite direction, depositing 99.95 percent pure nickel metal:



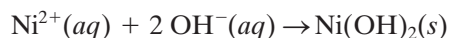
The carbon monoxide can then be reused.

### Nickel(II) Compounds

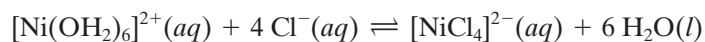
The hexaaquanickel(II) ion is a pale green color. Addition of ammonia gives the blue hexaamminenickel(II) ion:



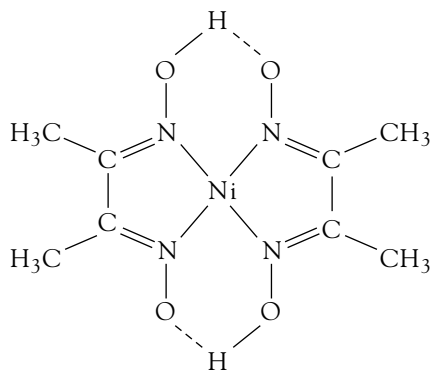
Nickel(II) hydroxide can be precipitated as a green gelatinous solid by adding sodium hydroxide solution to a solution of a nickel(II) salt:



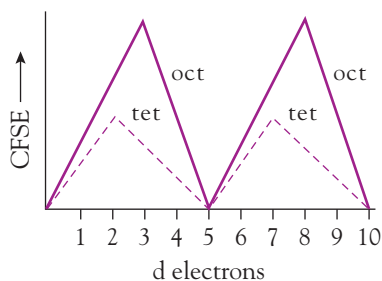
Like cobalt(II), the only common complexes having tetrahedral geometry are the halides, such as the blue tetrachloridonickelate(II) ion. This complex is formed by adding concentrated hydrochloric acid to aqueous nickel(II) ion:



In addition to octahedral and tetrahedral complexes, nickel forms a few square-planar complexes. One such complex is the yellow tetracyanonickelate(II) ion,

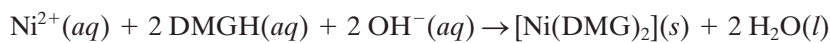


**FIGURE 20.15** Structure of the nickel(II)-dimethylglyoxime complex.



**FIGURE 20.16** Variation of CFSE for octahedral and tetrahedral environments for  $M^{2+}$  ions with a high-spin electron configuration.

$[\text{Ni}(\text{CN})_4]^{2-}$ , and another is bis(dimethylglyoximato)nickel(II),  $[\text{Ni}(\text{C}_4\text{N}_2\text{O}_2\text{H}_7)_2]$ , which precipitates as a red solid when dimethylglyoxime is added to a solution of a nickel salt made just alkaline by the addition of ammonia. The formation of this characteristic red complex (Figure 20.15) is used as a test for nickel(II) ions. Abbreviating dimethylglyoxime ( $\text{C}_4\text{N}_2\text{O}_2\text{H}_8$ ), a bidentate ligand, as DMGH, we write the equation for its formation as



### Octahedral versus Tetrahedral Stereochemistry

Cobalt(II) readily forms tetrahedral complexes, but as we have just seen, nickel(II) complexes are usually octahedral; however, a few are square planar, and very few are tetrahedral. Several factors determine the choice of stereochemistry, but one in particular is the CFSE. We can calculate this for each configuration and plot the values as a function of the number of d-orbital electrons. Because  $\Delta_{\text{tet}}$  is four-ninths that of  $\Delta_{\text{oct}}$ , the CFSE for a tetrahedral environment will always be less than that of the isoelectronic octahedral environment. Figure 20.16 shows the variation of CFSE with high-spin electron configurations. The differences between octahedral and tetrahedral CFSE energies are greatest for the high-spin  $d^3$  and  $d^8$  cases, and these are the electron configurations for which we find the fewest tetrahedral complexes.

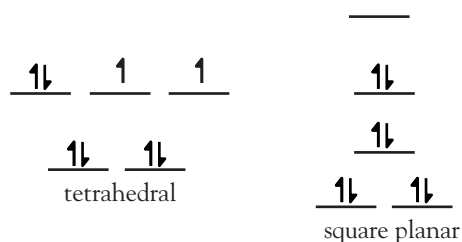
Nevertheless, there are a few tetrahedral nickel(II) complexes. Such complexes are formed with large, negatively charged, weak field ligands (that is, ligands low in the spectrochemical series). In these cases, there will be considerable electrostatic repulsion between neighboring ligands, so four ligands would be preferred over six. Thus, the tetrahalidonickelate(II) ions,  $[\text{NiX}_4]^{2-}$ , where X is chloride, bromide, or iodide, are the most common examples. Even then, to crystallize the tetrahedral ion, it is necessary to use a large cation; otherwise, the nickel ion will acquire other ligands (such as water molecules) to attain an octahedral environment.

**WORKED EXAMPLE 20.3**

A nickel complex  $[\text{NiX}_4]^{2-}$  has an experimentally measured magnetic moment of  $2.96 \mu_{\text{BM}}$ . Deduce whether the complex is tetrahedral or square planar.

**Answer**

Ni(II) ions have eight d electrons which can be arranged as follows, using the tetrahedral and square planar orbital energy diagrams (see Chapter 19, Section 19.7):



The square planar arrangement has no unpaired electrons and will be diamagnetic (Section 19.8). So the complex must be tetrahedral. The two unpaired electrons give a theoretical magnetic moment of  $2.83 \mu_{\text{BM}}$  which is close to the measured value. ■

**20.11 Group 11: Copper**

Copper is one of the two common yellow metals (the other being gold), although a thin coating of copper(I) oxide,  $\text{Cu}_2\text{O}$ , often makes copper look reddish. The color of copper is caused by the filled d band in the metal being only about  $220 \text{ kJ} \cdot \text{mol}^{-1}$  lower in energy than the s-p band. As a result, electrons can be excited to the higher band by photons of the corresponding energy range; that is, the blue and green regions of the spectrum. Hence, copper reflects yellow and red.

**Chemistry of Copper**

Pure copper has the highest thermal conductivity of all metals. For this reason, copper is used in premium cookware so that the heat is distributed rapidly throughout the walls of the container. An alternative approach is to apply a copper coating to the base of cookware made from other materials. Copper is second only to silver as an electrical conductor; hence, electrical wiring represents a major use of this metal. Copper is comparatively expensive for a common metal. To make penny coins of copper would now cost more than one cent, so more recent coins have an outer layer of copper over a core of the lower-priced zinc.

**TABLE 20.7** Important alloys of copper

Alloy	Approximate composition	Properties
Brass	77% Cu, 23% Zn	Harder than copper
Bronze	80% Cu, 10% Sn, 10% Zn	Harder than brass
Nickel coins	75% Ni, 25% Cu	Corrosion resistant
Sterling silver	92.5% Ag, 7.5% Cu	More durable than pure silver

Although copper is normally considered an unreactive metal, over time it is slowly oxidized in moist air to give a coating of green *verdigris*, a copper(II) carbonate hydroxide, also called *basic copper(II) carbonate*,  $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ . This characteristic green color can be seen on copper-covered roofs, such as the Parliament buildings in Ottawa, Canada, and buildings in parts of northern Europe.

Copper is a soft metal, and it is often used in alloys, including brass (for plumbing fixtures) and bronze (for statues). Nickel and silver alloys often contain small proportions of copper. Some of the common alloy compositions are shown in Table 20.7.

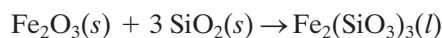
### Extraction of Copper

Although copper does not occur abundantly in nature, many copper-containing ores are known. The most common ore is copper(I) iron(III) sulfide,  $\text{CuFeS}_2$ , a metallic-looking solid that has the two mineralogical names of *chalcopyrites* and *copper pyrites*. A rarer mineral,  $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ , is the valued blue gemstone turquoise.

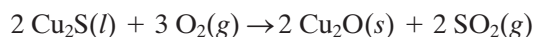
The extraction of copper from the sulfide can be accomplished by using either a thermal process (*pyrometallurgy*) or an aqueous process (*hydrometallurgy*). For the pyrometallurgical process, the concentrated ore is heated (a process called *roasting*) in a limited supply of air. This reaction decomposes the mixed sulfide to give iron(III) oxide and copper(I) sulfide:



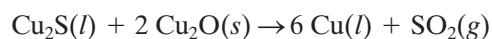
Sand is added to the molten mixture, converting the iron(III) oxide into a slag of iron(III) silicate:



This liquid floats on the surface and can be poured off. Air is again added, causing sulfide to be oxidized to sulfur dioxide, and simultaneously copper(I) sulfide is converted to copper(I) oxide:



The air supply is discontinued after about two-thirds of the copper(I) sulfide has been oxidized. The mixture of copper(I) oxide and copper(I) sulfide then undergoes an unusual redox reaction to give impure copper metal:





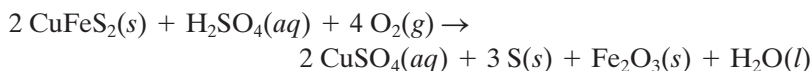
The pyrometallurgical process has a number of advantages: its chemistry and technology are well known; there are many existing copper smelters; it is a fast process. The process also has disadvantages: the ore must be fairly concentrated; a large quantity of thermal energy is required for the smelting process; and metal production also generates large quantities of sulfur dioxide.

Most metals are extracted by pyrometallurgical processes, using high temperatures and a reducing agent such as carbon monoxide. However, as mentioned, pyrometallurgy requires high-energy input, and the wastes are often major air and land pollutants.

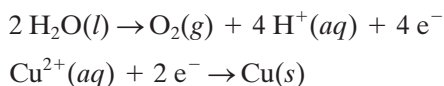
Hydrometallurgy, the extraction of metals by using solution processes, had been known for centuries but did not become widely used until the twentieth century and then only for specific metals, such as silver and gold. This method has many advantages: its by-products are usually less of an environmental problem than the flue gases and slag of a smelter; plants can be built on a small scale and then expanded, whereas a smelter needs to be built on a large scale to be economical; high temperatures are not required, so less energy is consumed than by smelting; hydrometallurgy can process lower-grade ores (less metal content) than can pyrometallurgy.

Hydrometallurgical processes usually consist of three general steps: leaching, concentration, and recovery. The leaching is often accomplished by crushing and heaping the ore, then spraying it with some reagent, such as dilute acid (for copper extraction) or cyanide ion (for silver and gold extraction). Sometimes, instead of chemicals, solutions of the bacterium *Thiobacillus ferrooxidans* are used (this process is actually *biohydrometallurgy*). This bacterium oxidizes the sulfide in insoluble metal sulfides to a soluble sulfate. The dilute metal ion solution is then removed and concentrated by a variety of means. Finally, the metal itself is produced either by chemical precipitation using a single replacement reaction or by an electrochemical process.

In the specific hydrometallurgical process for copper, copper pyrites is air oxidized in acid suspension to give a solution of copper(II) sulfate:

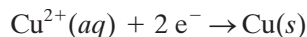
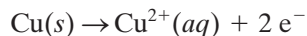


Thus, in this method, sulfur is released in the forms of sulfate ion solution and solid elemental sulfur rather than as the sulfur dioxide produced in the pyrometallurgical method. The copper metal is then obtained by electrolysis, and the oxygen gas formed can be utilized in the first step of the process:



Copper is refined electrolytically to give a product that is about 99.95 percent pure. This impure copper (formerly the cathode) is now made the anode of an electrolytic cell that contains pure strips of copper as the cathode and an electrolyte of copper(II) sulfate solution. During electrolysis, copper is transferred from the anode to the cathode; an anode sludge containing silver and

gold is produced during this process, thus helping to make the process economically feasible:

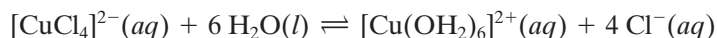


Because there is no net electrochemical reaction in this purification step, the voltage required is minimal (about 0.2 V), and the power consumption is very small. Of course, the environmentally preferred route for our copper needs is that of recycling copper.

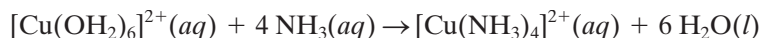
## Copper(II) Compounds

Although copper forms compounds in both the +1 and +2 oxidation states, it is the +2 state that dominates the aqueous chemistry of copper. In aqueous solution, almost all copper(II) salts are blue, the color being due to the presence of the hexaaquacopper(II) ion,  $[\text{Cu}(\text{OH}_2)_6]^{2+}$ .

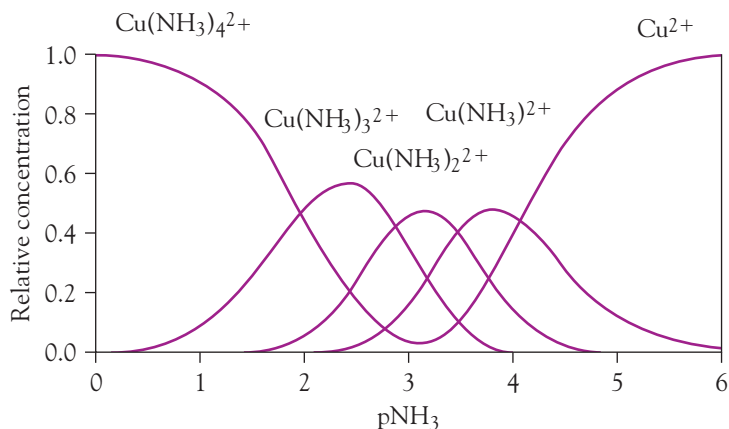
The common exception is copper(II) chloride. A concentrated aqueous solution of this compound is green, the color caused by the presence of complex ions such as the nearly planar tetrachloridocuprate(II) ion,  $[\text{CuCl}_4]^{2-}$ . When diluted, the color of the solution changes to blue. These color transformations are due to the successive replacement of chloride ions in the complexes by water molecules, the final color being that of the hexaaquacopper(II) ion. The overall process can be summarized as



If a solution of ammonia is added to a copper(II) ion solution, the pale blue color of the hexaaquacopper(II) ion is replaced by the deep blue of the square-planar tetraamminecopper(II) ion,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ :



Although we commonly depict the process as a single reaction, the substitution of water ligands by ammonia is a stepwise process. Figure 20.17 shows the distribution of species with ammonia concentration. Because it is a log

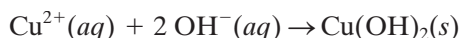


**FIGURE 20.17** The relative concentrations of copper(II) species with increasing  $\text{pNH}_3$  (to left). [Adapted from A. Rojas-Hernández, et al., *J. Chem. Educ.* **72**, 1100 (1995).]

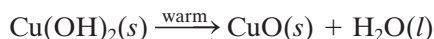
scale,  $\text{pNH}_3$  (like pH), increasing ammonia concentration is to the left. For simplicity, the coordinated water molecules are not included. We see that, as the concentration of ammonia is increased, so the  $[\text{Cu}(\text{NH}_3)_n]^{2+}$  complexes are formed in sequence.



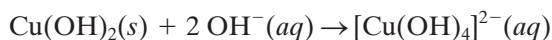
Addition of hydroxide ion to a copper(II) ion solution causes the precipitation of the copper(II) hydroxide, a blue-green gelatinous solid:



However, warming the suspension causes the hydroxide to decompose to the black copper(II) oxide and water:



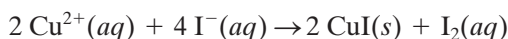
Copper(II) hydroxide is insoluble in dilute base, but it dissolves in concentrated hydroxide solution to give the deep blue tetrahydroxidocuprate(II) ion,  $[\text{Cu}(\text{OH})_4]^{2-}$ :



Copper(II) hydroxide also dissolves in an aqueous solution of ammonia to give the tetraamminecopper(II) ion:



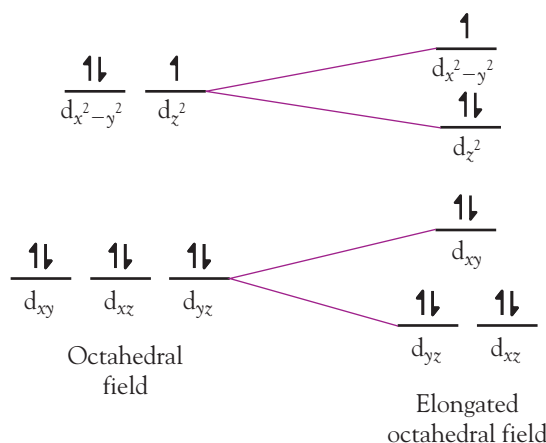
For most ligands, the copper(II) oxidation state is the more thermodynamically stable, although reducing ligands, such as iodide, will reduce copper(II) ions to the copper(I) state:



### Distortions in Copper(II) Complexes

In Chapter 19, Section 19.9, we introduced the Jahn-Teller effect. Although this effect can occur with other electron configurations, it has been studied most in copper(II) compounds. As a result of the Jahn-Teller effect, six-coordinate copper(II) compounds usually have two axial ligands more distant from the metal than those in the equatorial plane. The corresponding crystal field diagram is shown in Figure 20.18. With certain ligands, the Jahn-Teller splitting is

**FIGURE 20.18** The most common splitting of the  $d^9$ -orbital energies as a result of the Jahn-Teller effect.



so strong that square planar complexes form (see Chapter 19, Section 19.7), with no ligands in the axial position.

### Copper(I) Compounds

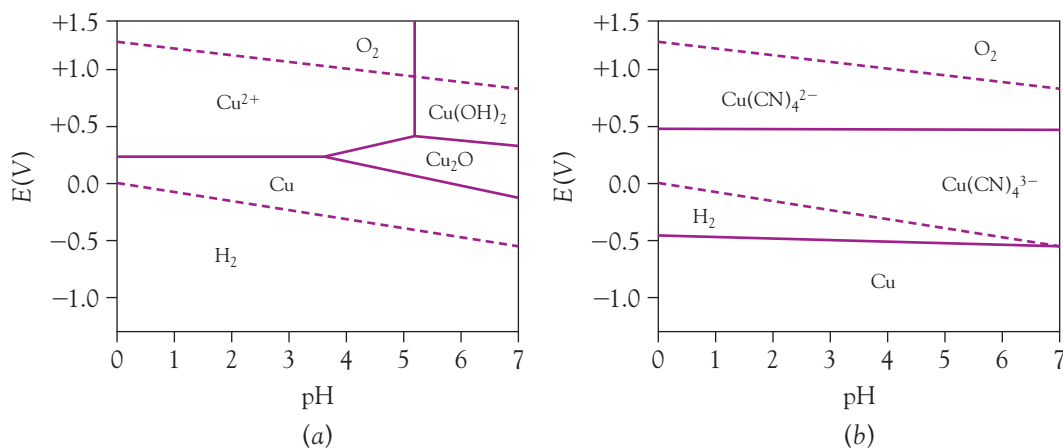
In aqueous solution, the hydrated copper(I) ion is unstable and disproportionates into the copper(II) ion and copper metal, as the Frost diagram in Figure 20.1 predicts:



The copper(I) ion is stabilized in the solid phase by low-charge anions. For example, we can synthesize copper(I) chloride, bromide, iodide, and cyanide. Generally, copper(I) compounds are colorless or white because the ion has a  $d^{10}$ -electron configuration. That is, with a filled set of d orbitals, there can be no d-d-electron transitions to cause visible light absorption.

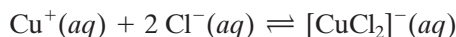
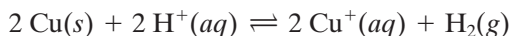
We can also use an appropriate choice of ligands to change the preference between the oxidation states, just as we did for cobalt(II) and cobalt(III). The Pourbaix diagram in Figure 20.19a shows the fields of stability for the various copper species in aqueous solution. As can be seen, aqueous copper(I) is not thermodynamically preferred anywhere within the range. However, addition of cyanide ion changes the stability fields dramatically. In particular, Figure 20.19b shows that cyano species dominate over the entire range of accessible pH and  $E$ . Thus, the tetracyanidocuprate(I) ion is preferred over all but the higher  $E$  values. This is not surprising, for as we discussed in Chapter 19, Section 19.7, cyanide stabilizes low oxidation states.

These two approaches to the formation of copper(I) compounds can be illustrated by the reaction of copper metal with boiling hydrochloric acid. This reaction is particularly unexpected because hydrochloric acid is not a strong oxidizing acid. The copper(I) ion formed in the oxidation is rapidly complexed by the chloride ion to produce the colorless dichloridocuprate(I)



**FIGURE 20.19** A comparison of (a) the "normal" Pourbaix diagram for copper with (b) the Pourbaix diagram for copper in the presence of cyanide ion. [Modified from A. Napoli and L. Pogliani, *Educ. Chem.* **34**, 51 (1997).]

ion,  $[\text{CuCl}_2]^-$ . It is this second equilibrium step that lies far to the right and “drives” the first step:



When the solution is poured into air-free distilled water, copper(I) chloride precipitates as a white solid:



It must be rapidly washed, dried, and sealed in the absence of air, because a combination of air and moisture oxidizes it to copper(II) compounds.

In organic chemistry, the dichloridocuprate ion is used for converting benzene diazonium chloride into chlorobenzene (the *Sandmeyer reaction*):



## 20.12 Biological Aspects

### Vanadium

Vanadium is not widely used in nature, yet it does appear to be vital to one of the simplest groups of marine organisms: the tunicates, or sea squirts. These organisms belong somewhere between invertebrates and vertebrates. One family of tunicates utilizes very high levels of vanadium in its blood plasma for oxygen transport. Why the tunicates should have picked such a unique element for a biochemical pathway is still unclear. The element also appears to be used by a very different organism, the poisonous mushroom *Amanita muscaria*. Here, too, the reason for this element being utilized is not well understood.

In Chapter 21, Section 21.5, we discuss the importance of molybdenum in the bacteria attached to the roots of leguminous plants (including alfalfa, beans, clover, lentils, mesquite, peanuts, and peas). These bacteria convert atmospheric nitrogen gas to absorbable and utilizable ammonia. In molybdenum-deficient soils, the bacteria utilize vanadium in place of molybdenum.

### Chromium

Although chromium(VI) is carcinogenic when ingested or absorbed through the skin, we require small quantities of chromium(III) in our diet. Insulin and the chromium(III) ion regulate blood glucose levels. A deficiency of chromium(III) or an inability to utilize the chromium ion can lead to one form of diabetes.

### Manganese

Manganese is a crucial element in a number of plant and animal enzymes. In mammals, it is used in the liver enzyme arginase, which converts nitrogen-containing wastes to the excretable compound urea. There is a group of enzymes in plants, the phosphotransferases, that incorporate manganese. Like most transition metals, the biological role of manganese seems to be as a redox reagent, cycling between the +2 and +4 oxidation states.

**TABLE 20.8** Major iron-containing proteins in an adult human

Name	Fe atoms per molecule	Function
Hemoglobin	4	O <sub>2</sub> transport in blood
Myoglobin	1	O <sub>2</sub> storage in muscle
Transferrin	2	Iron transport
Ferritin	Up to 4500	Iron storage in cells
Hemosiderin	10 <sup>3</sup> –10 <sup>4</sup>	Iron storage
Catalase	4	Metabolism of H <sub>2</sub> O <sub>2</sub>
Cytochrome <i>c</i>	1	Electron transfer
Iron-sulfur proteins	2–8	Electron transfer

## Iron

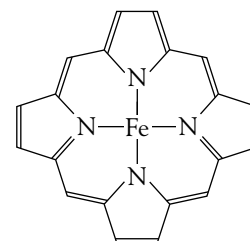
The biological roles of iron are so numerous that whole books have been written on the subject. Table 20.8 summarizes some major iron-containing proteins in an adult human.

Here we focus on three specific types of iron-containing macromolecules: hemoglobin, ferritin, and the ferredoxins. In hemoglobin, iron has an oxidation state of +2. (We mentioned this compound in the context of oxygen uptake in Chapter 16, Section 16.21.) There are four iron ions in each hemoglobin molecule, with each iron ion surrounded by a porphyrin unit (Figure 20.20). Each hemoglobin molecule reacts with four molecules of dioxygen to form oxyhemoglobin. The bonding to the dioxygen molecules is weak enough that, on reaching the site of oxygen utilization such as the muscles, the oxygen can be released. Carbon monoxide is extremely toxic to mammals because the carbonyl ligand bonds very strongly to the iron of the hemoglobin, preventing it from carrying dioxygen molecules.

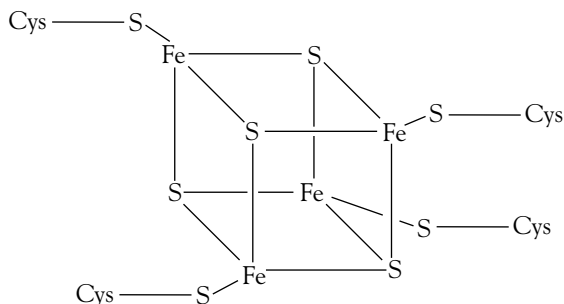
In oxyhemoglobin, the iron(II) is in the diamagnetic, low-spin state. It is just the right radius (75 pm) to fit in the plane of the porphyrin ring. Once the dioxygen is lost, iron in the deoxyhemoglobin molecule shifts below the plane of the porphyrin ring and away from the vacant coordination site because it has become a larger (radius 92 pm), paramagnetic, high-spin iron(II) ion. Throughout the cycle, the iron stays in the iron(II) state, merely alternating between high- and low-spin forms. It is only when exposed to air that the red iron(II)-containing hemoglobin is oxidized to the brown iron(III) species, an irreversible reaction.

Both plants and animals need to store iron for future use. To accomplish this, members of an amazing protein family, the ferritins, are utilized. They consist of a shell of linked amino acids (peptides) surrounding a core of an iron(III) oxohydroxidophosphate. This core is a cluster of iron(III) ions, oxide ions, hydroxide ions, and phosphate ions of average empirical formula  $[\text{FeO}(\text{OH})]_8[\text{FeO}(\text{OPO}_3\text{H}_2)]$ . The molecule is very large, containing up to 4500 iron ions. With its hydrophilic coating, this large aggregate is water soluble, concentrating in the spleen, liver, and bone marrow.

Plants and bacteria use a family of iron(III)-sulfur structures as the core of their redox proteins, the ferredoxins. These proteins contain covalently bonded

**FIGURE 20.20** The simplified structure of an iron-porphyrin complex.

**FIGURE 20.21** The 4Fe-4S atom core of some of the ferredoxins; the cube is covalently bonded to cysteine amino acid units.



iron and sulfur, and they act as excellent electron transfer agents. Figure 20.21 shows the 4Fe-4S atom core of some of the ferredoxins.

### Cobalt

Cobalt is yet another essential biological element. Of particular importance, vitamin B<sub>12</sub> has cobalt(III) at the core of the molecule, surrounded by a ring structure similar to the porphyrin ring. Injections of this vitamin are used in the treatment of pernicious anemia. Certain anaerobic bacteria use a related molecule, methylcobalamin, in a cycle to produce methane. Unfortunately, this same biochemical cycle converts elemental mercury and insoluble inorganic mercury compounds in mercury-polluted waters to soluble, highly toxic methyl mercury(II),  $[\text{HgCH}_3]^+$ , and dimethyl mercury(II),  $\text{Hg}(\text{CH}_3)_2$ .

Cobalt is also involved in some unidentified enzyme functioning in sheep. A deficiency (white liver) disease among sheep in Florida, Australia, Britain, and New Zealand was traced to a lack of cobalt in the soil. To remedy this, sheep are given a pellet of cobalt metal in their food, some of which remains in their digestive system for life.

### Nickel

The biochemistry of nickel is the most poorly understood of all the 3d transition elements. Nickel ions are present in some enzyme systems in the form of porphyrin-type complexes. Certain bacteria, such as those that reduce carbon dioxide to methane, need nickel. The requirement for nickel was explained when it was found that most types of the enzyme *hydrogenase* contain nickel together with iron-sulfur clusters. Although in normal chemistry the +3 oxidation state of nickel is very rare, nickel(III) is involved in the enzyme redox cycle. Nickel is also found in some plants that accumulate metals. In fact, certain tropical trees (nickel hyperaccumulators) concentrate nickel to such an extent that it makes up about 15 percent of their dry mass.

### Copper

Copper is the third most biologically important d-block metal after iron and zinc. About 5 mg are required in the daily human diet. A deficiency of this element renders the body unable to use iron stored in the liver. There are numerous copper proteins throughout the living world, the most intriguing being the hemocyanins. These molecules are common oxygen carriers in the

**TABLE 20.9** Some parallels between iron and copper proteins

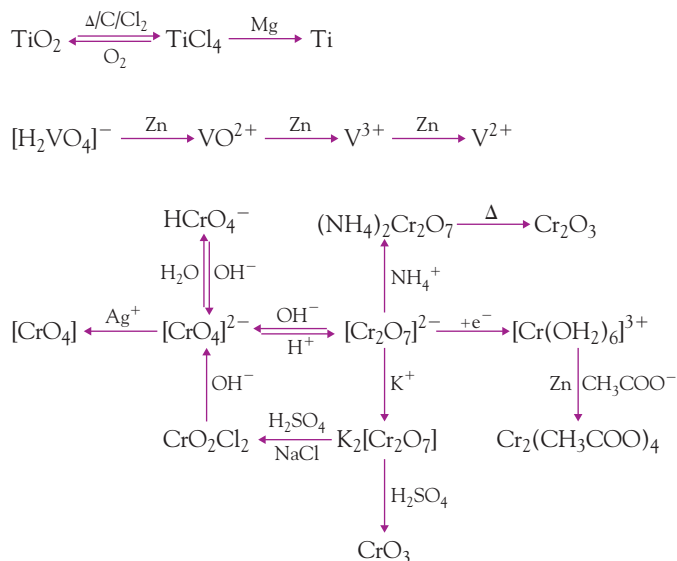
Function	Iron protein	Copper protein
Oxygen transport	Hemoglobin	Hemocyanin
Oxygenation	Cytochrome P-450	Tyrosinase
Electron transfer	Cytochromes	Blue copper proteins
Antioxidative function	Peroxidases	Superoxide dismutase
Nitrite reduction	Heme containing Nitrite reductase	Copper containing Nitrite reductase

invertebrate world: crabs, lobsters, octopi, scorpions, and snails all have bright blue blood. In fact, there are parallel iron and copper compounds (with very different structures) for many biological functions (Table 20.9). Because it is the invertebrates that contain the copper systems, it can be argued that early life developed with copper as the functional metal and that only later did iron systems develop.

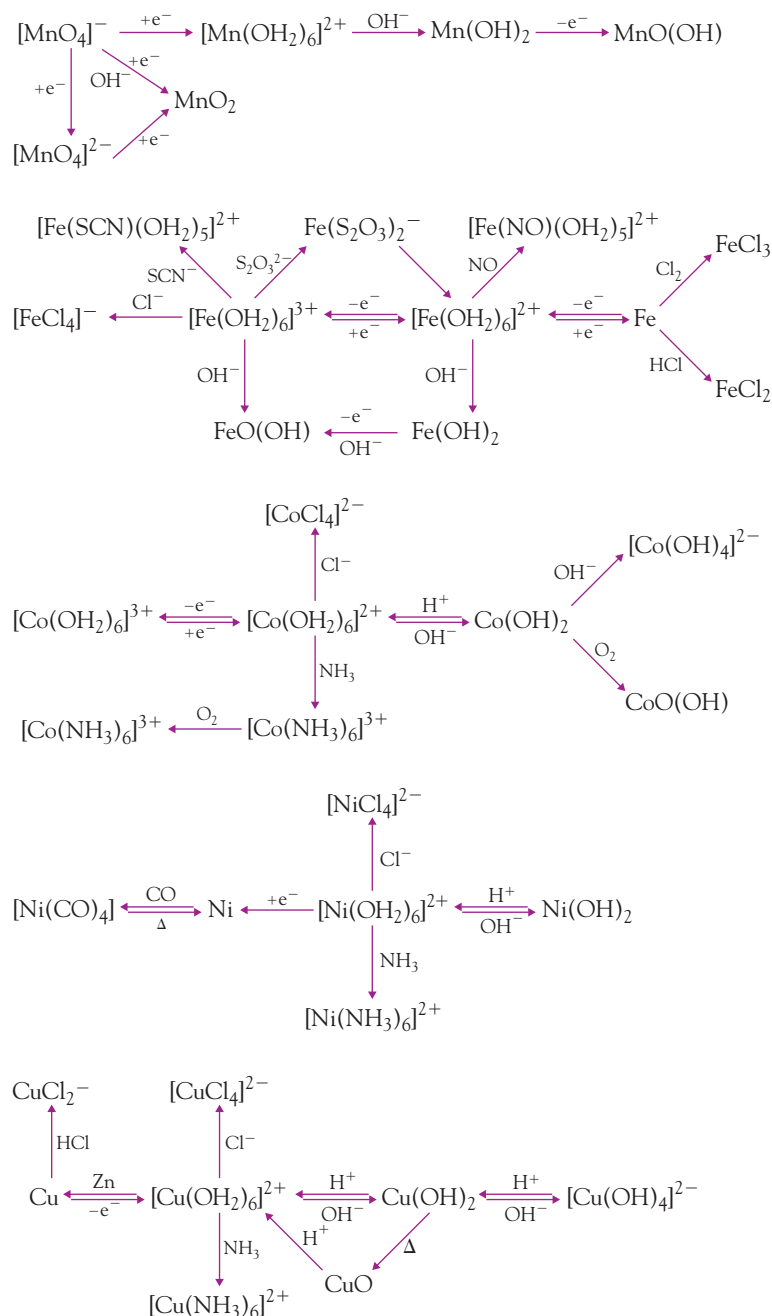
At the same time, an excess of copper is highly poisonous, particularly to fish. This is why copper coins should never be thrown into fish pools for “good luck.” Humans usually excrete any excess, but a biochemical (genetic) defect can result in copper accumulation in the liver, kidneys, and brain. This illness, Wilson’s disease, can be treated by administering chelating agents, which complex the metal ion and allow it to be excreted harmlessly.

## 20.13 Element Reaction Flowcharts

Flowcharts are shown for titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper.







## KEY IDEAS

- The early transition metals show higher oxidation states than the later members.
- The most important compound of titanium is titanium (IV) oxide.
- Vanadium can be reduced easily from vanadium(V) to vanadium(II).
- Chromate and dichromate ion dominate the chemistry of chromium.

- Manganese exhibits common oxidation states from +2 to +7, and their relative stability depends on the pH of the environment.
- Iron compounds exist in the +2 and +3 oxidation states.
- Cobalt(II) complexes can have octahedral or tetrahedral environments, depending on the ligands.
- Cobalt(III) can be formed by oxidation using an appropriate choice of ligands and oxidizing agents.
- In addition to forming octahedral and tetrahedral complexes, nickel(II) forms a few square-planar complexes.
- Copper compounds are almost all in the +2 oxidation state.

## EXERCISES

**20.1** Write balanced equations for (a) the reaction between titanium(IV) chloride and oxygen gas; (b) sodium dichromate with sulfur at high temperature; (c) the warming of copper(II) hydroxide.

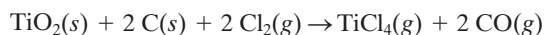
**20.2** Write balanced equations for (a) the reduction of vanadyl ion by zinc metal in acidic solution (two equations); (b) the oxidation of chromium(III) ion to dichromate ion by ferrate ion, which itself is reduced to iron(III) ion in acid solution (write initially as two half-equations); (c) the addition of excess hydroxide ion to copper(II) hydroxide; (d) the reaction between copper(II) ion and iodide ion.

**20.3** Discuss briefly how the stability of the oxidation states of the 3d transition metals changes along the row.

**20.4** Identify uses for (a) titanium(IV) oxide; (b) chromium(III) oxide; (c) silver nitrate.

**20.5** What evidence do you have that titanium(IV) chloride is a covalent compound? Suggest why this is to be expected.

**20.6** The equation for the first step in the industrial extraction of titanium is



Which element is being oxidized and which is being reduced in this process?

**20.7** Write balanced half-equations for the reduction of permanganate ion in (a) acidic solution; (b) basic solution.

**20.8** Aluminum is the most abundant metal in the Earth's crust. Discuss the reasons why iron, not aluminum, is the more important metal in the world's economy.

**20.9** Contrast how iron(II) chloride and iron(III) chloride are synthesized.

**20.10** In the purification of nickel metal, tetracarbonylnickel(0) is formed from nickel at a lower temperature, while the compound decomposes at a higher temperature. Qualitatively discuss this equilibrium in terms of the thermodynamic factors, enthalpy, and entropy.

**20.11** Identify each metal from the following tests and write balanced equations for each reaction: (a) Addition of chloride ion to a pink aqueous solution of this cation gives a deep blue solution. (b) Concentrated hydrochloric acid reacts with this metal to give a colorless solution. On dilution, a white precipitate is formed. (c) Addition of acid to this yellow anion results in an orange-colored solution.

**20.12** Identify each metal from the following tests and write balanced equations for each reaction: (a) Acidifying a solution of this cation gives a pale violet solution and, on addition of chloride ion, a yellow solution is formed. (b) Addition of ammonia to this pale blue cation gives a deep blue solution. (c) Addition of thiocyanate solution to this almost colorless cation gives a deep red color.

**20.13** A solution containing a colorless anion is added to a cold solution containing a pale yellow solution of a cation. A violet solution is formed that becomes colorless on warming to room temperature. Identify the ions and write a balanced chemical equation for each step.

**20.14** You wish to prepare a tetrahedral complex of vanadium(II). Suggest the best choice of a ligand (two reasons).

**20.15** The highest oxidation state for nickel in a simple compound is found in the hexafluoronickelate(IV) ion,  $[\text{NiF}_6]^{2-}$ . (a) Why would you expect fluoride to be the ligand? (b) Would you expect the complex to be high spin or low spin? Give your reasoning.

**20.16** When iron(III) salts are dissolved in water, a yellow-brown color is observed. Only after addition of a few drops of dilute nitric acid can the very pale purple color of the hexaaquairon(III) ion be seen. Explain.

**20.17** The ferrate(VI) ion,  $[\text{FeO}_4]^{2-}$ , is such a strong oxidizing agent that it will oxidize aqueous ammonia to nitrogen gas, itself being reduced to iron(III) ion. Write a balanced equation for the reaction.

**20.18** When iron(III) forms a complex with dimethylsulfoxide,  $(\text{CH}_3)_2\text{SO}$ , is the ligating atom likely to be the oxygen or the sulfur? Explain your reasoning.

**20.19** Of the two common oxides of chromium, chromium(VI) oxide and chromium(III) oxide, which should have the lower melting point? Explain your reasoning.

**20.20** Of the two common oxides of chromium, chromium(VI) oxide and chromium(III) oxide, which should be acidic? Explain your reasoning.

**20.21** Suggest why chromium(III) nitrate dissolves in water to form an acidic solution.

**20.22** There is only one simple anion of cobalt(III) that is high spin. Identify the likely ligand and write the formula of this octahedral ion.

**20.23** Suggest why copper(I) chloride is insoluble in water.

**20.24** Taking the Jahn-Teller effect into account, how many absorptions would you expect from d-electron transitions for the octahedral copper(II) ion?

**20.25** Use the Pourbaix diagrams in Figures 8.6 and 20.12 to suggest what is the most likely form of iron in (a) a well-aerated lake; (b) a lake suffering from the effects of acid rain; (c) bog water.

**20.26** Identify each of the following ions and write net ionic equations for each reaction: (a) A pale pink cation that gives a deep blue color with chloride ion. The cation gives a blue solid with hydroxide ion. (b) A yellow anion that gives a yellow precipitate with barium ion. Addition of acid to the anion causes a color change to orange. The orange anion is reduced by sulfur dioxide to give a green cation; the other product is a colorless anion that gives a white precipitate with barium ion. (c) A pale blue cation that reacts with zinc metal to give a red-brown solid. Addition of the pale blue cation to excess ammonia gives a deep blue color.

**20.27** What are the similarities and differences between aluminum and iron(III) chemistry?

**20.28** Identify which transition metal(s) is(are) involved in each of the following biochemical molecules: (a) hemocyanin; (b) ferredoxin; (c) vitamin B<sub>12</sub>.

**20.29** Write balanced chemical equations corresponding to each transformation in the element reaction flowcharts for titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper (pages 601–602).

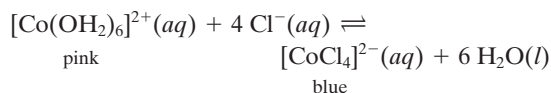
## BEYOND THE BASICS

**20.30** On the basis of the following thermodynamic data: (a) Calculate the equilibrium constant,  $K$ , for the formation of tetracarbonylnickel(0) from nickel and carbon monoxide under standard conditions. (b) Calculate the temperature above which the complex is favored, that is, when  $K$  becomes 1.00 or greater.

	$\Delta_f H^\circ$ (kJ·mol <sup>-1</sup> )	$S^\circ$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
Ni(s)	0.0	29.9
CO(g)	-110.5	197.7
[Ni(CO) <sub>4</sub> ](g)	-602.9	410.6

Explain how these calculations relate to the purification of nickel metal. Assume that  $\Delta H$  and  $S$  are temperature independent.

**20.31** Cobalt(II) undergoes the equilibrium



Suggest an explanation why addition of an anhydrous calcium compound to the mixture drives the equilibrium to the right, while addition of an anhydrous zinc compound drives the equilibrium to the left.

**20.32** Copper(I) fluoride crystallizes in a sphalerite structure, whereas copper(II) fluoride adopts a rutile structure. Calculate the enthalpy of formation of each of these compounds. What are the crucial terms in the respective Born-Haber cycles that contribute to the stability of each one? Qualitatively, what influence does the entropy of formation play in the feasibility of the reactions?

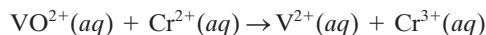
**20.33** When lead(II) ion is added to a solution of dichromate ion, lead(II) chromate precipitates. Using chemical equations, explain why this happens.

**20.34** Cobalt(II) perchlorate reacts with dimethylsulfoxide, (CH<sub>3</sub>)<sub>2</sub>SO, abbreviated DMSO, to form a pink compound that is a 1:2 (one cation to two anions) electrolyte in DMSO solution. Cobalt(II) chloride reacts with DMSO to give a 1:1 electrolyte. The cations are the same in both cases, but the anion in the latter compound also contains a complex ion of cobalt. Deduce the identity of the two compounds.

**20.35** (a) When potassium cyanide is added to aqueous nickel(II) ions, a green precipitate initially forms. What is the identity of the product? (b) Further addition of cyanide ion results in the dissolution of the precipitate to give a yellow solution. A salt can be isolated from the yellow solution. What is the identity of this product? What is the geometry

of the complex ion? (c) A large excess of potassium cyanide gives a red solution. Isolation of the product gives a compound that is a 3:1 electrolyte. What is the identity of the compound?

**20.36** For the (unbalanced) reaction



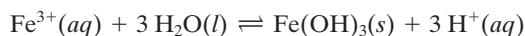
write a balanced redox equation, then use appropriate data tables to calculate the equilibrium constant and deduce a probable two-step mechanism for the process.

**20.37** Explain why: (a) Iron(III) perchlorate is soluble in water, whereas iron(III) phosphate is insoluble in water. (b) Complexes with the ligands  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are very common, whereas those of  $\text{PH}_3$  and  $\text{H}_2\text{S}$  are quite unusual. (c) Iron(III) bromide is more intensely colored than iron(III) chloride.

**20.38** Tungsten forms iodides of empirical formula  $\text{WI}_2$  and  $\text{WI}_3$ . What do you suggest is the likely product from the reaction of tungsten metal with fluorine gas? Give your reasoning.

**20.39** Nickel forms a compound of formula  $\text{NiS}_2$ . What are the probable oxidation states of nickel and sulfur? Give your reasoning.

**20.40** The precipitation of iron(III) hydroxide is used to clarify wastewaters because the gelatinous compound is very efficient at the entrapment of contaminants. Ignoring the many hydroxidoiron(III) species, we can write a simplified equilibrium as



(a) Using the ion product constant at  $25^\circ\text{C}$  of  $1.0 \times 10^{-14}$  and given the solubility product for iron(III) hydroxide as  $2.0 \times 10^{-39}$ , calculate the mathematical relationship between  $[\text{Fe}^{3+}]$  and  $[\text{H}^+]$ .

(b) If iron(III) hydroxide is used to clarify a water supply, what concentration of free iron(III) ion will enter the water system if the water supply has a pH of 6.00?

(c) What mass of iron(III) hydroxide will be dissolved during the passage of  $1 \times 10^6 \text{ L}$  of water?

**20.41** Dilute hydrochloric acid was added to a metallic-looking compound (A). A colorless gas (B) with a characteristic odor was formed together with a pale green solution of the cation (C).

The gas (B) was burned in air to give another colorless gas (D) that turned yellow dichromate paper green. Mixing (B) and (D) gave a yellow solid element (E). Depending on the mole ratios, (E) reacted with chlorine gas to give two possible chlorides, (F) and (G).

Addition of ammonia to a sample of the green cation solution (C) gave a pale blue complex ion (H). Addition of hydroxide ion to another sample of the green solution gave a green gelatinous precipitate (I). Addition of zinc metal to a third sample of the green solution gave a metal (J) that on drying could be reacted with carbon monoxide to give a compound (K) with a low boiling point.

Identify each of the substances and write balanced chemical equations for each reaction.

**20.42** When a very pale pink salt (A) is heated strongly, a brown-black solid (B) is produced; a deep brown gas (C) is the only other product. Addition of concentrated hydrochloric acid to (B) gives a colorless solution of salt (D), a pale green gas (E), and water. When the pale green gas is bubbled into a solution of sodium bromide, the solution turns brown. The yellow-brown substance (F) can be extracted into dichloromethane and other low-polarity solvents.

The brown solid (B) can also be produced when a deep purple solution of the anion (G) is reacted in basic solution with a reducing agent, such as hydrogen peroxide. The other product is a gas (H), which will relight a glowing splint. The anion of compound (A) does not form any insoluble salts, whereas the gas (C) is in equilibrium with colorless gas (I), the latter being favored at low temperatures.

Identify (A) through (I), writing balanced equations for each step.

**20.43** A transition metal, M, reacts with dilute hydrochloric acid in the absence of air to give  $\text{M}^{3+}(\text{aq})$ . When the solution is exposed to air, an ion,  $\text{MO}^{2+}(\text{aq})$ , is formed. Suggest the identity of metal M.

**20.44** When chromium(II) oxide,  $\text{CrO}$ , is synthesized from pure chromium and oxygen, the actual stoichiometry is found to be  $\text{Cr}_{0.92}\text{O}_{1.00}$ , yet the crystals are electrically neutral. Suggest an explanation.

**20.45** Suggest why 84 percent of all chromium atoms are the chromium-52 isotope.

**20.46** Iron(III) iodide has been synthesized in the total absence of air and water. Suggest a mechanism for the decomposition of this compound involving these two reagents.

**20.47** Chromium forms a variety of dimeric species such as the blue  $[(\text{H}_3\text{N})_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]^{4+}$  ion. What is the formal oxidation state of each chromium atom? The ion has a linear  $\text{Cr}-\text{O}-\text{Cr}$  arrangement. Suggest an explanation for this. If it existed, would the equivalent ion with cobalt instead of chromium probably be linear or bent? Explain.

**20.48** To stoichiometrically oxidize a particular solution of iron(II) ion to iron(III) ion, 20 mL of an acidified permanganate ion solution was required. However, in the presence of a large excess of fluoride ion, 25 mL of the permanganate ion solution was required. Suggest an explanation.

**20.49** Sulfur dioxide will reduce iron(III) ion to iron(II) ion in a solution acidified with a few drops of dilute hydrochloric acid. However, in a solution of concentrated hydrochloric acid, very little reduction occurs. Suggest an explanation.

**20.50** Copper(I) cyanide, although insoluble in water, dissolves in aqueous potassium cyanide. Write a balanced net ionic equation to explain why the solution process occurs.

**20.51** The colors of the silver halides are the result of charge transfer processes. Explain why the color becomes more intense in the order  $\text{Cl} < \text{Br} < \text{I}$ .

**20.52** A mixed nickel-cobalt oxide,  $\text{NiCo}_2\text{O}_4$ , is known but not  $\text{CoNi}_2\text{O}_4$ . Suggest an explanation.

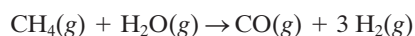
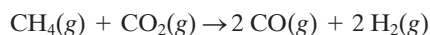
**20.53** The mineral braunite has the ideal composition  $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ . In fact, the ore usually contains small proportions of the following elements: aluminum, calcium, iron, and titanium. Suggest at which element/ion site each substituted element would probably be found.

**20.54** Manganese forms five common oxides:  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\text{Mn}_2\text{O}_7$ . (a) Calculate the oxidation number of manganese in each oxide. (b) Suggest an explanation for your answer for the oxidation number of manganese in  $\text{Mn}_3\text{O}_4$ . Which other transition metal forms an oxide

of this stoichiometry? (c) Which oxide should be basic? Which oxide should be strongly acidic? Give your reasoning. (d) Which common oxide of manganese has the same element-to-oxygen ratio as a common oxide of its main group analog, chlorine?

**20.55** The nickel-dimethylglyoxime complex is planar. From the structure (Figure 20.16), suggest a reason why planar geometry would be favored.

**20.56** Calculate the enthalpy change for the two methane re-forming reactions used for the production of direct-reduced iron:



**20.57** The iron produced by the DRI process is a low-density porous lump material. The high surface area makes it more reactive than bulk iron. DRI is usually stored in heaps open to the air. (a) Write a chemical equation for the reaction that will occur over the surface air-exposed layer. (b) A sodium silicate solution can be sprayed over the surface to minimize oxidation. Explain why this treatment is effective. (c) In 1996, there was a fire and explosion on a freighter carrying DRI. The DRI had begun to oxidize rapidly and exothermically. The crew had sprayed seawater over the DRI to cool it down. How would the water have reacted with the hot iron? What would have caused the explosion?

**20.58** Why is there so much nickel in the core of the Earth? Use Chapter 2, Section 2.3 to suggest an answer.

## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# PROPERTIES OF THE 4d AND 5d TRANSITION METALS

## CHAPTER 21

Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

The so-called heavy transition metals (those of the 4d and 5d periods) are often overlooked in the study of the transition metals. This is unfortunate since there is so much rich chemistry to be found among them. Whereas there are clear trends down each of the main groups, this is not the case with the transition metals. In most aspects of their chemistry, the metals of each 4d-5d pair are much more similar in properties than consecutive members of main groups and, at the same time, significantly different from the 3d member of the Group.

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 21.1** Comparison of the Transition Metals
- 21.2** Features of the Heavy Transition Metals
- 21.3** Group 4: Zirconium and Hafnium
- 21.4** Group 5: Niobium and Tantalum
- 21.5** Group 6: Molybdenum and Tungsten
- 21.6** Group 7: Technetium and Rhenium
- 21.7** The Platinum Group Metals
- 21.8** Group 8: Ruthenium and Osmium
- 21.9** Group 9: Rhodium and Iridium
- 21.10** Group 10: Palladium and Platinum
- 21.11** Group 11: Silver and Gold
- 21.12** Biological Aspects

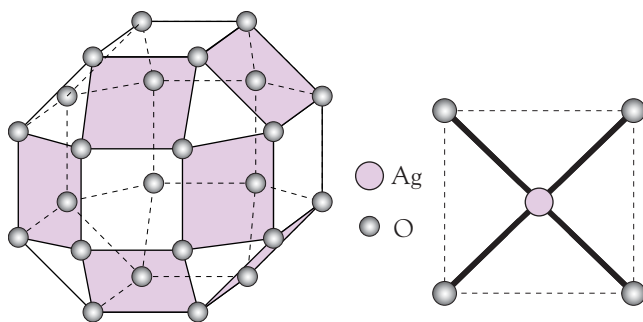
### Context: Bacteria and Viruses Beware! Silver Kills

The chemistry of silver (see Section 21.11) typifies two important aspects of 4d-5d transition metals: a wide range of oxidation states (for silver, +1, +2, and +3) and an ability to form cluster compounds. The compounds of silver are not only of academic interest, but also for their use in medicine as bactericides. Silver has well-established

antibacterial properties; in fact, in ancient Greece, silver coins were used to “purify” water. During World War I, wound dressings were impregnated with silver nitrate, but that was superseded as an antibacterial with the advent of antibiotics. More recently, drops of silver nitrate solution were placed in newborn babies’ eyes to prevent bacterial eye infections.

However, embedded silver nanoparticles in the size range of 1 to 50 nm have now become a popular method of controlling bacteria and viruses in products ranging from vacuum cleaners and washing machines to wound dressings and medical devices. This nanomaterial is also popular as a coating in antibacterial kitchenware, socks and other textiles, cleaning products and air filters, toothbrushes and toothpaste, and baby pacifiers and other baby products. In some countries, silver nanoparticles, in combination with titanium(IV) oxide coating, are applied to touchable surfaces in train stations, to railroad car interior surfaces, and to surfaces in shopping malls.

For wound-care products, even more effective than nanoparticle silver, is  $\text{Ag}_7\text{O}_8\text{NO}_3$ . This unusual stoichiometry consists of  $\text{Ag}_6\text{O}_8$  clusters with a nitrate ion trapped inside as a clathrate (see Chapter 10, Section 10.6). Thus, it is more accurately written as  $\text{Ag}^+[(\text{Ag}_6\text{O}_8)\text{NO}_3]^-$ . As we describe in Section 21.2, clusters are very common among the heavy transition metals. For the silver atoms in the cluster, five would have to be  $\text{Ag}^{3+}$  and the sixth an  $\text{Ag}^+$  ion. In reality, all the silver atoms are equivalent; thus, the charge seems to be distributed equally throughout the cluster. The clusters are linked into interlocking 26-hedra (see below), with the silver ions at the center of each square and the oxide ions at each corner. As we saw in Chapter 19, Section 19.7, a square-planar geometry is characteristic of  $d^8$  electron configurations, including silver(III).



(a)

Structure of the 26-hedron arrangement of oxide ions in  $\text{Ag}_6\text{O}_8$  clusters. A nitrate ion is trapped within each polyhedron.

(b)

Each square of the 26-hedron has the four oxide ions at the corners with a square-planar coordinated silver ion at the center.



## 21.1 Comparison of the Transition Metals

The heavy transition metals are differentiated from the 3d transition metals by being much denser and having significantly higher melting points. In fact, 10 of the 4d-5d metals have melting points above 2000°C and 3 above 3000°C (tantalum, tungsten, and rhenium), indicative of the strong metallic bonds within the structures. The densities increase as  $3d < 4d < 5d$ , with the highest values being those of osmium and iridium ( $23 \text{ g}\cdot\text{cm}^{-3}$ ). Chemically, the metals themselves are relatively unreactive, with later metals such as gold and platinum being particularly chemically inert.

One consistent factor found in each transition metal group is the increase in the crystal field splitting,  $\Delta$  (see Chapter 19, Section 19.7), from Period 4 to Period 6 elements. For example, in the series  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Rh}(\text{NH}_3)_6]^{3+}$ , and  $[\text{Ir}(\text{NH}_3)_6]^{3+}$ , the  $\Delta_{\text{oct}}$  values are 23 000, 34 000, and 41 000  $\text{cm}^{-1}$ , respectively. Because of the larger crystal field splittings for the 4d and 5d transition metals, almost all compounds of these elements are low spin.

A football made of iridium or osmium would have a mass of 320 kg.

### Ionic Radii

For the main group elements, there are clear trends down each group. For the transition metals, the 4d and 5d elements show very strong similarities in their chemistry within a group. This similarity is, to a large extent, a result of the filling of the 4f orbitals in the elements that lie between these two rows. Electrons in these orbitals are poor shielders of electrons in the outer 6s and 5d orbitals. With the greater effective nuclear charge, the atomic, covalent, and ionic radii of the Period 6 transition elements are reduced to almost the same as those in Period 5. This *lanthanoid contraction* is illustrated in Table 21.1, where the ionic radii of the Groups 2 and 5 metals are compared. The radii of the Group 2 metals increase down the group, whereas the niobium and tantalum ions have almost identical radii. It is the similarity in radii (and hence charge densities) that results in the strong resemblance in properties between the 4d and 5d members of a group.

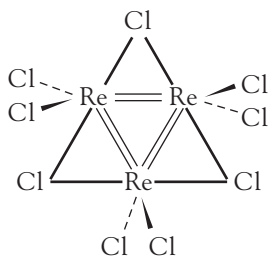
### Trends in Formulas

There are some superficial similarities in the chemistries of the 4d and 5d transition metals to those of the 3d elements. For example, chromium, molybdenum, and tungsten all form oxides with an oxidation number of +6.

**TABLE 21.1** Comparison of the metallic radii of the Group 2 and Group 5 metals

Group 2	Radius (pm)	Group 5	Radius (pm)
Calcium	194	Vanadium	171
Strontium	219	Niobium	198
Barium	253	Tantalum	200





**FIGURE 21.1** Structure of  $\text{Re}_3\text{Cl}_9$ .

However, parallel formulas can be misleading. For example, manganese forms manganese(III) fluoride,  $\text{MnF}_3$ , and rhenium forms an apparently analogous chloride,  $\text{ReCl}_3$ . However, the latter compound is actually  $\text{Re}_3\text{Cl}_9$  in which the three rhenium atoms are linked together by double covalent bonds (Figure 21.1). Such metal-bonded structures are called *metal cluster compounds* (see Section 21.2).

### Trends in Oxidation States

In Chapter 20, Section 20.1, we saw that for the 3d transition metals, the oxidation numbers are higher for the first half of each row than for the later members. Table 21.2 shows the common oxidation states for the 3d-4d-5d transition metal series. For Groups 4 to 7, although the preferred oxidation states do not differ significantly, it is the relative stability that does (see later). Among the later transition elements, higher oxidation states are found on descending the Group. As an example, osmium in Group 8 exhibits even the +8 oxidation state in some compounds, such as osmium(VIII) oxide,  $\text{OsO}_4$  (see Section 21.8).

**TABLE 21.2** Common oxidation states of the 3d-4d-5d transition metals

Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
+2, +3, +4	+2, +3, +4, +5	+3, +4, +6	+2, +3, +4, +7	+2, +3	+2, +3	+2	+1, +2
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
+4	+2, +4, +5	+2, +4, +6	+4, +7	+4	+3, +4	+2, +3	+1
Hf	Ta	W	Re	Os	Ir	Pt	Au
+4	+2, +4, +5	+4, +6	+3, +4, +6, +7	+4, +8	+3, +4	+2, +4, +6	+3

## 21.2 Features of the Heavy Transition Metals

As mentioned earlier, there is usually an abrupt change in chemical behavior between the 3d and 4d members of a group, while the 4d and 5d members tend to have very similar chemistries as a result of the lanthanoid contraction. The following subsections provide some examples of these behaviors.

### Comparative Stability of Oxidation States

Whereas the high oxidation states for the 3d transition metals are strongly oxidizing, those of the 4d and 5d metals are often the more stable oxidation states. For example, chromium(VI) oxide,  $\text{CrO}_3$ , is a powerful oxidizing agent, while molybdenum(VI) oxide,  $\text{MoO}_3$ , and tungsten(VI) oxide,  $\text{WO}_3$ , are the “normal” oxides of these metals. Conversely, the +2 state, which is often the most stable for the 3d metals, is rare for the earlier 4d and 5d metals.

**TABLE 21.3** The hexafluoro-anions in the +5 oxidation state of the heavy transition metals

Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11
$[\text{NbF}_6]^-$ $[\text{TaF}_6]^-$	$[\text{MoF}_6]^-$ $[\text{WF}_6]^-$	$[\text{TcF}_6]^-$ $[\text{ReF}_6]^-$	$[\text{RuF}_6]^-$ $[\text{OsF}_6]^-$	$[\text{RhF}_6]^-$ $[\text{IrF}_6]^-$	$[\text{PtF}_6]^-$	$[\text{AuF}_6]^-$

### Coordination Number

As we discussed in Chapter 20, four- and six-coordination is most common for the 3d transition metals. For the later heavy transition metals, six-coordination is also common. Stereochemistry and charge sometimes seem to be deciding factors in the existence and stability of ions over periodic trends in oxidation state. For example, all of the 5d transition elements from tantalum to gold form mono-negative octahedral fluorido-complexes in which the metal has a +5 oxidation state (Table 21.3).

Among the early 4d and 5d metal complexes, with the large size of the atoms, we find coordination numbers greater than six. For example, they all form octafluorido-anions with the highest oxidation state of the metal (Table 21.4).

### Metal Cluster Compounds

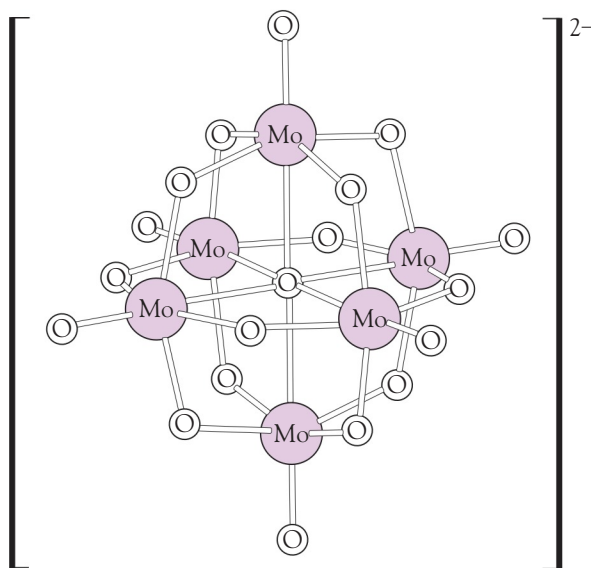
For the 3d metals, most of the common complexes are monomeric—a single metal ion or atom surrounded by ligands. For the early 4d and 5d metals particularly, cluster compounds are very common. Figure 21.2 shows the  $[\text{Mo}_6\text{O}_{19}]^{2-}$  cluster, with oxygen atoms linking six molybdenum atoms bonded to a central octahedrally coordinated oxygen atom.

### Quadruple Bonds

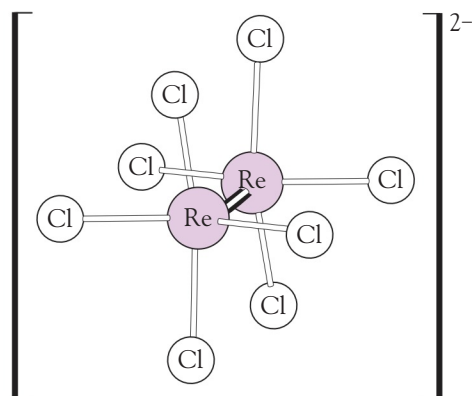
A feature of the mid 4d and 5d metals is the formation of quadruple metal-metal bonds. The first quadruple bond complex ion to be identified was  $[\text{Re}_2\text{Cl}_8]^{2-}$  (Figure 21.3). Quadruple bonds are now known to be particularly common among molybdenum and tungsten compounds, and since then iso-electronic  $[\text{W}_2\text{Cl}_8]^{4-}$  has been synthesized, together with  $[\text{Mo}_2\text{Cl}_8]^{4-}$ . The crystal structures shows that the chlorine atoms are locked in the eclipsed position, with no rotation about the quadruple bond.

**TABLE 21.4** The octafluoro-anions in the highest oxidation states of the early heavy transition metals

Group 4	Group 5	Group 6	Group 7
$[\text{ZrF}_8]^{4-}$ $[\text{HfF}_8]^{4-}$	$[\text{NbF}_8]^{3-}$ $[\text{TaF}_8]^{3-}$	$[\text{MoF}_8]^{2-}$ $[\text{WF}_8]^{2-}$	$[\text{ReF}_8]^-$



**FIGURE 21.2** Structure of the  $[\text{Mo}_6\text{O}_{19}]^{2-}$  ion.



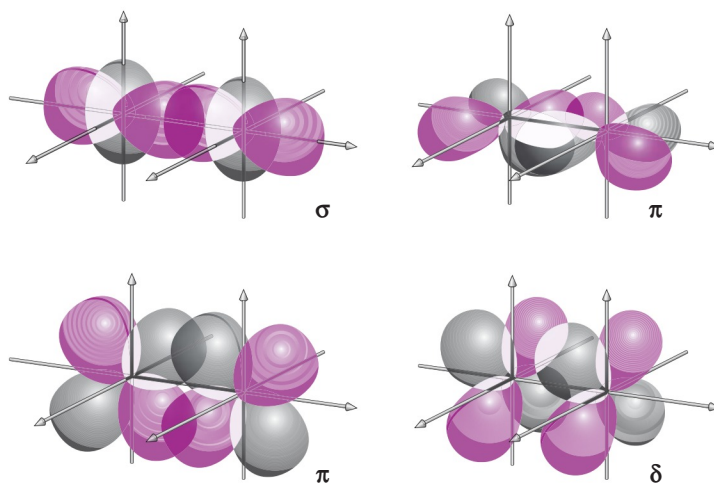
**FIGURE 21.3** Structure of the  $[\text{Re}_2\text{Cl}_8]^{2-}$  ion.

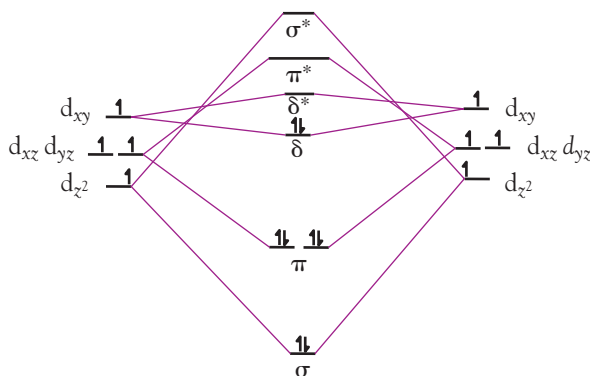
The bonding is believed to consist solely of d-orbital overlap. A  $\sigma$  bond can form by end-to-end overlap of  $d_{z^2}$  orbitals, a  $\pi$  bond can be formed by diagonal overlap of a pair of  $d_{xz}$  or  $d_{yz}$  orbitals, and a  $\delta$  bond can be formed by side-to-side overlap of a pair of  $d_{xy}$  orbitals (Figure 21.4).

A molecular orbital diagram can be constructed for the d orbitals involved in the quadruple metal-metal bond. Then the four electrons on each metal atom which occupy the atomic orbitals can be inserted. As is shown in Figure 21.5, the electrons will occupy the four lowest energy levels, each of which is a bonding molecular orbital: one  $\sigma$  bond, two  $\pi$  bonds, and one  $\delta$  bond.

For the isostructural  $[\text{Os}_2\text{Cl}_8]^{2-}$  ion, which has two more electrons, the bond length is greater (a triple bond) and the chlorine atoms are not locked in the

**FIGURE 21.4** Orbitals involved in the formation of the quadruple bond [computer-generated representations by Andrzej Okuniewski].





**FIGURE 21.5** Orbital energy levels involved in the formation of the quadruple bond.

eclipsed position. As can be seen from Figure 21.5, an added electron pair would occupy the  $\delta^*$  (antibonding) orbital, reducing the bond order from four to three. Without the  $\delta$  bond, with d orbitals, rotation about the Os—Os bond can occur.

### WORKED EXAMPLE 21.1

Rutherfordium, element 104, has to be synthesized atom-by-atom and all the known isotopes have very short half-lives. Nevertheless, it is possible to make some predictions about the chemical behavior of this element.

- What is the most likely oxidation state of rutherfordium in its compounds?
- What is the probable formula of its fluoro-anion?

#### Answer

Rutherfordium is in Group 4, therefore its chemistry should resemble that of zirconium and hafnium.

- +4
- $[\text{RfF}_8]^{4-}$  ■

## 21.3 Group 4: Zirconium and Hafnium

Zirconium is the fourth most common transition metal in the Earth's crust (only iron, titanium, and manganese are more abundant). Zirconium and hafnium are usually found together in ores, with the rarer hafnium constituting about 2 percent of the mixture, although the uncommon ore alvite,  $(\text{Hf,Zr})\text{SiO}_4 \cdot x\text{H}_2\text{O}$ , can sometimes contain more hafnium than zirconium.

### The Similarity of Zirconium and Hafnium

Of all the 4d-5d transition metal pairs, zirconium and hafnium are the most similar, having almost identical ionic radii. It was not until 1923 that chemists realized a second element lurked within the samples of zirconium and its compounds.

**TABLE 21.5** A comparison of titanium(IV), zirconium(IV), and hafnium(IV) species

	Very acidic	Acidic	Basic	Very basic
Titanium	$\text{TiO}^{2+}(\text{aq})$		$\text{TiO}_2(\text{s})$	
Zirconium	$\text{ZrO}^{2+}(\text{aq})$		$\text{ZrO}_2(\text{s})$	
Hafnium	$\text{HfO}^{2+}(\text{aq})$		$\text{HfO}_2(\text{s})$	

Zirconium and hafnium are both silvery lustrous metals with very high melting and boiling points. The only major difference is in density, where, like the other 4d-5d pairs, hafnium is much denser than zirconium ( $13.3 \text{ g}\cdot\text{cm}^{-3}$  compared with  $6.5 \text{ g}\cdot\text{cm}^{-3}$ ). Although the two metals are very chemically reactive, a tenacious coating of the respective oxide (analogous to aluminum; see Chapter 13, Section 13.6) makes zirconium useful as an alternative to stainless steel.

Zirconium metal is used to make containers for nuclear fuel because it has a low capture cross-section for neutrons; that is, it does not absorb the neutrons that propagate the fission process. By contrast, hafnium has a high capture cross-section. So for containers of the uranium used in the fission reaction, it is crucial to ensure that the zirconium metal has the lowest-possible hafnium content.

### Zirconium and Hafnium Chemistry

Not only is the chemistry of zirconium and hafnium similar, but uniquely for the 4d-5d Groups, the chemistry also resembles that of the 3d member of Group 4, titanium. For all three of the Group 4 metals, the only common oxidation state is +4, and over most of the pH range, the solid oxide is the predominant species (Table 21.5). Zirconium(IV) oxide exists in two crystal forms, baddleyite, in which the zirconium ion is seven-coordinate, and cubic zirconia, in which the zirconium ion is eight-coordinate zirconium ions, the fluorite structure (see Chapter 5, Section 5.8). The use of cubic zirconia as a gemstone instead of diamond was described in Chapter 14, Section 14.5.

#### WORKED EXAMPLE 21.2

Suggest two other stable metallic elements for which the  $\text{MO}_2$  oxide can be predicted. Give your reasoning.

#### Answer

The corresponding actinide to the Group 4 series, thorium, is likely to show a strong resemblance and should form  $\text{ThO}_2$  as its most stable oxide (see Chapter 9, Section 9.7)

Among the lanthanoids (Chapter 9, Section 9.8), cerium is the only metal to have a common oxidation state of +4 and to form the corresponding  $\text{CeO}_2$ . ■

## 21.4 Group 5: Niobium and Tantalum

Just as zirconium and hafnium are found together in ores, so niobium and tantalum are found together in the same mineral. The ore,  $(\text{Fe}^{2+}, \text{Mn}^{2+})(\text{Nb}^{5+}, \text{Ta}^{5+})_2(\text{O}^{2-})_6$ , is called *columbite* if it is richer in niobium and *tantalite* if it is richer in tantalum.

### Naming Element 41

The strong similarity between the two metals delayed the definite discovery of niobium. The discovery of a new element, columbium, was claimed in 1801, although this was possibly a mixture of niobium and tantalum. It was not until the 1860s that the element, named after the Niobe, daughter of Tantalus, of Greek mythology, was definitively identified. Element 41 retained the name *columbium* in the United States while Europe adopted *niobium*. In 1950, the name *niobium* was officially chosen by the International Union of Pure and Applied Chemistry (IUPAC). This was part of a nationalistic compromise: at the same time, IUPAC recommended the American preference of tungsten over the European preference for wolfram for element 74. Thus, each continent had its choice for one of the two elements. Nevertheless, the name *columbium* and the symbol Cb are still used in the United States, especially in mining and mineral contexts.

### Niobium and Tantalum Chemistry

Just as the chemistry of the 4d-5d Group 4 elements is dominated by the +4 oxidation state, so that of the heavier Group 5 elements is dominated by the +5 oxidation state. The +5 oxidation state is found for vanadium, too, as we saw in Chapter 20, Section 20.4. However, for vanadium, the +5 oxidation state is oxidizing, and compounds in the lower oxidation states are common. For niobium and tantalum, the +5 state is the predominant oxidation state.

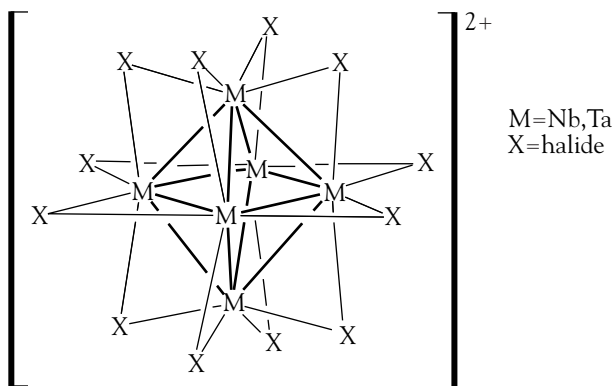
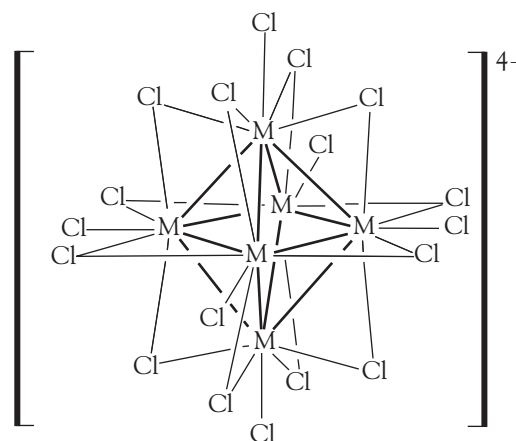
With these two elements, the chemical behavior shows a divergence; with the soluble anionic species  $[\text{Nb}_6\text{O}_{19}]^{8-}$  occurring in basic solution for niobium, while the insoluble oxide dominates across the common pH range for tantalum. What is interesting for this Group is that the  $(n)$  and  $(n + 10)$  relationship seems to have some validity for the lower members of Group 5 and Group 15. In particular, the chemistry of niobium(V) has some significant similarities to that of antimony(V). For example, antimony(V) also forms polymeric oxoanions in solution, and for both ions, the clusters involve shared  $[\text{MO}_6]$  octahedra. Table 21.6 summarizes the similarity of niobium(V) and antimony(V), in particular the amphoteric behavior of these two ions.

**TABLE 21.6** A comparison of niobium(V) and antimony(V) species

	Very acidic	Acidic	Basic	Very basic
Niobium		$\text{Nb}_2\text{O}_5(s)$		isopolyniobates(aq)
Antimony	$\text{Sb}_2\text{O}_5(s)$		isopolyantimonates(aq)	

**TABLE 21.7** A comparison of tantalum and bismuth species under oxidizing conditions

	Very acidic	Acidic	Basic	Very basic
Tantalum	$\text{Ta}_2\text{O}_5(s)$			
Bismuth	$\text{Bi}_2\text{O}_5(s)$			

**FIGURE 21.6** Structure of the  $[\text{M}_6\text{X}_{12}]^{2+}$  ion, where  $M = \text{Nb or Ta}$  and  $X = \text{halide}$ .**FIGURE 21.7** Structure of the  $[\text{M}_6\text{X}_{18}]^{2-}$  ion, where  $M = \text{Nb or Ta}$  and  $X = \text{a halogen}$ .

Just as there are similarities between the chemistry of niobium(V) and antimony(V), so there are similarities between the chemistry of tantalum(V) and bismuth(V). These two ions exhibit much more “metallic” behavior, with the insoluble oxide being the dominant species over the whole pH range (Table 21.7).

### Metal Cluster Compounds

The most interesting feature of these two metals is the formation of metal cluster halides. An example is the series of generic formula  $\text{M}_6\text{X}_{14}$ , where  $M$  is niobium or tantalum and  $X$  is a halide. In fact, the compounds have the true formulation of  $[\text{M}_6\text{X}_{12}]^{2+} \cdot 2\text{X}^-$ . The  $[\text{M}_6\text{X}_{12}]^{2+}$  cluster consists of an octahedron of metal atoms with the halogen atoms bridging each pair of metal atoms (Figure 21.6). This cluster is remarkably stable and can undergo oxidative addition to form  $[\text{M}_6\text{X}_{18}]^{2-}$  clusters, in which one halogen atom has attached terminally to each metal atom (Figure 21.7).

### WORKED EXAMPLE 21.3

In this section, the similarity of tantalum(V) and bismuth(V) is mentioned. Write the comparative noble gas core electron configurations of the  $\text{Ta}^{5+}$  and  $\text{Bi}^{5+}$  ions.

**Answer**

The noble-gas core electron configuration of tantalum would be expected to be  $[\text{Xe}]6s^24f^{14}5d^3$ .

Thus,  $\text{Ta}^{5+}$  would form by losing the outer 6s and 5d electrons to give  $[\text{Xe}]4f^{14}$ .

The noble-gas core electron configuration of bismuth would be expected to be  $[\text{Xe}]6s^24f^{14}5d^{10}6p^3$ .

Thus,  $\text{Bi}^{5+}$  would form by losing the outer 6s and 6p electrons to give  $[\text{Xe}]4f^{14}5d^{10}$ . ■

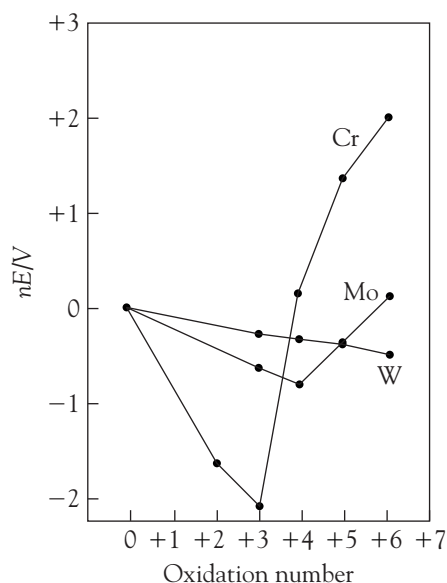
## 21.5 Group 6: Molybdenum and Tungsten

Unlike the other 4d-5d heavy metal pairs, molybdenum and tungsten are rarely found together in ores. Instead, molybdenum is usually found as molybdenite,  $\text{MoS}_2$ , while tungsten is found as the tungstate anion in scheelite,  $\text{CaWO}_4$ , and wolframite,  $(\text{Fe}, \text{Mn})\text{WO}_4$ . The formation of the sulfide by molybdenum might indicate it is a “softer” metal using the hard-soft acid-base (HSAB) concept than tungsten. The oxidation number of +6 is thermodynamically preferred for both these metals, but lower-oxidation-state compounds do exist.

Tungsten has the highest melting point of all metals ( $3422^\circ\text{C}$ ).

### Molybdenum and Tungsten Chemistry

In Chapter 20, Section 20.5, we showed that the +6 oxidation state for chromium in such species as the chromate ion,  $[\text{CrO}_4]^{2-}$ , is strongly oxidizing. By contrast, the molybdate ion,  $[\text{MoO}_4]^{2-}$ , and tungstate ion,  $[\text{WO}_4]^{2-}$ , are very stable in aqueous solution (Figure 21.8)



**FIGURE 21.8** A comparative generic Frost diagram for chromium, molybdenum, and tungsten in acid solution.



**TABLE 21.8** A comparison of molybdenum and tungsten species under oxidizing conditions

	Very acidic		Acidic	Basic	Very basic
Molybdenum	$\text{MoO}_2^{2+}(\text{aq})$	$\text{MoO}_3(\text{s})$	isopolymolybdates( $\text{aq}$ )	$[\text{MoO}_4]^{2-}(\text{aq})$	
Tungsten	$\text{WO}_3(\text{s})$		isopolytungstates( $\text{aq}$ )	$[\text{WO}_4]^{2-}(\text{aq})$	

The simple oxoanions only exist in basic solution. As the pH decreases, the anions polymerize. For example, decreasing the pH below 6, results in the formation of the  $[\text{Mo}_7\text{O}_{24}]^{6-}$  ion for molybdenum. Decreasing the pH further causes precipitation of the solid oxides. Then, in strongly acidic conditions, the molybdenum(VI) oxide dissolves to form the dioxomolybdenum(VI) ion,  $\text{MoO}_2^{2+}$ , analogous to the dioxouranium(VI) ion,  $\text{UO}_2^{2+}$ , a link between the chemistry of molybdenum and uranium previously discussed in Chapter 9, Section 9.7. The pH dependence of highly oxidized species is summarized in Table 21.8.

### Molybdenum(IV) Sulfide

Molybdenum(IV) sulfide, commonly called *molybdenum disulfide*, is the only industrially important compound of molybdenum. It is the common ore of the metal, and nearly half of the world's supply is in the United States, mostly in Colorado and New Mexico. The purified black molybdenum(IV) sulfide,  $\text{MoS}_2$ , has a layer structure of tetrahedrally coordinated molybdenum atoms linked by sulfide bridges that resembles graphite. This property has led to its use as a lubricant, both alone and as a slurry mixed with hydrocarbon oils.

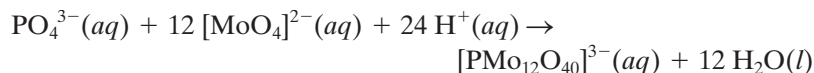
### Tungsten Bronzes

In Chapter 5, Section 5.6, we described the perovskite unit cell, which is common for oxides of formula  $\text{MM}'\text{O}_3$ , where M is a large, lower-charge cation and M' is a small, higher-charge cation. Sodium tungstate,  $\text{NaWO}_3$ , which adopts the perovskite structure, has very unusual properties. This compound can be prepared with less than stoichiometric proportions of sodium ion; that is,  $\text{Na}_x\text{WO}_3$ , where  $x < 1$ . The stoichiometric tungstate is white, but as the mole proportion of sodium drops to 0.9, it becomes a metallic golden yellow. As the proportion drops from 0.9 to 0.3, colors from metallic orange to red to bluish black are obtained. This material and its relatives, called the *tungsten bronzes*, are often used for metallic paints.

Not only do the compounds look metallic but also their electrical conductivity approaches that of a metal. In the crystal, increasing proportions of the cell centers, where the large alkali metal would be found, are vacant. As a result, the conduction band, which in the stoichiometric compound would be full, is now partially empty. In these circumstances, electrons can move through the  $\pi$  system along the cell edges by using tungsten ion d orbitals and oxide ion p orbitals. It is this electron mobility that produces the color and the electrical conductivity.

### Heteropolymolybdates and Heteropolytungstates

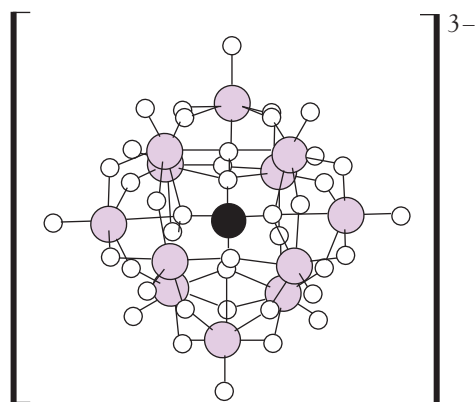
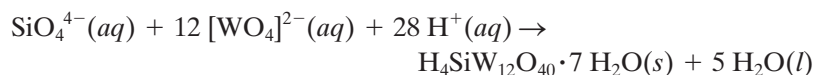
Just as silicates can form clusters of  $\text{SiO}_4$  tetrahedra to give polysilicates (see Chapter 14, Section 14.15), so molybdates,  $[\text{MoO}_4]^{2-}$ , and tungstates,  $[\text{WO}_4]^{2-}$ , can form clusters of octahedral  $\text{MO}_6$  units. What is particularly interesting about this class of clusters is that they can incorporate within them a hetero-ion, such as phosphate,  $\text{PO}_4^{3-}$ , and silicate,  $\text{SiO}_4^{4-}$ . For example, mixing molybdate and phosphate ions and acidifying give the phosphomolybdate ion,  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ :



The structure of the phosphomolybdate ion is shown in Figure 21.9. The phosphorus(V) sits in a tetrahedral hole, surrounded by four oxygens, in the center of the cluster. The heteropoly-ions are sometimes called *Keggin clusters* after J. F. Keggin, who first determined their structures. The 1:12 clusters are formed by both molybdenum and tungsten, while the hetero-ion can be any small ion that can fit into the tetrahedral hole.

The formation of the phosphomolybdate is a useful test for the qualitative and quantitative analysis of phosphate ion; the intensity of the yellow color indicates the concentration of the complex ion. Alternatively, addition of a reducing agent reduces some of the molybdenum(VI) ions to molybdenum(V). With the resulting charge defects, the ion becomes very deep blue—the *heteropoly-blues*—a very sensitive test for phosphate.

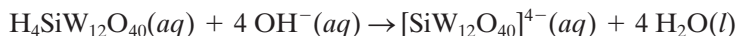
The salts of small cations and the parent acids are very water soluble, while salts of the larger cations, such as cesium and barium, are insoluble. With the 3- or 4-ion charge delocalized over such an enormous cluster, the low charge density results in the acid being very strong and the conjugate base essentially neutral. The heteropoly-acid itself can be synthesized at very low pH. The compound 12-tungstosilicic acid is one of the simplest to prepare:



Phosphomolybdate salts are good flame retardants on fabrics.

**FIGURE 21.9** Structure of the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  ion.

The acid can then be titrated against sodium hydroxide like any typical strong acid:



## 21.6 Group 7: Technetium and Rhenium

As mentioned in Chapter 2, Section 2.3, technetium is the only transition element for which no stable isotopes exist. One artificially synthesized isotope, technetium-99, has a long half-life of  $2 \times 10^5$  y. Considerable quantities have been synthesized, and with such a long half-life, the radiation is low enough that the chemistry of the isotope can be studied in a conventional laboratory. Technetium has medical uses in radiotherapy and radioimaging.

Rhenium, the last element to be discovered for which stable isotopes exist, is found in concentrations of up to 0.2 percent in molybdenite,  $\text{MoS}_2$ . This kind of “diagonal relationship” (see Chapter 9, Section 9.5) between a 4d transition metal and the 5d metal of the following group may be a result of the similar atom radius (190 pm for molybdenum and 188 pm for rhenium). The inclusion of rhenium(IV) within molybdenum(IV) sulfide is also a reflection of the fact that, like manganese, rhenium readily forms the +4 oxidation state (together with +6 and +7).

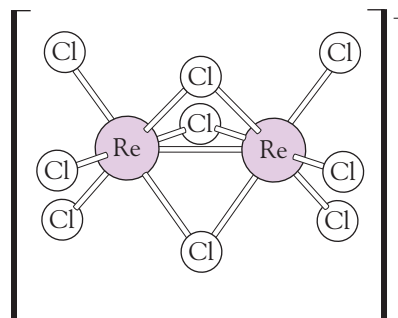
### Rhenium-Rhenium Bonds

In Section 21.2, we described how rhenium forms a quadruple-bonded blue  $[\text{Re}_2\text{Cl}_8]^{2-}$  species. Much of rhenium chemistry in its lower oxidation states involves compounds containing rhenium-rhenium bonds; for example, addition of chlorine to  $[\text{Re}_2\text{Cl}_8]^{2-}$  gives  $[\text{Re}_2\text{Cl}_9]^-$  with a very different structure: a single  $\text{Re}-\text{Re}$  bond and three chlorine atoms bridging the two rhenium atoms (Figure 21.10).

### Rhenium Diboride

The search for new superhard materials has traditionally focused on borides, carbides, and nitrides of the lighter elements. This changed with the synthesis of rhenium diboride,  $\text{ReB}_2$ , in 2007. Not only is the compound almost as hard as

**FIGURE 21.10** Structure of the  $[\text{Re}_2\text{Cl}_9]^-$  ion.

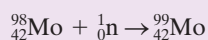


## Technetium: The Most Important Radiopharmaceutical

The inside of a human body can be imaged in several different ways, such as with magnetic resonance imaging (MRI). However, it is particularly useful to be able to highlight a particular location of interest, such as a specific organ or a tumor. Metal compounds play a valuable role since they often concentrate in certain organs or in tumors. The reason why they concentrate in tumors is not well understood but probably relates to the increased metabolism and altered chemistry of the tumor cells.

To be an effective radioactive isotope for diagnostic imaging, the nucleus must be a gamma emitter with a half-life long enough that the isotope can be produced and inserted into the patient's body before much has decayed. However, the half-life must be short enough that the emission intensity is measurable at very low concentrations. A short half-life also means that the patient is exposed to the radiation for only a brief period. A half-life of less than eight days is preferable. The nuclear excited-state technetium-99m fits this role superbly, and it is used for over 80 percent of all radiodiagnostics.

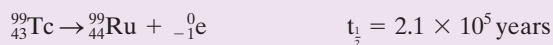
The technetium is obtained as the pertechnetate ion,  $[\text{TcO}_4]^{2-}$ , from the radioactive decay of the molybdate ion,  $[\text{MoO}_4]^{2-}$ . The synthesis is as follows. Nonradioactive molybdenum-98 is placed in a neutron source to give radioactive molybdenum-99:



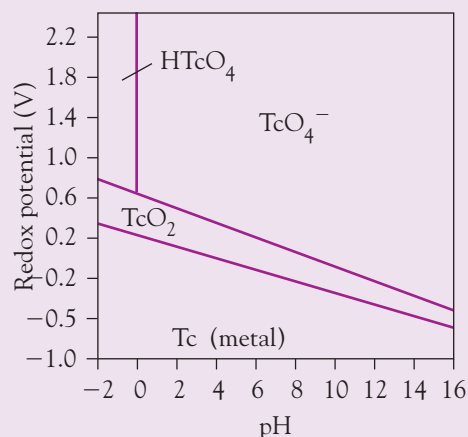
Molybdenum-99 decays with a half-life of 66 hr to technetium-99m, the *m* indicating that the technetium-99 is in a nuclear excited state. That is, just as electrons can be in excited states and release visible, ultraviolet, or infrared electromagnetic radiation as the electron descends to the ground state, so the proton formed in the nuclear decay is in an excited state and emits a gamma ray as it drops to the nuclear ground state. It is the emission of the gamma ray that is recorded in the radiodiagnostic procedure.



The ground-state technetium-99 has such a long half-life that the radiation level is low enough to be a negligible hazard:

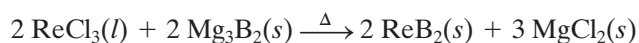


Although the nuclear chemistry is of great importance in diagnostic imaging, the aqueous chemistry is also crucial. The technetium must be in forms that are soluble in body fluids. These fluids are typically near neutral and slightly oxidizing. The Pourbaix diagram in Figure 21.11 shows that the pertechnetate ion is stable over much of the physiologically relevant range. This is unlike the element above it in the periodic table, manganese, where most of the physiological range is occupied by insoluble oxides and hydroxides and the permanganate ion is only stable under highly oxidizing conditions.



**FIGURE 21.11** Pourbaix diagram for technetium. [From W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life* (New York: Wiley-VCH, 1994), ch. 18, p. 360.]

diamond, it is remarkably easy to synthesize without resorting to ultrahigh pressures and temperatures. For example, it can even be synthesized in a high-temperature double-replacement reaction, with the magnesium chloride removed subsequently by washing with water:



Rhenium diboride is a metallic-looking material with a high density close to that of rhenium itself since the boron atoms fit in the interstices between the rhenium atoms. The hardness comes from the very strong covalent bonds, which are almost nonpolar, since rhenium and boron have similar electronegativities.

### WORKED EXAMPLE 21.4

Calculate the theoretical oxidation state of rhenium in  $[\text{Re}_2\text{Cl}_8]^{2-}$  and  $[\text{Re}_2\text{Cl}_9]^-$ .

#### Answer

For  $[\text{Re}_2\text{Cl}_8]^{2-}$

$$2[(N_{\text{ox}}(\text{Re})) + 8[(N_{\text{ox}}(\text{Cl}))] = -2$$

As chlorine, the more electronegative element will have its  $-1$  oxidation state:

$$2[(N_{\text{ox}}(\text{Re})) + 8[-1] = -2$$

$$[(N_{\text{ox}}(\text{Re}))] = +3$$

For  $[\text{Re}_2\text{Cl}_9]^-$

$$2[(N_{\text{ox}}(\text{Re})) + 9[(N_{\text{ox}}(\text{Cl}))] = -1$$

$$2[(N_{\text{ox}}(\text{Re})) + 9[-1] = -1$$

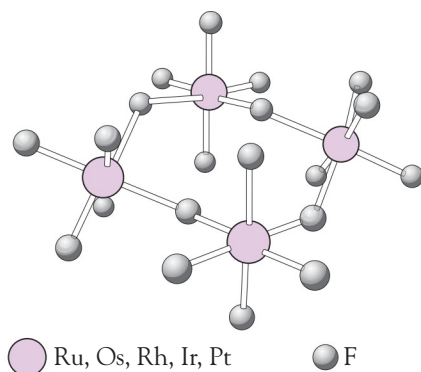
$$[(N_{\text{ox}}(\text{Re}))] = +4 \blacksquare$$

## 21.7 The Platinum Group Metals

Under the old nomenclature system, Groups 8, 9, and 10 were collectively called Group VIII. This made chemical sense, for ruthenium, osmium, rhodium, iridium, palladium, and platinum share enough common chemistry to have the collective name the *platinum metals*. The platinum metals are very inert to all but the most extreme reagents, such as *aqua regia*, a mixture of concentrated hydrochloric and nitric acids. As a result of the platinum metals' lack of chemical reactivity, they are sometimes called the *noble metals*, by analogy with the noble gases.

One source of all these metals is the nickel deposit at Sudbury, Ontario, Canada. This deposit resulted from a 10-km meteorite impact that occurred 1.85 billion years ago. Even though the platinum metals are present in very small concentrations, so much nickel is mined that significant quantities of the platinum metals are extracted. These “soft” metals are usually found as sulfides and arsenides, such as sperrylite,  $\text{PtAs}_2$  (see Chapter 7, Section 7.7). The annual total production is about 300 tonnes.

These elements are all unreactive, silvery, lustrous metals, some of which are used to produce jewelry and bullion coinage, but most are used in the chemical industry as catalysts for various reactions, as we discuss in Chapter 23, Section 23.17. The densities of these metals show a strong horizontal relationship: the 4d platinum metals have densities of about  $12 \text{ g}\cdot\text{cm}^{-3}$ , whereas the



**FIGURE 21.12** Structure of  $M_4F_{20}$ , where  $M = \text{Ru, Os, Rh, Ir, or Pt}$ .

densities of the 5d metals are about  $21 \text{ g}\cdot\text{cm}^{-3}$ . The melting points of the platinum metals are also high, with values ranging from 1500 to 3000°C.

One of the several similarities among the platinum metals is the fluorides with the generic empirical formula  $MF_5$ . In fact, these fluorides are all isostructural (but not isoelectronic) tetramers,  $M_4F_{20}$ , where  $M$  is ruthenium, osmium, rhodium, iridium, or platinum. The fluorine-bridged, eight-member ring structure of these compounds is shown in Figure 21.12.

## 21.8 Group 8: Ruthenium and Osmium

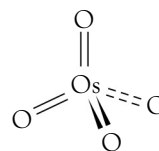
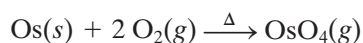
Although all the platinum metals have many similarities, in their chemical compounds ruthenium and osmium behave more like a continuation of the earlier transition metals, with their highest oxidation state +8, the  $d^0$  electron configuration. In fact, the only important compound of osmium is osmium(VIII) oxide,  $\text{OsO}_4$ .

### Osmium(VIII) Oxide

Osmium(VIII) oxide, usually called *osmium tetroxide*, has many similarities to xenon tetroxide (another example of the Group ( $n$ ) and ( $n + 10$ ) parallel; see Chapter 9, Section 9.4). Like the xenon analog, the  $\text{OsO}_4$  molecule has a tetrahedral geometry with osmium-oxygen double bonds (Figure 21.13).

The compound is a pale yellow solid that melts at 40°C and boils at 130°C. It has a high vapor pressure at room temperature, resulting in an ozone-like odor. The vapor is highly poisonous, even at low exposure levels, and in particular, inhalation at concentrations well below those at which a smell can be perceived can lead to pulmonary edema and subsequent death. Chronic exposure to very low levels of osmium(VIII) oxide can result in vision abnormalities, particularly seeing “halos” around light sources, as a result of the reaction of the compound with the cornea.

Heating osmium metal in oxygen gas provides a simple synthetic method, the vapor being collected and cooled to form the pure solid compound:



**FIGURE 21.13** Structure of  $\text{OsO}_4$ .

Osmium(VIII) oxide is widely used in organic synthesis, particularly to oxidize alkenes to diols, adding two hydroxyl groups on the same side (*syn* addition). The compound is also a widely used staining agent in transmission electron microscopy (TEM) to provide contrast to the image. As a lipid stain, it is also useful in scanning electron microscopy (SEM).

### WORKED EXAMPLE 21.5

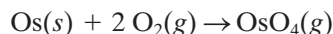
Calculate the Os—O bond energy, given:

$$\Delta_{\text{sublimation}}H(\text{Os}(s)) = 782 \text{ kJ}\cdot\text{mol}^{-1}; \text{O}=\text{O} \text{ bond energy} = 496 \text{ kJ}\cdot\text{mol}^{-1};$$

$$\Delta_f H^\circ(\text{OsO}_4(g)) = -337 \text{ kJ}\cdot\text{mol}^{-1}$$

Comment upon the value.

#### Answer



$$\Delta_f H^\circ(\text{OsO}_4(g)) = [\Delta_{\text{sublimation}}H(\text{Os}(s))] + 2[\text{B.E. O}=\text{O}] - 4[\text{B.E. Os}=\text{O}]$$

$$4[\text{B.E. Os}=\text{O}] = [782 \text{ kJ}\cdot\text{mol}^{-1}] + [992 \text{ kJ}\cdot\text{mol}^{-1}] - [-337 \text{ kJ}\cdot\text{mol}^{-1}]$$

$$= 528 \text{ kJ}\cdot\text{mol}^{-1}$$

This is a very high bond energy and suggests that the Os—O bond is about a double bond in strength. ■

## 21.9 Group 9: Rhodium and Iridium

Of the platinum metals, the chemistries of rhodium, iridium, palladium, and platinum are much closer to one another than to the chemistry of ruthenium and osmium. For example, the highest oxidation state for both Group 9 and Group 10 platinum metals is +6 instead of the group number, and the lower oxidation states are the “normal” ones.

Both rhodium and iridium readily form complexes with the +3 oxidation state, which, like the cobalt analogs, are kinetically inert. Also closely resembling the 3d member of the group, rhodium and iridium both form simple aqueous ions  $[\text{M}(\text{OH}_2)_6]^{3+}$ , where M = Rh or Ir. However, it is with these later groups of elements that we also find the most noticeable differences between the 4d and 5d members; for example, the +4 oxidation state is quite common for iridium but rare for rhodium.

## 21.10 Group 10: Palladium and Platinum

The most common oxidation states for palladium and platinum are +2 and +4 (isoelectronic with the +1 and +3 states of rhodium and iridium, respectively). In the +2 state, the complexes are square planar; thus, their aqueous ions are  $[\text{M}(\text{OH}_2)_4]^{2+}$ , where M = Pd or Pt. As we mentioned in Section 21.1, with the 4d and 5d transition metals, formulas are not always what they seem, and as

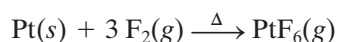
another example, palladium forms a fluoride of empirical formula  $\text{PdF}_3$ , which is actually palladium(II) hexafluoridopalladate(IV),  $(\text{Pd}^{2+})[\text{PdF}_6]^{2-}$ .

### Palladium Hydrides

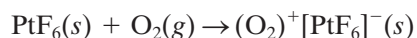
Palladium has the unusual property of absorbing hydrogen gas; in fact, it can reversibly absorb 900 times its own volume of hydrogen. In the crystal, palladium adopts a face-centered cubic lattice. As the hydrogen molecules are absorbed, they dissociate into atoms and rapidly diffuse through the structure, each hydrogen atom occupying an octahedral hole in the palladium lattice. Metallic conductivity slowly decreases with increasing hydrogen absorption until at about  $\text{PdH}_{0.5}$ , the substance becomes a semiconductor. The maximum absorption corresponds to an empirical formula of about  $\text{PdH}_{0.7}$ . The palladium-hydrogen standard reference electrode is now favored over the traditional platinum-hydrogen electrode since the former does not require continuous bubbling of hydrogen gas over the electrode surface, the hydrogen being internally absorbed instead.

### Platinum(VI) Fluoride

We discussed platinum(VI) fluoride in the context of the discovery of the first noble gas compounds (see Chapter 18, Section 18.4). The compound is a dark-red solid which melts at  $61^\circ\text{C}$  and boils at  $69^\circ\text{C}$  to give a deep red gas. It is simply formed by reacting platinum metal and fluorine gas:



Platinum(VI) fluoride is one of the strongest oxidizing agents known, even oxidizing molecular oxygen to the oxygenyl ion, itself being reduced to the more stable hexafluoridoplatinate(V) ion:



The fact that platinum(VI) fluoride was capable of removing an electron from dioxygen led to the realization that the ionization energy of xenon had about the same value as that of dioxygen. It was the successful reaction of platinum(VI) fluoride with xenon gas which led to the synthesis of the first proven compound of the noble gases (As it transpired, the reaction with xenon was not as simple as that with dioxygen and instead a mixture of compounds, including  $[\text{XeF}]^+[\text{PtF}_5]^{-}$ , is formed).

## 21.11 Group 11: Silver and Gold

Copper, silver, and gold are sometimes called the *coinage metals* because historically they were the three metals used for this purpose. The reasons for this were fourfold: they can be found in the metallic state; they are malleable, so disks of the metal can be stamped with a design; they are quite unreactive chemically; and, in the cases of silver and gold, the comparative rarity of the metals meant that the coins had the intrinsic value of the metal itself.



**TABLE 21.9** Similarity of the pH dependence of the silver(I) and thallium(I) species

	Very acidic	Acidic	Basic	Very basic
Silver	$\text{Ag}^+(aq)$		$\text{Ag}_2\text{O}(s)$	$\text{AgO}^-(aq)$
Thallium	$\text{Tl}^+(aq)$			$\text{TlO}^-(aq)$

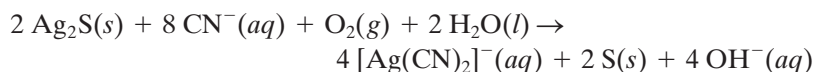
In Chapter 20, Section 20.11, we mentioned that the yellow color of copper results from visible-region electron absorptions from the d band to the s-p band. The band separation in silver is greater, and the absorption is in the ultraviolet part of the spectrum. Relativistic effects (see Chapter 2, Section 2.5) lower the s-p band energy in the case of gold, again bringing the absorption into the blue part of the visible range, resulting in the characteristic yellow color.

### Silver

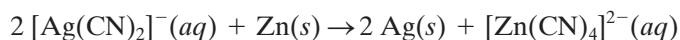
The chemistry of silver is dominated by the  $d^{10} \text{Ag}^+$  ion. As a result, silver often behaves more like a main group metal, and in its chemistry, it has many similarities to thallium (see Chapter 9, Section 9.8). For example, under weakly oxidizing conditions, Table 21.9 shows the similar pH dependence of the silver(I) and thallium(I) species.

### Extraction of Silver

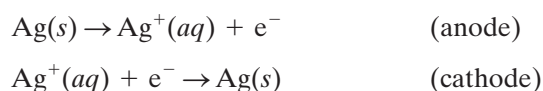
Silver is found mostly as the free element and as silver(I) sulfide,  $\text{Ag}_2\text{S}$ . Significant amounts of silver are also obtained during the extraction of lead from its ores and from the electrolytic refining of copper. One method of extraction of the metal involves the treatment of pulverized silver(I) sulfide with an aerated solution of sodium cyanide, a process that extracts the silver as the dicyanidoargentate(I) ion,  $[\text{Ag}(\text{CN})_2]^-$ :



Addition of metallic zinc causes a single replacement reaction in which the very stable tetracyanidozincate ion,  $[\text{Zn}(\text{CN})_4]^{2-}$ , is formed:



The pure metal is obtained by electrolysis, using an electrolyte of acidified silver nitrate solution with the impure silver as the anode and a strip of pure silver as the cathode:

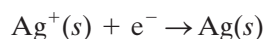


As discussed in the opening chapter Context section, silver metal is used increasingly for its antibacterial properties. Of concern, laws are lacking to control the use of nanomaterials—particularly nanosilver. Existing regulatory

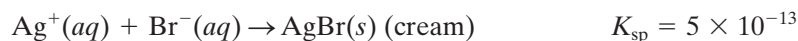
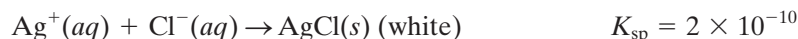
systems fail to treat nanomaterials as new chemicals and remain based on the flawed assumption that the hazard of nanomaterials can be predicted from the same materials in their bulk form. For this reason, a large group of leading nanotoxicologists have called for nanomaterials to be screened using particle number and surface area in addition to mass as critical dose characteristics. Until this is done, nanosilver particles will enter the environment, where they may have negative effects, such as killing the anaerobic bacteria that are essential for the breakdown of wastes in landfills.

## Silver Halides

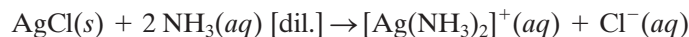
In almost all the simple compounds of silver, the metal has a +1 oxidation number, and the  $\text{Ag}^+$  ion is the only water-stable ion of the element. Hence, it is common to write “silver” for “silver(I).” The insolubility of silver chloride, bromide, and iodide was explained in terms of covalent character in Chapter 5, Section 5.3. The silver fluoride,  $\text{AgF}$ , is a white, water-soluble solid and is considered to be ionic in both solid and aqueous solution. Silver chloride, bromide, and iodide are sensitive to light, and the ready reduction of the silver ion results in a darkening of the solid (which is why silver compounds and their solutions are stored in dark bottles):



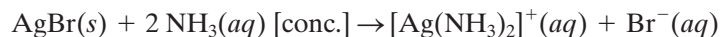
In the laboratory, a standard solution of soluble silver nitrate is used to test for the presence of chloride, bromide, and iodide ion. In qualitative analysis, the halide can be identified by color:



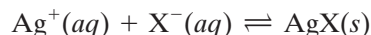
Because the intensity of the color depends on particle size, it can be difficult to differentiate chloride from bromide or bromide from iodide. Hence, there is a secondary confirmatory test. This test involves addition of dilute ammonia solution. Silver chloride reacts with dilute ammonia solution to give the diamminesilver(I) ion:



Silver bromide is only slightly soluble, and silver iodide is insoluble in dilute ammonia. However, silver bromide will react with concentrated ammonia:



To understand this difference in behavior, we must compare the equation for the precipitation reaction (where X is any of the halides) with the equation for the complexation reaction:



There are two competing equilibria for the silver ion. In qualitative terms, it is the one with the larger equilibrium constant that will predominate. Hence, in the case of very insoluble silver iodide, it is the precipitation equilibrium that will dominate. Conversely, the more soluble silver chloride will result in a silver ion concentration high enough to drive the complexation reaction to the right.

## Gold

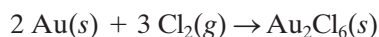
With its very high reduction potential, this element is usually found in nature as the free metal. Because gold is a very soft acid, the gold minerals that are known, such as calaverite,  $\text{AuTe}_2$ , and sylvanite,  $\text{AuAgTe}_4$ , involve the very soft base tellurium. For extraction of metallic gold from rock, the same cyanide process as that for silver metal is used.

The element forms a wide variety of complexes but few simple inorganic compounds. Gold(I) oxide,  $\text{Au}_2\text{O}$ , is one of the few stable gold compounds in which the metal has an oxidation number of +1. Like copper, this oxidation state is only stable in solid compounds because aqueous solutions of all gold(I) salts disproportionate to gold metal and gold(III) ions:



## Gold(III) Chloride

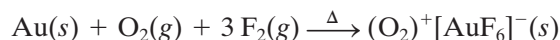
One of the most common compounds of gold is gold(III) chloride,  $\text{Au}_2\text{Cl}_6$ , which has a chlorine-bridged structure analogous to that of aluminum chloride (see Chapter 13, Section 13.7) though the geometry around the gold atoms is square planar. It can be prepared simply by reacting the two elements together:



Dissolving gold(III) chloride in concentrated hydrochloric acid gives the tetrachloridoaurate(III) ion,  $[\text{AuCl}_4]^-$ , an ion that is one of the components in “liquid gold,” a solution of gold species with thiol ligands that will deposit a film of gold metal when heated.

## The Hexafluoridoaurate(V) Ion

Gold, in its chemistry, has more resemblance to the platinum metals than to the other members of Group 11. For example, like platinum (and the other 5d transition metals; see Section 21.2), gold forms a hexafluoridoaurate(V) ion. The dioxygenyl salt,  $(\text{O}_2)^+[\text{AuF}_6]^-$ , can be isolated, analogous to  $(\text{O}_2)^+[\text{PtF}_6]^-$ :



The fluoridokrypton compound can also be prepared:



To diminish the need for summer air conditioning, the windows in some high-rise office buildings are coated with a reflective layer of  $10^{-11}$  m of gold.

**WORKED EXAMPLE 21.6**

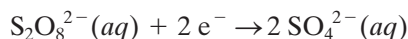
Silver(I) ion can be oxidized to silver(II) ion by the peroxodisulfate ion (usually in the presence of a complexing ligand, which will be ignored here). Write a balanced net ionic equation for the reaction.

**Answer**

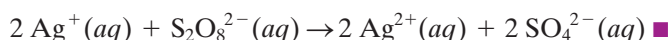
The oxidation step will be:



The peroxodisulfate ion (a strong oxidizing agent) is reduced to the sulfate ion (see Chapter 16, Section 16.19).



The net ionic equation will be:

**WORKED EXAMPLE 21.7**

In an earlier section, we mention that the gold(III) ion has similarities in its chemistry to the aluminum(III) chemistry. Another similarity is in the gold species which predominate under highly oxidizing conditions over the middle of the pH range and under very basic conditions. By comparison with aluminum(III), what would these two species be?

**Answer**

Aluminum exists as  $\text{Al}_2\text{O}_3$  over the central pH range and as  $[\text{Al}(\text{OH})_4]^-$  in very basic conditions (see Chapter 13, Section 13.6). Gold, therefore, should be present as  $\text{Au}_2\text{O}_3$  under highly oxidizing conditions over most of the pH range and as  $[\text{Au}(\text{OH})_4]^-$  in very basic solution.  $\blacksquare$

## 21.12 Biological Aspects

### Molybdenum

Molybdenum is the most biologically important member of Group 6. It is the heaviest (highest atomic number) element to have a wide range of functions in living organisms. Dozens of enzymes are known to rely on molybdenum, which is usually absorbed as the molybdate ion,  $[\text{MoO}_4]^{2-}$ . The most crucial molybdenum enzyme (which contains iron as well) is nitrogenase. This family of enzymes occurs in bacteria that reduce the “inert” dinitrogen of the atmosphere to ammonia, which is used in protein synthesis by plants. Some of these bacteria have a symbiotic relationship with the leguminous plants forming nodules on the roots. These bacteria process about  $2 \times 10^8$  tonnes of nitrogen per year in the soils of this planet! We discussed the  $\text{Fe}_7\text{MoS}_9$  core of the nitrogenase enzyme in the Context section of Chapter 8.

**TABLE 21.10** Some common molybdopterin enzymes

Name	Metal atoms per molecule	Source
Sulfite reductase	2 Mo	Mammalian livers
Nitrate reductase	2 Mo, 2 Fe	Plants, fungi, algae, bacteria
Trimethylamine N-oxide reductase	2 Mo, 1 Fe, $1\frac{1}{2}$ Zn	<i>Escherichia coli</i>
Xanthine oxidase	2 Mo, 4 Fe <sub>2</sub> S <sub>2</sub>	Cow's milk, mammalian liver, kidney
Formate dehydrogenase	Mo, Se, Fe <sub>n</sub> S <sub>n</sub>	Fungi, yeast, bacteria, plants
Carbon monoxide dehydrogenase	2 Mo, 4 Fe <sub>2</sub> S <sub>2</sub> , 2 Se	Bacteria

Outside of the nitrogenases is a family of molybdenum-containing enzymes, the molybdopterins, that have a core containing a MoS<sub>2</sub> group and an organic ring structure known as a *pterin system*. These enzymes often contain another metal, particularly an iron-sulfur system, and they perform the vital role of oxidants or reductants of toxic species in organisms. For example, sulfite oxidase oxidizes sulfite ion to sulfate ion, carbon monoxide dehydrogenase oxidizes carbon monoxide to carbon dioxide, and nitrate reductase reduces nitrate ion to nitrite ion. Some common pterin-containing molybdenum enzymes are listed in Table 21.10.

Why is a metal as rare as molybdenum so biologically important? There are a number of possible reasons. The molybdate ion has a high aqueous solubility at near-neutral pH values, making it easily transportable by biological fluids. The ion has a negative charge, making it more suitable for different environments than are the cations of the 3d transition metals. In fact, it is argued that the molybdate ion is transported by the same mechanism as the sulfate ion, SO<sub>4</sub><sup>2-</sup>, another example of the similarities of ions of Group 6 and Group 16 (see Chapter 9, Section 9.4). The element has a wide range of oxidation states (+4, +5, and +6) whose redox potentials overlap with those of biological systems. Finally, molybdenum is about eighteenth in the order of abundances of metals in seawater, and much of the choice of elements for biochemical processes was probably determined when the only life on this planet was in the sea.

## Tungsten

Tungsten-containing enzymes are found in some extremophile bacteria, the hyperthermal *Archaea*. The tungsten center acts as an electron sink and source, oscillating among tungsten +4, +5, and +6 oxidation states. Because these bacteria exist at very high temperatures, up to 110°C in some cases, it is argued that tungsten rather than molybdenum is utilized by the enzyme since tungsten has the stronger metal-ligand bond, enabling the enzyme to function at high temperatures without disintegrating. Linked to the bond strength, the rate of reaction of the tungsten enzyme at about 110°C is comparable to that of the molybdenum enzyme at 37°C.

## Gold in Medicine

The application of gold compounds in medicine began in 1935 and is known as *chrysotherapy* or *aurotherapy*. Gold compounds are particularly efficacious in the treatment of rheumatoid arthritis by reducing inflammation, although the mechanism of action is still debated. Several gold compounds are used for this purpose; one of the most common has the pharmaceutical name *auranofin*,  $(\text{C}_{14}\text{H}_{19}\text{O}_9)\text{—S—Au=P}(\text{C}_2\text{H}_5)_3$ .

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## KEY IDEAS

- The 4d and 5d transition elements show close similarities within each group.
- The early 4d-5d transition metals exhibit higher oxidation states than the later members.
- Metal cluster compounds are common among the earlier 4d-5d transition metals.
- Quadruple bonds are found among some of the earlier 4d-5d transition metals.
- The later 4d-5d transition metals have sufficiently similar chemistry that they are collectively known as the platinum metals.

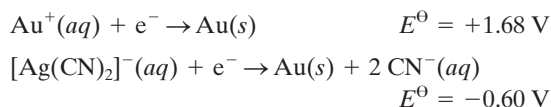
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## EXERCISES

- 21.1** Write balanced equations for (a) the reaction between the dicyanoargentate ion and zinc metal; (b) the reaction between gold and dichlorine.
- 21.2** Write balanced equations for (a) the heating of osmium in oxygen; (b) the reaction of zirconium(IV) chloride with magnesium.
- 21.3** Discuss briefly how the stability of the oxidation states of the 4d-5d transition metals changes along the row, using the fluorides as examples.
- 21.4** Discuss briefly how the stability of the oxidation states of the 4d-5d transition metals differ from those of the 3d transition metals, using the fluorides as examples.
- 21.5** Identify a use for (a) molybdenum(IV) sulfide and (b) silver nitrate.
- 21.6** Identify a use for (a) osmium(VIII) oxide and (b) zirconium(IV) oxide.
- 21.7** What evidence do you have that osmium(VIII) oxide is a covalent compound? Suggest why this is to be expected.
- 21.8** Identify the elements that are called the coinage metals.
- 21.9** Identify the elements that are called the noble metals.
- 21.10** Suggest why silver bromide and iodide are colored even though both silver and halide ions are colorless.
- 21.11** Suggest two possible reasons why the highest oxidation-state fluoride of manganese is  $\text{MnF}_4$ , while that of technetium is  $\text{TcF}_6$  and of rhenium is  $\text{ReF}_7$ .
- 21.12** What is the common coordination number of the silver(I) ion? What other ion in this group has the same coordination number?
- 21.13** What are the common oxidation states of palladium and platinum? What are the common stereochemistries of these oxidation states?
- 21.14** What is meant by (a) a Keggin cluster and (b) a heteropoly blue.
- 21.15** Explain briefly how a quadruple bond can be explained in terms of combinations of atomic orbitals.
- 21.16** Platinum(IV) fluoride has a melting point of about  $600^\circ\text{C}$ , while platinum(VI) fluoride has a melting point of  $61^\circ\text{C}$  and a boiling point of  $69^\circ\text{C}$ . Comment.
- 21.17** The rare nickel(III) oxidation state is found in the fluoride  $\text{NiF}_3$ ; thus, the existence of  $\text{PdF}_3$  was used as an illustration of a group trend. Why is this parallel invalid?
- 21.18** Suggest reasons why molybdenum is utilized in many biological systems.

## BEYOND THE BASICS

**21.19** Calculate the equilibrium constant (stability constant) for the complexation of gold(I) ion with cyanide ion, given



**21.20** Tungsten forms iodides of empirical formula  $\text{WI}_2$  and  $\text{WI}_3$ . What do you suggest is the likely product from the reaction of tungsten metal with fluorine gas? Give your reasoning.

**21.21** Rhenium forms the unusual compound  $\text{K}_2[\text{ReH}_9]$ . What is the oxidation state of rhenium in this compound? Is this an expected oxidation state of rhenium? Is the oxidation state expected with hydrogen as a ligand?

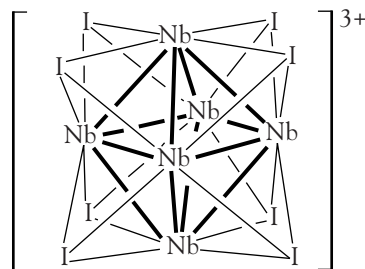
**21.22** Contrast the solubilities of the silver halides with those of calcium. Suggest an explanation for the difference.

**21.23** On the basis of its chemistry, should silver be regarded as a transition metal? Discuss. Which main group element does silver most resemble?

**21.24** The 4d-5d Group 4 ore, alvite, often has the formula  $(\text{Hf}, \text{Th}, \text{Zr})\text{SiO}_4 \cdot x\text{H}_2\text{O}$ . Suggest why thorium would be an isostructural substitute for hafnium or zirconium in the mineral structure.

**21.25** The most common ore of niobium is  $\text{NaCaNb}_2\text{O}_6\text{F}$ . What is the oxidation state of niobium in this compound?

**21.26** The octahedral niobium core also forms an iodide, the complex cation of which is shown below. In what way does this cluster differ from those described in Section 21.4? What is the empirical formula of the iodide?



**21.27** Reaction of the  $[\text{Nb}_6\text{Br}_{18}]^{4-}$  ion with azide ion gives  $[\text{Nb}_6\text{Br}_{12}(\text{N}_3)_6]^{4-}$ . Suggest why only six bromide ions are replaced. What is the azide ion acting as?

**21.28** From the compound,  $\text{Re}_3\text{Cl}_9$  (Figure 21.1), it is possible to synthesize the  $[\text{Re}_3\text{Cl}_{12}]^{3-}$  ion. To where do the additional chloride ions bond? Why is this expected?

## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

# THE GROUP 12 ELEMENTS

## CHAPTER 22

Zn
Cd
Hg

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 22.1** Group Trends
- 22.2** Zinc and Cadmium
- 22.3** Mercury
- 22.4** Biological Aspects
- 22.5** Element Reaction Flowchart

The Group 12 elements, although at the end of the transition metal series, behave like main group metals. Zinc is the most commonly encountered member of the group, both chemically and biochemically.

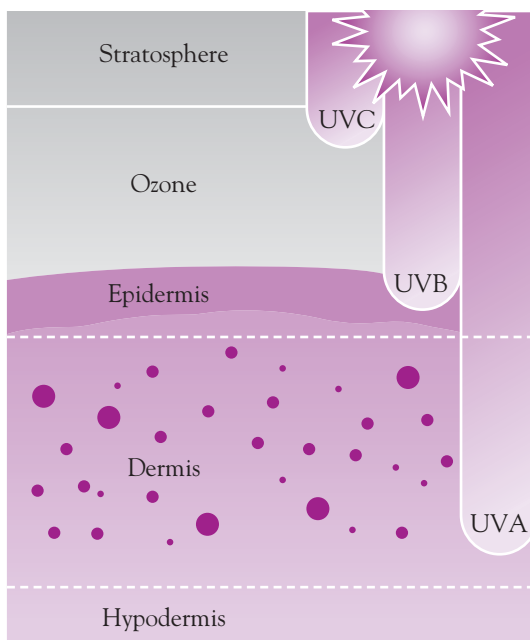
### Context: Metal Oxides for Sun Protection

Western society's love affair with tanning through sunbathing and tanning beds has waned in recent years as we come to understand the potentially harmful effects of ultraviolet (UV) light on the skin. Yet there are many misconceptions about UV radiation. First, not all UV radiation has the same properties. Scientists subdivide the ultraviolet region of the spectrum into three parts: starting from the edge of the visible region: UVA (about 400 to 315 nm), UVB (about 315 to 280 nm), and UVC (about 280 to 100 nm). The following figure shows that it is only the UVC which is blocked by the Earth's ozone layer, while it is the UVA which is the most penetrating and destructive of cells.

Most sunscreen products containing organic compounds only shield against UVB rays. Most people think that UVB protection is all that one needs, but it is not. UVB protection stops skin reddening, but the UVA rays continue to penetrate deep into the skin and cause long-term damage. It is oxides of two elements from either end of the 3d series which provide protection against both UVA and UVB rays: zinc

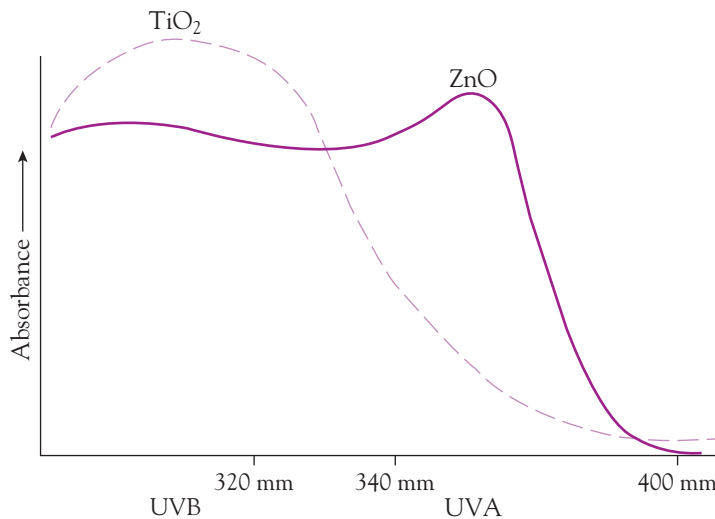


The comparative penetrating power of UVA, UVB, and UVC radiation into skin.



oxide, ZnO (see Section 22.2) and titanium(IV) oxide,  $\text{TiO}_2$  (see Chapter 20, Section 20.2). The oxides are both bright white, stable, nontoxic solids which scatter (through their high refractive index) and absorb (through charge-transfer transitions) ultraviolet radiation very effectively. Zinc oxide is more effective over the UVA range, but less effective over the UVB range (see following figure). Thus, a combination of the two oxides is generally preferable. In the past, the large crystals used resulted in a white appearance, but application of nano-size particles of these compounds produces a colorless suspension.

A comparison of the absorptivity of different wavelengths of ultraviolet rays by zinc oxide and titanium(IV) oxide.



## 22.1 Group Trends

This group of silvery metals superficially appears to belong to the transition metals, but in fact the chemistry of these elements is distinctly different. For example, the melting points of zinc and cadmium are 419 and 321°C, respectively, which is much lower than the typical values of the transition metals, which are close to 1000°C. The liquid phase of mercury at room temperature can be best explained in terms of relativistic electron effects—namely, that the contraction of the outer orbitals makes the element behave more like a “noble liquid.”

The Group 12 elements have filled d orbitals in all their normal compounds, so they are better considered to be main group metals. Consistent with this assignment, most of the compounds of the Group 12 metals are white, except when the anion is colored. Zinc and cadmium are very similar in their chemical behavior, having an oxidation number of +2 in all their simple compounds. Mercury exhibits oxidation numbers of +1 and +2, although the  $\text{Hg}^+$  ion itself does not exist; instead, an  $\text{Hg}_2^{2+}$  ion is formed. The only real similarity between the Group 12 elements and the transition metals is complex formation, particularly with ligands such as ammonia, cyanide ions, and halide ions. All of the metals, but especially mercury, tend to form covalent rather than ionic compounds.

As we discussed in Chapter 9, Section 9.4, there are strong similarities in behavior between the chemistry of magnesium and that of zinc (the  $n$  and  $n + 10$  relationship). Also, we mentioned in Chapter 9, Section 9.6, that there is a “knight’s move” link between  $\text{Zn(II)}$  and  $\text{Sn(II)}$  and between  $\text{Cd(II)}$  and  $\text{Pb(II)}$ .

### WORKED EXAMPLE 22.1

In the chapter opening Context section, it was mentioned that zinc oxide works as a UV protectant by a charge-transfer absorption. Write an equation of the likely process.

#### Answer

In Chapter 20, Section 20.5 (and elsewhere), we describe how energy can be absorbed by an electron shifting from the oxide ion to the metal ion. So in the crystal of zinc oxide, the process should be:



(the energy would then be lost as thermal vibration). ■

### WORKED EXAMPLE 22.2

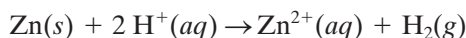
As discussed later, all of the Group 12 metals occur in nature as the metal sulfides. Only one of the Group can also be found as the metal carbonate,  $\text{MCO}_3$ . Suggest the identity of the metal, M.

**Answer**

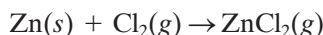
As we discussed in Chapter 7, Section 7.6, sulfide is a very soft hard-soft acid-base (HSAB), whereas carbonate ion is a harder base. Mercury is a soft HSAB acid, so it is least likely to exist as a common carbonate. Conversely, zinc will be the most borderline in its HSAB acid properties and is most likely to form a carbonate mineral. Thus, M should be zinc (as it is, in fact). ■

**22.2 Zinc and Cadmium**

These two soft metals are chemically reactive. For example, zinc reacts with dilute acids to give the zinc ion:

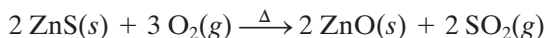


The metal also burns when heated gently in chlorine gas:

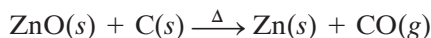
**Extraction of Zinc**

The principal source of zinc is zinc sulfide, ZnS, the mineral sphalerite (or zinc blende), the prototypical structure for tetrahedral ionic lattice structures (see Chapter 5, Section 5.4). Sphalerite occurs in Australia, Canada, and the United States.

The first step in the extraction of zinc is *roasting* the zinc sulfide in air at about 800°C, converting it to the oxide:



It is then possible to use coke to reduce the metal oxide to the metal:



The hot gaseous zinc metal is rapidly cooled by spraying it with molten lead. The two metals are then easily separated because the liquid metals are immiscible. The zinc (density  $7 \text{ g}\cdot\text{cm}^{-3}$ ) floats on the lead (density  $11 \text{ g}\cdot\text{cm}^{-3}$ ), and the lead is recycled.

Zinc is mainly used as an anticorrosion coating for iron. This process is called *galvanizing*, a term that recognizes the electrochemical nature of the process. Actually, the metal is not quite as reactive as one would expect. This results from the formation of a protective layer in damp air. Initially this is the oxide, but over a period of time the basic carbonate,  $\text{Zn}_2(\text{OH})_2\text{CO}_3$ , is formed. The advantage of zinc plating is that the zinc will be oxidized in preference to the iron, even when some of the iron is exposed. This is a result of the more negative reduction potential of the zinc than of the iron, the zinc acting as a sacrificial anode:



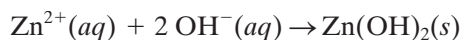
## Reactions of the Zinc Ion

Most zinc salts are soluble in water, and these solutions contain the colorless hexaaquazinc(II) ion,  $[\text{Zn}(\text{OH}_2)_6]^{2+}$ . The solid salts are often hydrated; for example, the nitrate is a hexahydrate and the sulfate, a heptahydrate, just like those of magnesium and cobalt(II). The structure of the sulfate heptahydrate is  $[\text{Zn}(\text{OH}_2)_6]^{2+}[\text{SO}_4 \cdot \text{H}_2\text{O}]^{2-}$ .

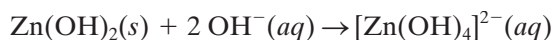
The zinc ion has a  $d^{10}$  electron configuration, so there is no crystal field stabilization energy. Hence, it is often the anion size and charge that determine whether the zinc ion adopts octahedral or tetrahedral stereochemistry. Solutions of zinc salts are acidic as the result of a multistep hydrolysis similar to that of aluminum or iron(III):



Addition of hydroxide ion causes precipitation of white, gelatinous zinc hydroxide,  $\text{Zn}(\text{OH})_2$ :



With excess hydroxide ion, the soluble tetrahydroxidozincate(II) ion,  $[\text{Zn}(\text{OH})_4]^{2-}$ , is formed:



The precipitate will also react with ammonia to give a solution of the tetraamminezinc(II) ion,  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ :



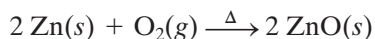
## Zinc Chloride

The most commonly used zinc compound is zinc chloride. It is obtainable as the dihydrate  $\text{Zn}(\text{OH}_2)_2\text{Cl}_2$  and as sticks of the anhydrous zinc chloride. The latter is very deliquescent and extremely soluble in water. It is also soluble in organic solvents such as ethanol and acetone, and this property indicates the covalent nature of its bonding.

Zinc chloride is used as a flux in soldering and as a timber preservative. Both uses depend on the ability of the compound to function as a Lewis acid. In soldering, the oxide film on the surfaces to be joined must be removed; otherwise, the solder will not bond to these surfaces. Above  $275^\circ\text{C}$ , the zinc chloride melts and removes the oxide film by forming covalently bonded complexes with the oxide ions. The solder can then adhere to the molecular-clean metal surface. When it is applied to timber, zinc chloride forms covalent bonds with the oxygen atoms in the cellulose molecules. As a result, the timber is coated with a layer of zinc chloride, a substance toxic to living organisms.

## Zinc Oxide

Zinc oxide can be obtained by burning the metal in air or by the thermal decomposition of the carbonate:



VIDEO CLIP

In the zinc oxide crystal, each zinc ion is surrounded tetrahedrally by four oxygen ions, and each oxygen ion is likewise surrounded by four zinc ions. Unlike other white metal oxides, zinc oxide develops a yellow color when heated. The reversible change in color that depends on temperature is known as *thermochromism*. In this case, the color change results from the loss of some oxygen from the lattice, leaving it with an excess negative charge. The excess negative charge (electrons) can be moved through the lattice by applying a potential difference; thus, this oxide is a semiconductor. Zinc oxide returns to its former color when cooled because the oxygen that was lost during heating returns to the crystal lattice.

Zinc oxide is the most important compound of zinc. It is used as a white pigment, as a filler in rubber, and as a component in various glazes, enamels, and antiseptic ointments, together with its role in sunscreens (see chapter opening Context). In combination with chromium(III) oxide, it is used as a catalyst in the manufacture of methanol from synthesis gas.

### WORKED EXAMPLE 22.3

Zinc and magnesium are related by the  $(n)$  and  $(n + 10)$  relationship. Yet, unlike zinc ion, magnesium ion does not form so many isolable complexes. Suggest a reason why.

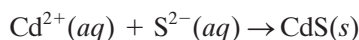
#### Answer

The primary difference between the two ions is that magnesium ion has a noble-gas electron configuration, while that of zinc ion has an additional  $d^{10}$  of electrons. According to Fajans' Third Rule, electrons in the  $d$  orbitals are more polarizable, leading to a greater preference for covalency in bonding, and hence complex formation. ■



### Cadmium Sulfide

The only commercially important compound of cadmium is cadmium sulfide, CdS. Whereas zinc sulfide has the typical white color of Group 12 compounds, cadmium sulfide is an intense yellow. As a result, the compound is used as a pigment. Cadmium sulfide is prepared in the laboratory and industry by the same route: the addition of sulfide ion to cadmium ion:

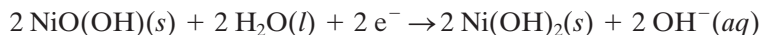
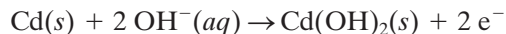


Even though cadmium compounds are highly toxic, cadmium sulfide is so insoluble that it presents little hazard.

### The NiCad Battery

The most significant use of cadmium is in the rechargeable NiCad battery. In the discharge cycle, cadmium is oxidized to cadmium hydroxide, while nickel is reduced from the unusual oxidation state of +3 in nickel(III) oxide hydroxide,

NiO(OH), to the more normal +2 state, as nickel(II) hydroxide. The electrolyte is hydroxide ion:



In the charging process, the reverse reactions occur. There are two major reasons for using a basic reaction medium: the nickel(III) state is only stable in base, and the insolubility of the hydroxides means that the metal ions will not migrate far from the metal surface, thus allowing the reverse reactions to happen readily at the same site. The major problem with this battery is its disposal; with toxic cadmium, it is important that such cells be returned for recycling.

## 22.3 Mercury

With the weakest metallic bonding of all, mercury is the only liquid metal at 20°C. Mercury's weak bond also results in a high vapor pressure at room temperature. Because the toxic metal vapor can be absorbed through the lungs, spilled mercury globules from broken mercury thermometers were a major hazard in the traditional chemistry laboratory. Mercury is a very dense liquid (13.5 g·cm<sup>-3</sup>). It freezes at -39°C and boils at 357°C.

### Extraction of Mercury

The only mercury ore is mercury(II) sulfide, HgS, the mineral cinnabar, although mercury is occasionally found as the free liquid metal. The deposits of mercury(II) sulfide in Spain and Italy account for about three-quarters of the world's supply of the metal. Many mercury ores contain considerably less than 1 percent of the sulfide, which accounts for the high price of the metal. Mercury is readily extracted from the sulfide ore by heating it in air. Mercury vapor is evolved and is then condensed to the liquid metal:



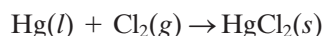
Mercury is used in thermometers, barometers, electrical switches, and mercury arc lights. Solutions of other metals in mercury are called *amalgams*. Sodium amalgam and zinc amalgam are used as laboratory reducing agents, and the most common amalgam of all, dental amalgam (which contains mercury mixed with one or more of the metals silver, tin, and copper), is used for filling cavities in back teeth. It is suitable for this purpose for several reasons. It expands slightly as the amalgam forms, thereby anchoring the filling to the surrounding material. It does not fracture easily under the extreme localized pressures exerted by our grinding teeth. And it has a low coefficient of thermal expansion; thus, contact with hot substances will not cause it to expand and crack the surrounding tooth. In terms of total consumption, the major uses of mercury compounds are in agriculture and in

horticulture; for example, organomercury compounds are used as fungicides and as timber preservatives.

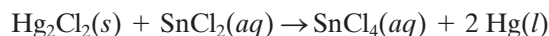
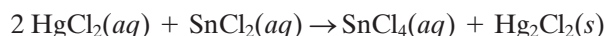
### Mercury(II) Compounds

Virtually all mercury(II) compounds utilize covalent bonding. Mercury(II) nitrate is one of the few compounds believed to contain the  $\text{Hg}^{2+}$  ion. It is also one of the few water-soluble mercury compounds.

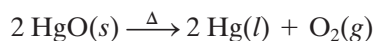
Mercury(II) chloride can be formed by bubbling chlorine gas through mercury:



This compound dissolves in warm water, but the nonelectrically conducting behavior of the solution shows that it is present as  $\text{HgCl}_2$  molecules, not as ions. Mercury(II) chloride solution is readily reduced to white insoluble mercury(I) chloride and then to black mercury metal by the addition of tin(II) chloride solution. This is a convenient test for the mercury(II) ion:



Mercury(II) oxide is thermally unstable and decomposes into mercury and dioxygen when heated strongly:



This decomposition is a visually interesting demonstration because mercury(II) oxide, a red powder, “disappears” as silvery globules of metallic mercury form on the cooler parts of the container. However, the reaction is very hazardous because a significant portion of the mercury metal escapes as vapor into the laboratory. The experiment is of historical interest, for it was the method used by Joseph Priestley to obtain the first sample of pure oxygen gas.

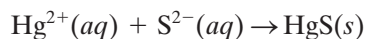
### Mercury(I) Compounds

A unique feature of mercury chemistry is its ability to form the  $[\text{Hg}—\text{Hg}]^{2+}$  ion, in which the two mercury ions are united by a single covalent bond. In fact, there are no known compounds containing the simple mercury(I) ion.

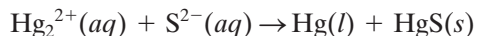
Although mercury(I) chloride,  $\text{Hg}_2\text{Cl}_2$ , and mercury(I) nitrate,  $\text{Hg}_2(\text{NO}_3)_2$ , exist, compounds with other common anions, such as sulfide, have never been synthesized. To understand the reason for this, we must look at the disproportionation equilibrium,



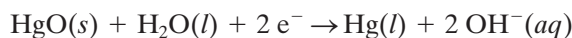
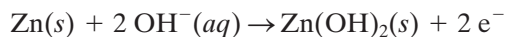
which has an equilibrium constant,  $K_{\text{dis}}$ , of about  $6 \times 10^{-3}$  at  $25^\circ\text{C}$ . The low value for the equilibrium constant implies that, under normal conditions, there is little tendency for the mercury(I) ion to disproportionate into the mercury(II) ion and mercury. However, anions such as sulfide form highly insoluble compounds with mercury(II) ion:



This precipitation “drives” the disproportionation equilibrium to the right. As a result, the overall reaction of mercury(I) ion with sulfide ion becomes:



For very compact power needs, such as hearing aids, mercury batteries are often used. In this cell, zinc is the anode and mercury(II) oxide (mixed with conducting graphite) is the cathode. The zinc is oxidized to zinc hydroxide, while the mercury(II) oxide is reduced to mercury metal:



Because the electrolyte (hydroxide ion) concentration remains constant, there is a steady cell potential.

### Mercury(IV) Fluoride

In Chapter 3, we discussed transient species, including molecules that can only be synthesized at very low temperatures and that decompose on warming. One such compound is mercury(IV) fluoride,  $\text{HgF}_4$ . The synthesis of small amounts of this compound at a temperature of 4 K has been claimed. In this particular compound, mercury(IV) is behaving as a transition metal with an incomplete set of d electrons, specifically  $[\text{Xe}]4\text{f}^{14}5\text{d}^8$ , isoelectronic with iridium(I), platinum(II), and gold(III). The compound  $\text{HgF}_4$  is square-planar and isoelectronic (and isostructural) with the known gold(III) ion,  $[\text{AuF}_4]^{-}$ . Nevertheless, the existence of such a compound under extreme conditions does not require the shifting of the transition metal boundary. For all mercury chemistry under realistic conditions, the element still behaves as a main group metal.

## 22.4 Biological Aspects

This group contains one essential element (zinc) and two very toxic elements.

### The Essentiality of Zinc

Among trace essential elements, zinc is second only to iron in importance. Around the world, a lack of zinc is the most common soil deficiency. Beans, citrus fruit, coffee, and rice are the crops most susceptible to zinc deficiency.

Zinc is an essential element for animals. Over 200 zinc enzymes have been identified in living organisms and their roles determined. Zinc enzymes that perform almost every possible type of enzyme function are known, but the most common function is hydrolysis; for example, the zinc-containing hydrolases are enzymes that catalyze the hydrolysis of  $\text{P—O—P}$ ,  $\text{P—O—C}$ , and  $\text{C—O—C}$  bonds. With such a dependence on zinc enzymes, it is understandable that zinc is one of the most crucial elements in our diet. Yet it has been estimated that up to one-third of people in the Western world suffer from zinc



deficiency. Such deficiencies are not life threatening, but they do contribute to fatigue, lethargy, and related symptoms (and possibly to diminished disease resistance).

The question arises as to what makes zinc such a useful ion, considering that it cannot serve a redox function. There are several reasons:

1. Zinc is widely available in the environment.
2. The zinc ion is a strong Lewis acid, and zinc functions as a Lewis acid in enzymes.
3. Zinc, unlike many other metals, prefers tetrahedral geometries, a key feature of the metal site in most zinc enzymes. Five- and six-coordinate geometries are also available, making transition states involving these coordination numbers possible.
4. The zinc ion has a  $d^{10}$  electron configuration, so there is no crystal field stabilization energy associated with exact geometries as there are with the transition metals. Hence, the environment around the zinc can be distorted from the exact tetrahedral to allow for the precise bond angles needed for its function without an energy penalty.
5. The zinc ion is completely resistant to redox changes at biological potentials; thus, its role cannot be affected by changing redox potentials in the organism.
6. The zinc ion undergoes extremely rapid ligand exchange, facilitating its role in enzymes.

### The Toxicity of Cadmium

Cadmium is a toxic element that is present in our foodstuffs and is normally ingested at levels that are close to the maximum safe level. The kidney is the organ most susceptible to cadmium; about 200 ppm causes severe damage. Cigarette smokers absorb significant levels of cadmium from tobacco smoke.

Exposure to cadmium from industrial sources is a major concern. In particular, the nickel-cadmium battery is becoming a major waste-disposal problem. Many battery companies now accept return of defunct NiCad batteries so that the cadmium metal can be safely recycled. Cadmium poisonings in Japan have resulted from cadmium-contaminated water produced by mining operations. The ensuing painful bone degenerative disease is called *itai-itai* (English translation: “it hurts—it hurts” disease).

### The Many Hazards of Mercury

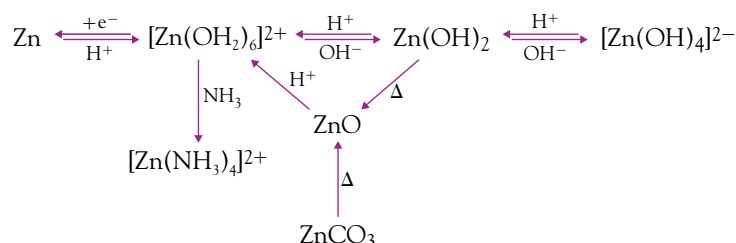
As mentioned earlier, mercury is hazardous because of its relatively high vapor pressure. The mercury vapor is absorbed in the lungs, dissolves in the blood, and is then carried to the brain, where irreversible damage to the central nervous system results. The metal is also slightly water soluble, again a result of its very weak metallic bonding. The escape of mercury metal from leaking chlor-alkali electrolysis plants into nearby rivers has led to major pollution problems in North America.

Inorganic compounds of mercury are usually less of a problem because they are not very soluble. A note of historical interest: At one time, mercury ion

solutions were used in the treatment of animal furs for hat manufacture. Workers in the industry were prone to mercury poisoning, and the symptoms of the disease were the model for the Mad Hatter in the book *Alice in Wonderland*. As we will show in Chapter 23, it is the nonpolar, covalently bonded organo-metallic form,  $\text{Hg}(\text{CH}_3)_2$ , which is the most hazardous.

## 22.5 Element Reaction Flowchart

The only flowchart shown is that for zinc. Notice the similarities with the flowchart for copper (see Chapter 20, Section 20.10).



### KEY IDEAS

- Zinc and cadmium are similar in their chemistry, whereas that of mercury is very different.
- All zinc compounds exist in the +2 oxidation state.
- Mercury occurs in both the +2 and +1 ( $\text{Hg}_2^{2+}$ ) oxidation states.
- Zinc is an essential element, whereas cadmium and mercury are both highly toxic.

### EXERCISES

- 22.1** Write balanced chemical equations for the following chemical reactions:
- zinc metal with liquid bromine
  - the effect of heat on solid zinc carbonate
- 22.2** Write balanced chemical equations for the following chemical reactions:
- aqueous zinc ion with ammonia solution
  - heating mercury(II) sulfide in air
- 22.3** Suggest a two-step reaction sequence to prepare zinc carbonate from zinc metal.
- 22.4** Explain briefly the reasons for considering the Group 12 elements separately from the transition metals.
- 22.5** Compare and contrast the properties of (a) zinc and magnesium; (b) zinc and aluminum.
- 22.6** Normally, metals in the same group have fairly similar chemical properties. Contrast and compare the chemistry of zinc and mercury by this criterion.
- 22.7** Write the two half-equations for the charging process of the NiCad battery.
- 22.8** Cadmium sulfide adopts the zinc sulfide (wurtzite and zinc blende) structure, but cadmium oxide adopts the sodium chloride structure. Suggest an explanation for the difference.
- 22.9** Cadmium-coated paper clips were once common. Suggest why they were used and why their use was discontinued.
- 22.10** Compare and contrast the chemistry of calcium (Group 2) and cadmium (Group 12).
- 22.11** Write balanced chemical equations corresponding to each transformation in the element reaction flowchart of zinc (see Section 22.5).

## BEYOND THE BASICS

**22.12** Both cadmium ion,  $\text{Cd}^{2+}$ , and sulfide ion,  $\text{S}^{2-}$ , are colorless. Suggest an explanation for the color of cadmium sulfide.

**22.13** Mercury(I) selenide is unknown. Suggest an explanation.

**22.14** Mercury(II) iodide is insoluble in water. However, it will dissolve in a solution of potassium iodide to give a di-negative anionic species. Suggest a formula for this ion.

**22.15** In the industrial extraction of zinc, molten lead is used to cool the zinc vapor until it liquefies. The molten zinc and molten lead do not mix; thus, they can be easily separated. Suggest why the two metals do not mix to any significant extent.

**22.16** You are an artist and you wish to make your “cadmium yellow” paint paler. Why is it not a good idea to mix in some “white lead,”  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ , to accomplish this?

**22.17** When mercury(II) forms a complex with dimethylsulfoxide,  $(\text{CH}_3)_2\text{SO}$ , is the ligating atom likely to be the oxygen or the sulfur? Explain your reasoning.

**22.18** The only common ore of mercury is mercury(II) sulfide, whereas zinc is found as a sulfide and a carbonate. Suggest an explanation.

**22.19** The acid-base chemistry of liquid ammonia often parallels that of aqueous solutions. On this basis, write a balanced equation for

- the reaction of zinc amide,  $\text{Zn}(\text{NH}_2)_2$ , with ammonium ion in liquid ammonia
- the reaction of zinc amide with amide ion,  $\text{NH}_2^-$ , in liquid ammonia

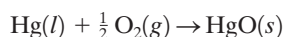
**22.20** A compound (A) of a di-positive metal ion is dissolved in water to give a colorless solution. Hydroxide ion is added to the solution. A gelatinous white precipitate (B) initially forms, but in excess hydroxide ion, the precipitate redissolves to give a colorless solution of complex ion (C). Addition of concentrated ammonia solution to the precipitate (B) gives a colorless solution of complex ion (D). Addition of sulfide ion to a solution of compound (A)

gives a highly insoluble white precipitate (E). Addition of silver ion to a solution of compound (A) results in a yellow precipitate (F). Addition of aqueous bromine to a solution of (A) gives a black solid (G), which can be extracted into an organic solvent and gives a purple solution. The solid (G) reacts with thiosulfate ion to give a colorless solution containing ions (H) and (I), the latter being an oxyanion.

Identify (A) to (I) and write balanced equations for each reaction.

**22.21** Which would you expect to have a higher melting point, zinc oxide or zinc chloride? Explain your reasoning.

**22.22** For the reaction



the value of the free energy change,  $\Delta G$ , reverses its sign from negative to positive above about  $400^\circ\text{C}$ . Explain why this happens.

**22.23** When hydrogen sulfide is bubbled into a neutral solution of zinc ion, zinc sulfide precipitates. However, if the solution is first acidified, no precipitate forms. Suggest an explanation.

**22.24** The following are four different forms of mercury, each of which poses a different level of health hazard:  $\text{Hg}(l)$ ,  $\text{Hg}(\text{CH}_3)_2(l)$ ,  $\text{HgCl}_2(aq)$ ,  $\text{HgS}(s)$ . Which of these forms, on ingestion,

- will pass unchanged through the digestive tract (for digestion, substances must be water or fat soluble)?
- will be most easily eliminated through the kidneys?
- will be the greatest hazard for absorption through the skin?
- will most readily pass from blood into the (nonpolar) brain tissue?
- will be absorbed by inhalation through the lungs?

## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)



For accompanying video clips: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

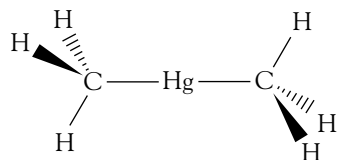
# ORGANOMETALLIC CHEMISTRY

## CHAPTER 23

Approximately half the world's research publications in chemistry are currently about organometallic compounds. This field, bridging inorganic and organic chemistry, will be of continuing importance throughout the twenty-first century. Organometallics play a vital role in the economy, with about 10 of the world's top 30 chemicals being produced using organometallic catalysts.

### Context: The Extreme Toxicity of Dimethylmercury

Many organometallic compounds are highly poisonous; for example, tetracarbonylnickel(0), was once referred to as “liquid death”. Thus, organometallic chemists are very safety conscious, but even they can underestimate the hazards. Dimethylmercury was known to be very toxic. In fact, the two British chemists who first synthesized the compound both died from mercury poisoning. However, no one realized the extreme toxicity of the compound.



Structure of dimethylmercury.

August 14, 1996, would seem like a normal day for Karen Wetterhahn, professor of chemistry at Dartmouth College, New Hampshire. Wetterhahn was one of the foremost experts on metal toxicology, the study of the effects of heavy metals on biological systems, and on that day, she was using dimethylmercury,  $(\text{CH}_3)_2\text{Hg}$ . She took all the required precautions: lab coat, goggles, and disposable latex gloves. Because of the compound's high vapor pressure, Wetterhahn handled it in a fume hood. As she transferred the compound to a tube, one or two drops of the liquid dripped from the pipette onto her left glove. Completing the task, she removed the gloves and thoroughly washed her hands.

Five months later, Wetterhahn found herself walking into walls and slurring her speech. She was admitted to the hospital, where her symptoms were matched to severe mercury poisoning. The only mercury incident that she could recall was the drips of dimethylmercury—but

						5	6	7	8
						B	C	N	O
						13	14	15	16
						Al	Si	P	S
25	26	27	28	29	30	31	32	33	34
Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
43	44	45	46	47	48	49	50	51	52
Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
75	76	77	78	79	80	81	82	83	84
Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
107	108	109	110	111	112	113	114	115	116

- 23.1** Introduction to Organometallic Compounds
- 23.2** Naming Organometallic Compounds
- 23.3** Counting Electrons
- 23.4** Solvents for Organometallic Chemistry
- 23.5** Main Group Organometallic Compounds
- 23.6** Organometallic Compounds of the Transition Metals
- 23.7** Transition Metal Carbonyls
- 23.8** Synthesis and Properties of Simple Metal Carbonyls
- 23.9** Reactions of Transition Metal Carbonyls
- 23.10** Other Carbonyl Compounds
- 23.11** Complexes with Phosphine Ligands
- 23.12** Complexes with Alkyl, Alkene, and Alkyne Ligands
- 23.13** Complexes with Allyl and 1,3-Butadiene Ligands
- 23.14** Metallocenes
- 23.15** Complexes with  $\eta^6$ -Arene Ligands
- 23.16** Complexes with Cycloheptatriene and Cyclooctatetraene Ligands
- 23.17** Fluxionality
- 23.18** Organometallic Compounds in Industrial Catalysis
- 23.19** Biological Aspects

she had used gloves as required. The chelation therapy administered had no effect. Three weeks later, she went into a coma and died on June 8, 1997.

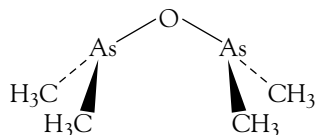
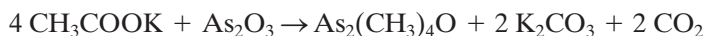
All of the material safety data sheets (MSDS) stated that gloves were needed when handling dimethylmercury, but they did not stipulate any type. To that time, no research had been done on the permeability of materials to dimethylmercury. Following the accident, a testing laboratory reported horrifying results: it took less than 15 seconds for the dimethylmercury to pass through the glove. Other glove types were no better. Only a special laminated glove, SilverShield, delayed the passage of the liquid for any significant length of time. As one chemist commented, if compounds were rated on a safety scale from 1 to 10, with 10 being the most toxic, we now realize dimethylmercury would rate a “15.”

Laboratory chemistry is always accompanied by some degree of risk, as is crossing a highway. For chemists, the MSDS provide an awareness of the hazards of particular compounds and of classes of compounds. It is essential for any practicing chemist to read such safety information. Unfortunately for Wetterhahn, the extreme risk of this particular volatile compound had not previously been realized.

### 23.1 Introduction to Organometallic Compounds

Organometallic compounds straddle both inorganic and organic chemistry. To be a member of this class, the compound must contain at least one direct metal-to-carbon covalent bond. The metal can be a transition, main group, or f-group metal, and the term “metal” is often stretched to include boron, silicon, germanium, arsenic, antimony, selenium, and tellurium. The carbon-containing group(s) may be carbonyl, alkyl, alkene, alkyne, aromatic, cyclic, or heterocyclic. Unlike inorganic compounds, many organometallic compounds are *pyrophoric* (spontaneously flammable) and thermodynamically unstable.

Although organometallic chemistry is sometimes perceived as a relatively new area of research, the first synthesis was performed in 1760. In that year, the French chemist Louis Claude Cadet de Gassicourt mixed potassium ethanoate (acetate) with diarsenic trioxide and obtained “Cadet’s fuming liquid.” This poisonous, oily red liquid with a garlic odor, we now know to be mainly cacodyl oxide,  $\text{As}_2(\text{CH}_3)_4\text{O}$  (Figure 23.1). The traditional name *cacodyl* derives from the Greek *kakodes*, for “evil smelling.” The reaction for the production of cacodyl oxide is:



**FIGURE 23.1** Structure of cacodyl oxide,  $\text{As}_2(\text{CH}_3)_4\text{O}$ .

However, it is the transition metal organometallic compounds which provide us with richness and variety in their structures and bonding types since transition metals can utilize s, p, and d orbitals in bonding. Each orbital type can either donate or accept electron density, and the d orbitals on the metal are particularly well suited to interact with s and p orbitals on the organic species in similar ways to the ligand field theory approach to bonding in coordination compounds (see Chapter 19, Section 19.10). Unlike conventional transition metal complexes, the central metal atom in an organometallic compound is often in a very low-oxidation state. As a result of the flexibility in bonding and

the ability to transfer electron density, transition metal organometallic compounds are of industrial importance as catalysts.

Unlike the other chapters in this text, this chapter does not show chemical equations with symbols indicating solid, gas, or liquid phase or solution. This is the normal convention in organometallic chemistry, and it should be assumed that all reactions are carried out in an organic solvent.

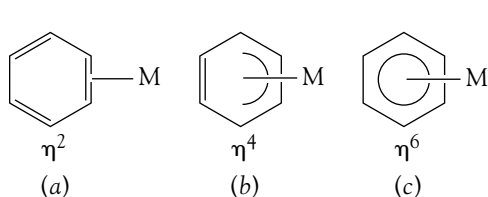
## 23.2 Naming Organometallic Compounds

In addition to the general rules that we use to name simple inorganic compounds or transition metal complexes, a few supplementary rules are used to give additional information about the nature of the bonding within the organometallic molecule. First, we need to introduce a selection of the many organic species that act as ligands in organometallic chemistry (Table 23.1).

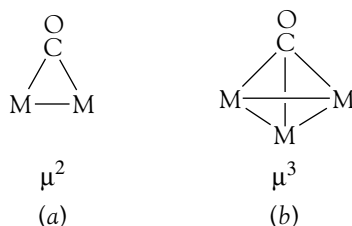
The number of carbon atoms within an organic species that are directly interacting with the metal is specified by the prefix  $\eta$  (the Greek letter eta). This is called *hapticity*, and most ligands bond through one atom only, so they are described as monohapto. Some ligands, especially those with multiple  $\pi$  bonds, may bond in more than one way. For example, benzene may bond to a metal center through one, two, or three of benzene's  $\pi$  bonds. Consequently, we can describe benzene as di-, tetra-, or hexahapto and use the notation  $\eta^2$ ,  $\eta^4$ , and  $\eta^6$ , respectively, depending on if the bonding is across two-, four-, or six-ligand atoms (Figure 23.2). Species that can bridge two metal centers, such as carbonyl (Figure 23.3), halide, or carbene ligands, are indicated by the prefix  $\mu$  (the Greek letter mu).

**TABLE 23.1** Some common ligands in organometallic chemistry

Formula	Name	Abbreviation
CO	Carbonyl	
CH <sub>3</sub>	Methyl	Me
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	<i>n</i> -Butyl	<sup>n</sup> Bu
(CH <sub>3</sub> ) <sub>3</sub> C	Tertiary-butyl	<sup>t</sup> Bu
[C <sub>5</sub> H <sub>5</sub> ] <sup>−</sup>	Cyclopentadienyl	Cp
C <sub>6</sub> H <sub>5</sub>	Phenyl	Ph
C <sub>6</sub> H <sub>6</sub>	Benzene	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	Triphenylphosphine	PPh <sub>3</sub>



**FIGURE 23.2** The benzene molecule bonded to a metal via (a) two carbon atoms, (b) four carbon atoms, and (c) all six carbon atoms.



**FIGURE 23.3** Carbonyl ligands bridging (a) two metal centers and (b) three metal centers.

In main group chemistry, covalent s-block compounds are named according to the substituent names used in organic chemistry, as in methyllithium,  $\text{Li}(\text{CH}_3)_4$ . Similarly, p-block compounds are named as simple organic species, such as trimethylboron,  $\text{B}(\text{CH}_3)_3$ . Alternatively, they may be named as derivatives of the hydride; for example, trimethylborane. Ionic compounds are named as salts, such as sodium naphthalide,  $\text{Na}^+[\text{C}_{10}\text{H}_8]^-$ . In d- and f-block species, the usual rules for naming coordination compounds are followed, with the additional use of  $\eta$  and  $\mu$ . For example,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$  is named pentahaptocyclopentadienyltricarbonylmanganese(I).

### WORKED EXAMPLE 23.1

Give the systematic name of  $[(\eta^6\text{-C}_6\text{H}_6)\text{W}(\text{CO})_3]$ .

#### Answer

The ligands are hexahaptobenzene and carbonyl and are named in alphabetical order. The tungsten is in oxidation state 0. As the molecule is neutral overall, the name is hexahaptobenzenetricarbonyltungsten(0). ■

## 23.3 Counting Electrons

Formal oxidation numbers (see Chapter 8) of metallic species can be useful in keeping track of electrons in both the structures and the reactions of organometallic compounds. For organometallics, the electron count helps in predicting compound stability.

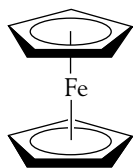
There are two conventions when it comes to counting electrons and charges on some organic ligands. As an example, the cyclopentadienyl ligand can be considered as an anionic species,  $\text{C}_5\text{H}_5^-$ , formed on removal of a proton from  $\text{C}_5\text{H}_6$ :



This is known as the *ionic convention*. Alternatively, the cyclopentadienyl ligand can be regarded as a neutral radical,  $\text{C}_5\text{H}_5\cdot$ , with the dot representing the single unpaired electron:



This is known as the *covalent* or *radical convention*. The choice has an effect on the formal charge that is assigned to the metal center, an important point when considering the relative stabilities of low- and high-oxidation states. The two conventions are shown here for  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$ , commonly called *ferrocene* (Figure 23.4):



**FIGURE 23.4**  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$ , ferrocene.

Ionic convention		Covalent or radical convention	
$\text{C}_5\text{H}_5^-$	$6\text{ e}^-$	$\text{C}_5\text{H}_5\cdot$	$5\text{ e}^-$
$\text{C}_5\text{H}_5^-$	$6\text{ e}^-$	$\text{C}_5\text{H}_5\cdot$	$5\text{ e}^-$
$\text{Fe}^{2+}$	$\text{d}^6$	Fe	$\text{d}^8$
Total electrons	$18\text{ e}^-$	Total electrons	$18\text{ e}^-$



**TABLE 23.2** Details of some common ligands for organometallic compounds

Ligand	Formal charge	Electrons donated
H	-1	2
F, Cl, Br, I	-1	2
CN	-1	2
$\mu$ -F, Cl, etc.	-1	4
CO	0	2
$\mu$ -CO	0	2
$\text{PR}_3$ , $\text{PX}_3$	0	2
$\text{CH}_3$ , $\text{C}_2\text{H}_5$ , etc.	-1	2
$\mu$ - $\text{CH}_3$	-1	2
NO	0	2
$\eta^5\text{-}[\text{C}_5\text{H}_5]^-$	-1	6
$\eta^6\text{-C}_6\text{H}_6$	0	6

The convention chosen makes no difference in the count of the final number of electrons. In fact, both systems are in widespread use, and, provided there is consistency, it really does not matter which one is adopted. The approach used throughout this chapter will be the ionic convention. Electron counts and charges for some common ligands are provided in Table 23.2.

**WORKED EXAMPLE 23.2**

What is the electron count for the complex  $[(\eta^6\text{-C}_6\text{H}_6)\text{W}(\text{CO})_3]$ ?

**Answer**

Both  $\eta^6\text{-C}_6\text{H}_6$  and CO have 0 charge, so tungsten is in oxidation state 0.

$$\begin{array}{rcl}
 \text{Tungsten (0) electrons (d}^6\text{)} & = & 6 \\
 \text{Carbon monoxide electrons} & = & 3 \times 2 = 6 \\
 \text{C}_6\text{H}_6 & = & 6 \\
 \text{total} & = & \underline{18} \blacksquare
 \end{array}$$

**23.4 Solvents for Organometallic Chemistry**

Synthesis and reactions of transition metal coordination compounds are often performed either in aqueous solution or in moderately polar solvents such as ethanol and acetone. However, as most organometallic compounds decompose in water, reactions are usually performed in organic solvents, many of which are of low polarity (see Chapter 7, Section 7.1). Some common solvents for



**TABLE 23.3** Some typical solvents for organometallic chemistry

Name	Formula	Common name/abbreviation
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	DCM
2-Propanol	CH <sub>3</sub> CH(OH)CH <sub>3</sub>	Isopropanol
2-Propanone	CH <sub>3</sub> COCH <sub>3</sub>	Acetone
Diethylether	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	Ether
Oxacyclopentane	(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O	Tetrahydrofuran, THF

organometallic chemistry are listed in Table 23.3. Many organometallic compounds also react with oxygen and thus must be prepared under an inert atmosphere, such as nitrogen or argon.

## 23.5 Main Group Organometallic Compounds

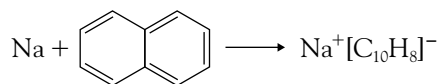
Organometallic compounds of the main group elements have many structural and chemical similarities to the analogous hydrogen compounds. This is because the electronegativities of carbon and hydrogen are similar; hence, M—C and M—H bonds have similar polarities.

### Organometallic Compounds of the Alkali Metals

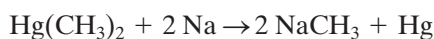
All organometallic compounds of Group 1 elements are labile and pyrophoric. Organic species that readily lose protons form ionic compounds with the Group 1 metals. For example, cyclopentadiene reacts with sodium metal:



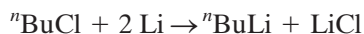
Sodium and potassium form intensely colored compounds with aromatic species. The oxidation of the metal results in transfer of an electron to the aromatic system, which produces a radical anion. A radical anion is an anion that possesses an unpaired electron; for example, the naphthalide anion in the deep blue sodium naphthalide:



Colorless sodium and potassium alkyls are solids that are insoluble in organic solvents and, when stable enough, have fairly high melting temperatures. They are produced by *transmetallation reactions*. Transmetallation is a common method for the synthesis of main group organometallic compounds. It involves the breaking of the metal-carbon bond and the forming of a metal-carbon bond to a different metal. Alkylmercury compounds are convenient starting materials in these reactions; for example, we can synthesize methylsodium by reacting sodium metal with dimethylmercury:

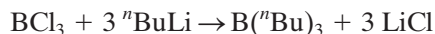


Lithium alkyls and aryls are by far the most important Group 1 organometallic compounds. They are liquids or low-melting-point solids, are more thermally stable than other Group 1 organometallic compounds, and are soluble in organic and nonpolar solvents. Synthesis can be accomplished from an alkyl halide and lithium metal or by reacting the organic species with *n*-butyl lithium,  $\text{Li}(\text{C}_4\text{H}_9)$ , commonly abbreviated to  $^n\text{BuLi}$ :



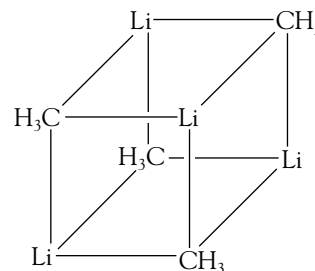
A feature of many main group organometallic compounds is the presence of bridging alkyl groups. When ethers are the solvent, methyllithium exists as  $\text{Li}_4(\text{CH}_3)_4$ , with a tetrahedron of lithium atoms and bridging methyl groups, with each carbon atom essentially six-coordinate (three hydrogens of the methyl and three lithiums; Figure 23.5). In hydrocarbon solvents,  $\text{Li}_6(\text{CH}_3)_6$  is present, and its structure is based on an octahedral arrangement of lithium atoms. Other lithium alkyls adopt similar structures except when the alkyl groups become very bulky, as in the case of *t*-butyl,  $(\text{CH}_3)_3\text{C}-$ , when tetramers are the largest species formed.

Organolithium compounds are very important in organic synthesis. They act in a similar way to Grignard reagents (see later) but are much more reactive. Among their many applications, organolithium compounds are used to convert p-block halides to organo compounds; for example, *n*-butyllithium can be reacted with boron trichloride to give the organoboron compound:



The driving force for this and many other reactions of organometallic compounds is the formation of the halide of the more electropositive metal. This is a common feature in organometallic chemistry.

Lithium alkyls are important industrially in the stereospecific polymerization of alkenes to form synthetic rubber. *n*-Butyllithium is used as an initiator in solution polymerization to produce a wide range of elastomers and polymers. The composition and molecular weight of the polymer can be carefully controlled to produce varied products suitable for a wide range of different uses, such as footwear, hoses and pipes, adhesives, sealants, and resins. Organolithium compounds are also used in the synthesis of a range of pharmaceuticals, including vitamins A and D, analgesics, antihistamines, antidepressants, and anticoagulants.

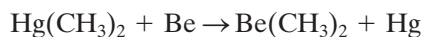


**FIGURE 23.5** Structure of methyl lithium,  $\text{Li}_4(\text{CH}_3)_4$ .

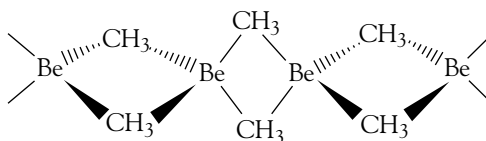
### Organometallic Compounds of the Alkaline Earth Metals

The organometallic compounds of calcium, strontium, and barium are generally ionic and very unstable, whereas those of beryllium and magnesium are covalent and more stable, although those of beryllium are pyrophoric and readily hydrolyzed. It is the compounds of beryllium and magnesium which are much more important and thus will be discussed in detail.

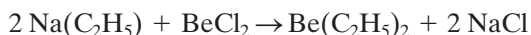
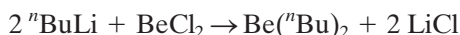
Methylberyllium can be prepared by transmetallation from methylmercury:



**FIGURE 23.6** Structure of methyl beryllium in the solid phase.

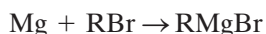


Another synthetic route is by *halogen exchange* or *metathesis* reactions, in which a metal halide reacts with an organometallic compound of a different metal. The products are the halide of the second metal and the organo-derivative of the first metal. In this way, the halide and organo groups are effectively “transferred” between the two metals. Once again, the halide of the more electropositive metal is formed. Two examples are:

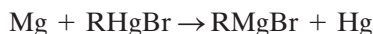


Methylberyllium,  $\text{Be}(\text{CH}_3)_2$ , is a monomer in the vapor phase and polymerizes in the solid (Figure 23.6). There are insufficient electrons, so the polymer is held together by three-center, two-electron bridging bonds. This bond type was described in Chapter 13, Section 13.4, in the context of diborane. Bulkier alkyl groups inhibit or prevent polymerization; for example, *t*-butylberyllium is a monomer even in the solid phase.

Alkyl and aryl magnesium halides are very well known as Grignard reagents and are widely used in synthetic organic chemistry. They are prepared from magnesium metal and an organohalide. The reaction is performed in ether and is initiated by a trace of iodine. A general reaction is shown in the following, where R is used as a generic symbol for any alkyl group.



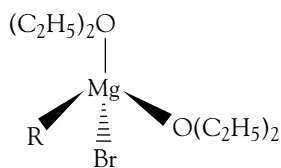
The compounds produced in this way are not pure, often containing other species such as  $\text{R}_2\text{Mg}$ . An alternative synthesis employs transmetallation, using a mercury compound:



The structure of these compounds is not simple. They have a coordination number of 2 only in solution and when the alkyl group is bulky. Otherwise, they are solvated with a tetrahedral magnesium atom (Figure 23.7).

Grignard reagents must be produced in an ether solvent, and the reagents must be absolutely dry. The reagent is never isolated but used in situ. Virtually all alkyl halides will form Grignard compounds. Reactions of Grignard reagents generally fall into two types: they either attack a hydrogen attached to an O, N, or S, or they add to a compound containing multiple bonds such as  $\text{C}=\text{O}$ ,  $\text{C}=\text{S}$ , or  $\text{N}=\text{O}$ .

Research has identified Grignard-type reagents that can be used in aqueous solution. These reagents are formed between an alkyl halide and tin, zinc, or indium. With tin, the yield is improved if powdered aluminum is also added



**FIGURE 23.7** A solvated molecule of a Grignard reagent,  $\text{RMgBr}[\text{O}(\text{C}_2\text{H}_5)_2]_2$ .

## Grignard Reagents

Victor Grignard, born in Cherbourg, France, in 1871, started his academic career in mathematics at the University of Lyons but later switched to chemistry. However, the reagent named after him was actually discovered by Phillipe Barbier in 1899. Barbier had been searching for a metal to replace zinc in reactions used to insert a methyl group into organic compounds. The disadvantage with zinc was that the zinc compounds caught fire on contact with air. Barbier found that magnesium was a superior substitute. (Of course, a link between zinc and magnesium would be expected on the basis of the (*n*) and (*n* + 10) relationship; see Chapter 9, Section 9.4.)

Barbier asked his junior colleague, Grignard, to study the reaction in more detail. The comprehensive study of

the reaction and of its applicability to a wide range of syntheses formed the basis of Grignard's doctoral thesis in 1901. Although originally called the Barbier-Grignard reaction, Barbier generously insisted that credit should go to Grignard, even though it had been Barbier who first synthesized the key species, methyl magnesium iodide (CH<sub>3</sub>)MgI. In 1912, Grignard was awarded the Nobel Prize in Chemistry and Barbier's contribution forgotten—until recently. There is now a reaction known as the *Barbier reaction*, which is part of the shift toward green chemistry, in which the Grignard-type reagent is generated in the same container as the other reactant, and often in aqueous solution. Thus, Barbier's name is again part of organometallic history.

or if the reaction mixture is heated. The zinc reaction needs traces of acid as a catalyst and tetrahydrofuran (THF) as an additional solvent. The reaction based on indium, however, requires no catalyst and will proceed under very mild conditions in 100 percent water.

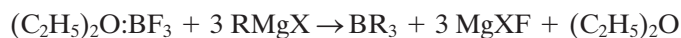
## Organometallic Compounds of the Group 13 Elements

In Group 13, the organometallic compounds of boron and aluminum are the most important, and we will focus mainly on them.

Organoboranes of the type BR<sub>3</sub> can be prepared by the reaction of an alkene with diborane. This is an example of *hydroboration* and involves insertion of the alkenyl group between a boron-hydrogen bond:

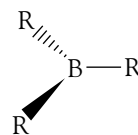
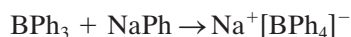


Alternatively, organoboranes can be produced from a Grignard reagent (where X is a halogen):

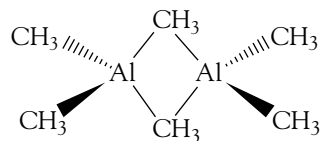


Alkylboranes are all stable to water but are pyrophoric, whereas the aryl species are more stable to oxidation. Organoboranes are monomeric and planar. Like boron trifluoride (see Chapter 13, Section 13.5), the organoboron species are electron deficient and consequently act as Lewis acids and form adducts easily (Figure 23.8).

An important anion is the tetraphenylborate ion, [B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sup>−</sup>, more commonly written as [BPh<sub>4</sub>]<sup>−</sup>, analogous to the tetrahydridoborate ion, [BH<sub>4</sub>]<sup>−</sup> (see Chapter 13, Section 13.4). The sodium salt can be obtained by a simple addition reaction:



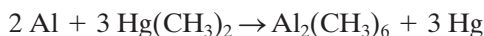
**FIGURE 23.8** A molecule of an alkyl borane, BR<sub>3</sub>.



**FIGURE 23.9** Representation of trimethylaluminum,  $\text{Al}_2\text{Me}_6$ .

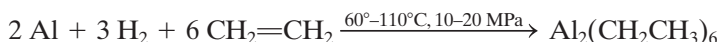
The sodium salt is water soluble, but the salts of most massive, monopositive ions are insoluble. Consequently, the anion is useful as a precipitating agent and can be used in gravimetric analysis.

Alkyl aluminum compounds can be prepared on a laboratory scale by transmetallation of a mercury compound. As an example, dimeric trimethylaluminum can be synthesized as follows:



Commercially, trimethylaluminum (Figure 23.9) is synthesized by the reaction of aluminum metal with chloromethane to give  $\text{Al}_2\text{Cl}_2(\text{CH}_3)_4$ . This compound is then reacted with sodium to give  $\text{Al}_2(\text{CH}_3)_6$ . These dimers are similar in structure to the dimeric halides (see Chapter 13, Section 13.7), but the bonding is different. In the halides, the bridging  $\text{Al}-\text{Cl}-\text{Al}$  bonds are three-center, two-electron bonds; that is, each  $\text{Al}-\text{Cl}$  bond involves an electron pair. In the alkyls, the  $\text{Al}-\text{C}-\text{Al}$  bonds are longer than the terminal  $\text{Al}-\text{C}$  bonds, suggesting that they are three-center, two-electron bonds with one bonding pair shared across the  $\text{Al}-\text{C}-\text{Al}$ , somewhat analogous to the bonding in diborane,  $\text{B}_2\text{H}_6$  (see Chapter 13, Section 13.4).

Triethylaluminum and higher alkyl compounds are prepared from the metal, an appropriate alkene, and hydrogen gas at elevated temperatures and pressures:



This cost-effective route has resulted in aluminum alkyls finding many commercial applications. In particular, triethylaluminum, often written as the monomer,  $\text{Al}(\text{C}_2\text{H}_5)_3$ , is of major industrial importance, as we will see in Section 23.18.

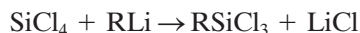
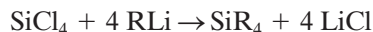
Steric factors have a powerful effect on the structures of aluminum alkyls. While dimers are favored, the long, weak, bridging bonds are easily broken, and this tendency increases with the bulkiness of the ligand. So, for example, triphenylaluminum is a dimer, but the mesityl, 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2-$ , compound is a monomer.

### Organometallic Compounds of the Group 14 Elements

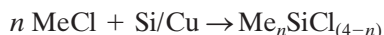
Some Group 14 organometallic compounds are of great commercial importance. Silicon forms the widely used silicones (see Chapter 14, Section 14.17), which can be oils, gels, or rubbers depending on the organic function. Organotin compounds are used to stabilize polyvinyl chloride (PVC) and as antifouling agents on ships, as wood preservatives, and as pesticides. Tetraethyllead was used as an antiknock agent in leaded fuels to increase the octane rating. Generally, organometallic compounds of these elements are tetravalent and have low-polarity bonds. Their stability decreases from silicon to lead.

All tetraalkyl and tetraaryl silicon compounds are monomeric with a tetrahedral silicon center, resembling the carbon analogs. The carbon-silicon bond

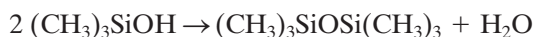
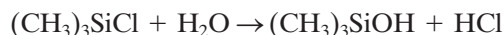
is strong, so all the compounds are fairly stable. They can be prepared in a variety of ways, such as



The *Rochow process* provides industry with a cost-effective route to methylchlorosilane, an important starting material:



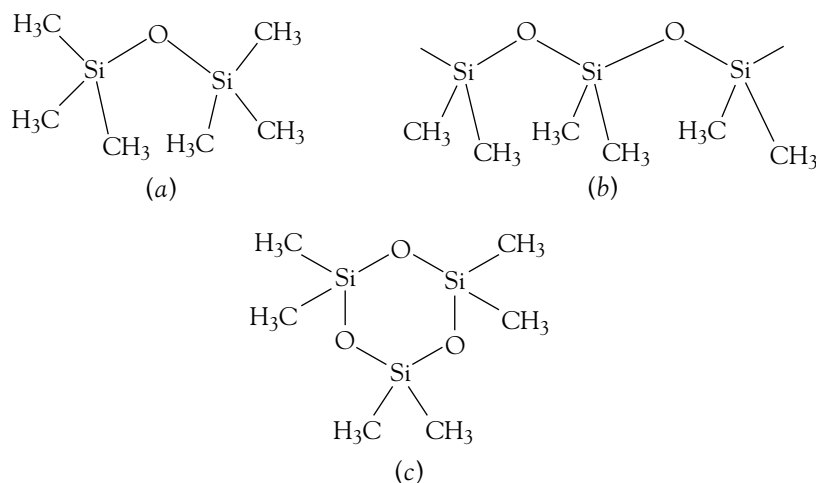
These methylchlorosilanes,  $\text{Me}_n\text{SiCl}_{(4-n)}$ , where  $n = 1-3$ , can be hydrolyzed to form silicones and siloxanes:



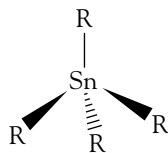
The reaction yields oligomers that contain the tetrahedral silicon group and oxygen atoms with Si—O—Si bridges. Dimers can condense to form chains or rings (Figure 23.10). The hydrolysis of  $\text{MeSiCl}_3$  produces a cross-linked polymer. Silicone polymers have a range of structures and uses, their properties depending on the degree of polymerization and cross-linking. The structures are determined by the choice and the mix of reactants and the use of dehydrating agents such as sulfuric acid and elevated temperatures.

Silicone products have many commercial uses. Silicones are responsible for the “silky” feel of personal-care products such as shampoos, conditioners, shaving foams, hair gels, and toothpastes. In industry, silicone greases, oils, and resins are used as sealants, lubricants, varnishes, waterproofing, synthetic rubbers, and hydraulic fluids.

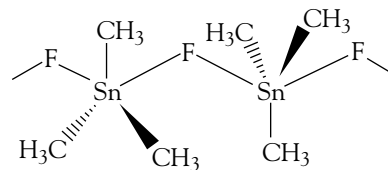
Organotin compounds differ from silicon and germanium compounds in several ways. There is a greater occurrence of the +2 oxidation state and a greater range of coordination numbers, and halide bridges are often present. Most organotin compounds tend to be colorless liquids or solids that are stable



**FIGURE 23.10** Structures of some silicones: (a) a dimer, (b) a chain, and (c) a ring structure.



**FIGURE 23.11** A tetraalkyl tin molecule.

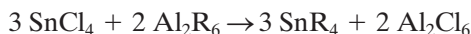
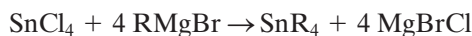


**FIGURE 23.12** The zigzag backbone in  $(\text{CH}_3)_3\text{SnF}$ .

to air and water. The structures of  $\text{R}_4\text{Sn}$  compounds are all similar, with a tetrahedral tin atom (Figure 23.11).

The halide derivatives,  $\text{R}_3\text{SnX}$ , often contain  $\text{Sn}-\text{X}-\text{Sn}$  bridges and form chain structures. The presence of bulky R groups may affect the shape; for example, in  $(\text{CH}_3)_3\text{SnF}$ , the  $\text{Sn}-\text{F}-\text{Sn}$  backbone is in a zigzag arrangement (Figure 23.12), in  $\text{Ph}_3\text{SnF}$  the chain has straightened, and  $(\text{Me}_3\text{SiCH}_2)\text{Ph}_2\text{SnF}$  is a monomer. The haloalkyls are more reactive than the tetraalkyls and are useful in the synthesis of tetraalkyl derivatives.

Alkyl tin compounds may be prepared in a variety of ways, including via a Grignard reagent and by metathesis:



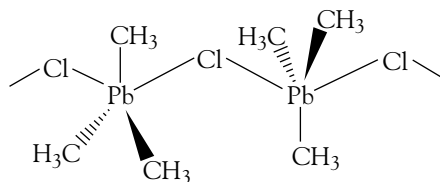
Organotin compounds have the widest range of uses of all main group organometallic compounds, and the worldwide industrial production of organotin complexes has probably now passed the 50 000-tonne level. The major use of tin organometallic compounds is in the stabilization of PVC plastics. Without the additive, halogenated polymers are rapidly degraded by heat, light, or atmospheric dioxygen to give discolored, brittle products.

Organotin(IV) compounds have a wide range of applications relating to their biocidal effects. They are used as fungicides, algicides, wood preservatives, and antifouling agents, but their widespread use has caused environmental concerns. High levels of organotin compounds have been found in harbor regions where boats are treated with organotin compounds to prevent fouling, barnacles, etc. There is evidence that high concentrations of organotin compounds kill some species of marine life and affect the growth and reproduction of others. Many nations now restrict the use of organotin compounds to vessels over 25 m long.

$\text{R}_4\text{Pb}$  compounds can be made in the laboratory via either a Grignard reagent or an organolithium compound:



They are all monomeric molecules with a tetrahedral lead center. However, the halide derivatives may contain bridging halide atoms to form chains,

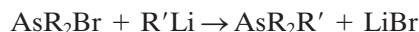
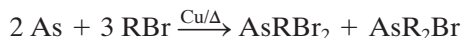
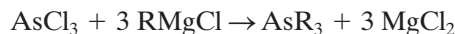


**FIGURE 23.13** Chain structure of  $\text{Pb}(\text{CH}_3)_3\text{Cl}$ .

although monomers are favored with more bulky organic substituents. For example,  $\text{Pb}(\text{CH}_3)_3\text{Cl}$  (Figure 23.13) exists as a chain structure with bridging chloride atoms, whereas the mesityl derivative,  $\text{Pb}(\text{Me}_3\text{C}_6\text{H}_2)_3\text{Cl}$ , is a monomer.

### Organometallic Compounds of the Group 15 Elements

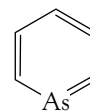
Organometallic compounds of arsenic(III), antimony(III), and bismuth(III) can be prepared by the use of a Grignard or organolithium compound or from the element and an organohalide. The three alternatives are shown in the following:



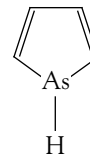
The compounds are all readily oxidized but stable to water. The aryl compounds are more stable than the alkyls. They are all trigonal pyramidal, and the  $\text{M}-\text{C}$  bond strength decreases for a given R group in the order  $\text{As} > \text{Sb} > \text{Bi}$ .

In addition to forming single  $\text{M}-\text{C}$  bonds, arsenic, antimony, and bismuth form  $\text{M}=\text{C}$  double bonds. Arsenine (commonly called *arsabenzene*),  $\text{C}_5\text{H}_5\text{As}$  (Figure 23.14), is stable up to  $200^\circ\text{C}$ ; stibabenzene,  $\text{C}_5\text{H}_5\text{Sb}$ , can be isolated but readily polymerizes; and bismabenzene,  $\text{C}_5\text{H}_5\text{Bi}$ , is very unstable. These compounds exhibit typical aromatic character, although *arsabenzene* is 1000 times more reactive than benzene. A related group of compounds have the Group 15 atom as part of a five-membered ring,  $\text{C}_4\text{H}_4\text{MH}$ : arsenole (commonly called *arsole*) (Figure 23.15), stibole, and bismuthole.

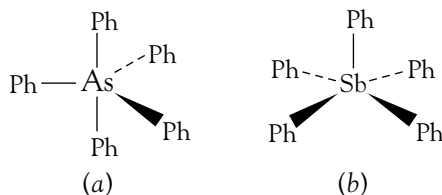
$\text{MR}_5$  compounds are usually trigonal bipyramidal; for example,  $\text{BiMe}_5$  and  $\text{AsPh}_5$  (Figure 23.16a). However,  $\text{SbPh}_5$  is a square-based pyramid (Figure 23.16b). All  $\text{MR}_5$  compounds are thermally unstable, and the stability decreases down the group.



**FIGURE 23.14** Structure of *arsabenzene*.



**FIGURE 23.15** Structure of *arsenole*.



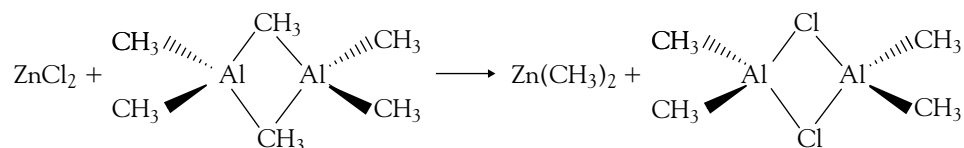
**FIGURE 23.16** Structures of (a)  $\text{AsPh}_5$  and (b)  $\text{SbPh}_5$ .



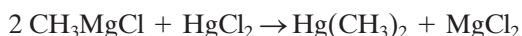
### Organometallic Compounds of the Group 12 elements

The chemistry of the organometallic compounds of zinc, cadmium, and mercury resembles the chemistry of the Group 2 elements much more than that of the transition metals.

The alkyl compounds are linear, monomeric species with two-center, two-electron bonds. Unlike the Group 2 analogs, they do not form polymeric chains through alkyl bridges. They can be prepared by metathesis with an aluminum alkyl. For example, dimethylzinc, first synthesized by Edward Frankland in 1849, can be obtained as follows:



Alkyl zinc compounds are pyrophoric and are readily hydrolyzed in air, whereas the alkyl cadmium compounds are less reactive. Alkyl mercury compounds are prepared by metathesis reactions between mercury(II) halides and a Grignard or organolithium compound.



Dimethylmercury is stable to air oxidation. Alkyl mercury compounds are versatile starting materials for the synthesis of the organometallic compounds of more electropositive metals.

## 23.6 Organometallic Compounds of the Transition Metals

Looking at the formulas of many transition metal organometallic compounds, one might expect their physical and chemical properties to be very similar to those of many of the coordination compounds. In fact, the properties of organometallics are much more “organic” in nature, as the contrast in the following list shows:

Properties of typical coordination compounds	Properties of typical organometallic compounds
Water-soluble	Hydrocarbon-soluble
Air-stable	Air-sensitive
High-melting solids ( $>250^\circ\text{C}$ )	Low-melting solids, or liquids

This difference in properties between transition metal complexes and transition metal compounds involving metal-carbon bonds can be explained in terms of bonding, as will be discussed in the following sections.

### The 18-Electron Rule

As we have seen, main group organometallic compounds generally obey the octet rule and share their valence electrons to form  $\sigma$  bonds with the organo group. For example, tin forms the stable tetramethyltin,  $\text{Sn}(\text{CH}_3)_4$ .

The *18-electron rule* for transition metal organometallics is based on a similar concept—the central transition metal ion can accommodate electrons in the d, s, and p orbitals, giving a maximum of 18. Thus, to the number of electrons in the outer electron set, a metal can add electron pairs from Lewis bases to bring the total up to 18. This rule is not satisfactory for “classic” transition metal complexes for, as we saw in Chapter 19, coordination chemistry (particularly of the 3d metals) is dominated by the presence of incompletely filled d orbitals. However, organometallic complexes of transition metals do commonly obey the 18-electron rule.

The classic examples are the complexes in which carbon monoxide is the ligand. In Chapter 20, Section 20.10, for example, we mentioned tetracarbonylnickel(0),  $[\text{Ni}(\text{CO})_4]$ , a compound used in the purification of nickel metal. In this compound, nickel has an oxidation state of zero. It is important to realize that, although in gaseous atoms the 4s level is filled before the 3d, for example,  $\text{Ni} = [\text{Ar}]4s^23d^8$ , in a chemical environment, the 4s is always higher in energy; that is,  $\text{Ni}^0 = [\text{Ar}]3d^{10}$ .

As we discussed in Section 23.3, each carbon monoxide molecule is taken as a two-electron donor. Thus, the bonding of four carbon monoxide molecules would provide eight additional electrons, resulting in a total of 18:

$$\begin{array}{rcl} \text{Nickel(0) electrons (3d}^{10}\text{)} & = & 10 \\ \text{Carbon monoxide electrons} & = & 4 \times 2 = 8 \\ \text{total} & = & \overline{18} \end{array}$$

Similarly, pentacarbonyliron(0),  $[\text{Fe}(\text{CO})_5]$ , has iron in a zero-oxidation state, giving 8 d electrons and a total of 10 electrons from the five CO groups. The total is once again 18, and this compound, too, is stable.

#### WORKED EXAMPLE 23.3

Deduce whether hexacarbonylchromium(0),  $[\text{Cr}(\text{CO})_6]$ , obeys the 18-electron rule.

#### Answer

Chromium has an electron configuration in a chemical environment in its zero-oxidation state of  $[\text{Ar}]3d^6$ . Each carbonyl is a two-electron donor. So the calculation is as follows:

$$\begin{array}{rcl} \text{Chromium(0) 3d}^6 & = & 6 \\ 6 \times \text{CO} & = & 6 \times 2 = 12 \\ \text{total} & = & \overline{18} \end{array}$$

Therefore, the molecule obeys the 18-electron rule. ■

**WORKED EXAMPLE 23.4**

Deduce whether  $[\text{CoH}(\text{PMe}_3)_4]$  obeys the 18-electron rule.

**Answer**

The hydrido ligand has a  $-1$  charge and  $\text{PMe}_3$  is neutral. Therefore, the cobalt has a formal oxidation state of  $+1$  and has the  $[\text{Ar}]3d^8$  electron configuration. We can calculate the number of valence electrons:

$$\begin{array}{rcl} \text{Cobalt(I)}\ 3d^8 & = & 8 \\ 4 \times \text{PMe}_3 = 4 \times 2 & = & 8 \\ \text{H} & = & 2 \\ \text{total} & = & \underline{18} \end{array}$$

Therefore, the molecule obeys the 18-electron rule. ■

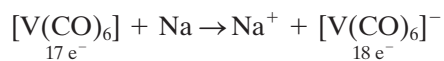
**16-Electron Species**

Although most stable organometallic compounds obey the 18-electron rule, stable complexes do exist with electron counts other than 18, since factors such as crystal field stabilization energy, steric bulk, and the nature of the bonding between the metal and the ligand affect the stability of the compound.

The most widely encountered exceptions to the rule are 16-electron complexes of the transition metals on the right-hand side of the d block, particularly Groups 9 and 10. These 16-electron, square-planar complexes commonly have  $d^8$  electron configurations; for example,  $\text{Rh(I)}$ ,  $\text{Ir(I)}$ ,  $\text{Ni(II)}$ , and  $\text{Pd(II)}$ . Examples of such complexes include the anion of *Zeise's salt*,  $\text{K}^+[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ , and the iridium complex  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ , *Vaska's compound*. Crystal field stabilization energy favors low-spin square-planar  $d^8$  configurations for large values of  $\Delta$ . Values of  $\Delta$  are larger in Periods 5 and 6. Consequently, there are many square-planar complexes of rhodium, iridium, palladium, and platinum. These square-planar complexes are all low spin (see Chapter 19, Section 19.7). The  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ , and  $d_{z^2}$  orbitals all contain two electrons, while the high-energy  $d_{x^2-y^2}$  orbital remains empty. The greater the crystal field splitting, the more stable the complexes will be.

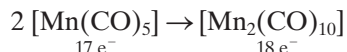
**Odd-Electron Species**

Odd-electron complexes do exist, although they often act as electron acceptors to give an even-electron species. For example,  $[\text{V}(\text{CO})_6]$ , a 17-electron species, readily attains the 18-electron configuration by accepting an electron from a reducing agent:



Other odd-electron species may acquire an additional electron by dimerizing with another molecule. For example,  $[\text{Mn}(\text{CO})_5]$  has 17 electrons. Two

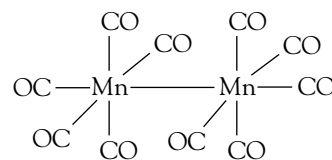
molecules “share” their odd electron in order to form an Mn–Mn bond (Figure 23.17). Consequently, each Mn becomes an 18-electron species.



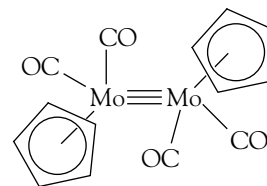
### Metal-Metal Bonding and the 18-Electron Rule

The 18-electron rule can be useful in predicting the number of metal-metal bonds in an organometallic compound that contains multiple metal atoms. Such a molecule will be most stable if the number of electrons around each metal atom is 18. As we have seen from the previous example, the metal may gain additional electrons by forming covalent bonds to another metal atom. For example, if we examine the compound  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_2]_2$ , we see that for each molybdenum center, there are five 4d electrons from the molybdenum(I), six electrons from the cyclopentadienyl ligand, and four electrons from the carbonyl ligands. This gives a total of 15 electrons per molybdenum, which is 3 short of 18. This deficit is made up by forming three bonds to the other molybdenum, and they result in the structure shown in Figure 23.18.

molybdenum(I) electrons ( $4d^5$ )	= 5
cyclopentadienyl electrons	= 6
carbon monoxide electrons = $2 \times 2$	= 4
Mo—Mo shared electrons	= 3
total	= 18



**FIGURE 23.17** Structure of  $\text{Mn}_2(\text{CO})_{10}$ .



**FIGURE 23.18** Structure of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_2]_2$ .

### WORKED EXAMPLE 23.5

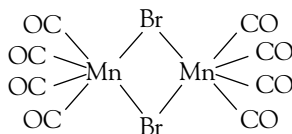
Predict the number of metal-metal bonds in  $[\text{Mn}(\mu\text{-Br})(\text{CO})_4]_2$  and suggest a structure.

#### Answer

Each bromine ligand has a charge of  $-1$ . Therefore, each manganese atom is in a formal oxidation state of  $+1$  and the electron configuration is  $[\text{Ar}]3d^6$ . The total number of valence electrons for each manganese atom can be calculated:

Mn(I) electrons ( $3d^6$ )	= 6
CO electrons = $4 \times 2$	= 8
$2 \times \mu\text{-Br}$ electrons	= 4
total	= 18

Note that the  $\mu\text{-Br}$  donates two electrons to each manganese atom. This molecule already has 18 electrons so there is no need for Mn—Mn bonding. The dimer is held together by the two bridging Br ligands. ■



## 23.7 Transition Metal Carbonyls

Transition metal carbonyls are the most important class of transition metal organometallic compounds. The classic  $\sigma$ -bonding ligands form complexes with both main group and transition metals, but this is not true of carbon monoxide as a ligand. With the exceptions of borane carbonyl,  $\text{H}_3\text{BCO}$ , and the potassium carbonyl,  $\text{K}_6(\text{CO})_6$ , the only known carbonyls are those of transition metals. In transition metal carbonyls, the  $\sigma$  bonding is reinforced by additional  $\pi$  bonding that stabilizes the complexes and also stabilizes very low-oxidation states of the metal. Many carbonyl compounds exist with the metal in a zero-oxidation state; for example, hexacarbonylchromium(0),  $[\text{Cr}(\text{CO})_6]$ . These very low-oxidation states are not found with  $\sigma$  bonding-only ligands such as water and ammonia.

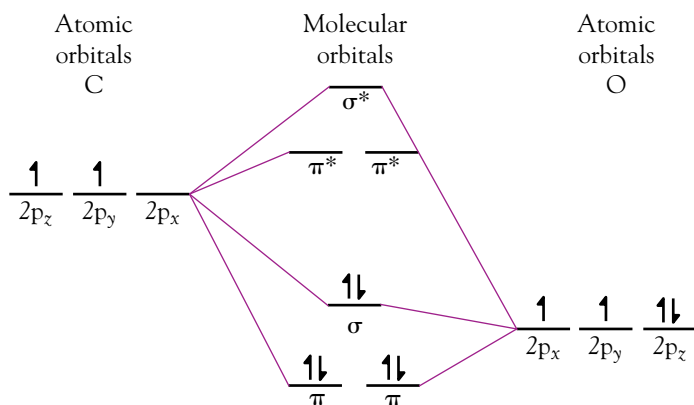
Carbonyl compounds are volatile and toxic. Their toxicity arises from their interaction with hemoglobin in red blood cells. In hemoglobin, iron has an oxidation state of +2. There are four iron ions in a hemoglobin molecule, each iron ion being surrounded by a porphyrin unit (see Chapter 20, Section 20.6). Each hemoglobin molecule reacts with four molecules of dioxygen to form oxyhemoglobin. The bonding to the dioxygen molecules is weak, and the oxygen can be released quite readily. However, the carbonyl ligand bonds almost irreversibly to the iron of the hemoglobin due to the strength of the  $\sigma$  and  $\pi$  contributions to the bonding, thus preventing the iron from carrying dioxygen molecules.

### Bonding in Carbonyl Compounds

As mentioned previously, it is the nature of the bonding between carbon monoxide and a transition metal that makes carbon monoxide so lethal. This bonding is also the reason why so many transition metal carbonyl compounds exist, why they are so stable, why they can exist in low-oxidation states, and why main group carbonyls are very rare. Thus, we need to look at the bonding between transition metals and carbon monoxide in some detail.

In Chapter 3, Section 3.5, we saw that the bonding in heteronuclear diatomic molecules can be represented by a molecular orbital diagram. Because the effective nuclear charge differs between the constituent atoms, the orbital energies are lower for the atom with the higher effective nuclear charge. Figure 23.19 shows a simplified molecular orbital diagram for the carbon monoxide molecule (a more sophisticated representation would mix in some 2s component to the bonding; see Chapter 3, Section 3.9).

For the carbon monoxide molecule, the highest-energy occupied molecular orbital (HOMO) is a  $\sigma_{2p}$  orbital essentially derived from the high-energy 2p carbon and oxygen atomic orbitals. We assume this orbital resembles a lone pair on the carbon atom. The lowest-energy unoccupied molecular orbitals (LUMOs) are the  $\pi^*_{2p}$  antibonding orbitals. Again, the predominant contribution comes from the 2p atomic orbitals of carbon, so they, too, are focused



**FIGURE 23.19** Partial simplified molecular-orbital-energy-level diagram for carbon monoxide.

around the carbon rather than around the oxygen atom. Approximate shapes of these orbitals are shown in Figure 23.20.

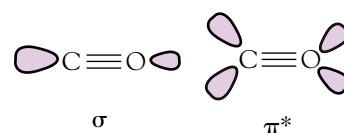
We can picture an overlap of the end of the  $\sigma$  HOMO of the carbon monoxide with an empty d orbital of the metal (Figure 23.21); that is, the carbon monoxide is acting as a Lewis base and donating a pair of electrons to the metal that acts as a Lewis acid.

This leads to high electron density on the metal. Imagine six ligands simultaneously donating electrons to a metal center, which, if it is in a low-oxidation state, will already be electron-rich. At the same time, there is an overlap of a full d orbital on the metal with the  $\pi^*$  LUMO of the carbon monoxide (Figure 23.22). These two orbitals have the correct symmetry to allow this interaction, and thus the electron density is removed from the metal center back onto the carbonyl ligand to some extent.

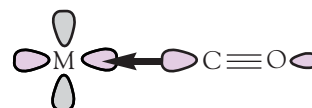
This additional bond is a  $\pi$  bond. So, the carbon monoxide is said to be a  $\sigma$  donor and a  $\pi$  acceptor, and the metal is a  $\sigma$  acceptor and a  $\pi$  donor. Thus, there would be a flow of electrons from the carbon monoxide to the metal through the  $\sigma$  system and a flow (*back bonding* or *synergistic bonding*) through the  $\pi$  system in the reverse direction. This *synergistic effect* leads to a strong, short, almost double covalent bond between the metal and carbon atoms.

It is the removal of electron density from the metal by the carbonyl ligand that enables us to account for the stabilization of low-oxidation states of transition metals. In a low- or zero-oxidation state, the metal would have a full, or nearly full, complement of electrons even before the bonding of the carbonyl ligands. The even higher electron density that results from coordination is then effectively removed to the ligands by the synergistic effect.

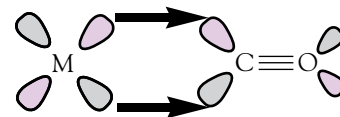
According to this representation of the bonding, electrons would be “pumped” into the  $\pi$  antibonding orbital of the carbon monoxide. An increased occupancy of antibonding orbitals would lead to a reduction of the bond order below its value of 3 in the free carbon monoxide molecule. Experimental measurements have shown that, indeed, the carbon-oxygen bond in these carbonyl compounds is longer and weaker than that in carbon monoxide itself. This is



**FIGURE 23.20** The highest-energy occupied molecular orbital ( $\sigma$ ) and the lowest-energy unoccupied molecular orbital ( $\pi^*$ ) for carbon monoxide.



**FIGURE 23.21** Sigma donation from the carbonyl ligand to the metal.



**FIGURE 23.22** Pi back bonding from the metal to the carbonyl ligand.

good evidence for the validity of our molecular orbital bonding model. As added evidence, nearly all stable neutral metal carbonyl compounds are found in the middle transition metal groups (Groups 6 to 9), where the metal has some d electrons available for donation into the carbonyl  $\pi$  system but few enough that other d orbitals are empty and capable of accepting electron pairs from carbonyl ligands.

Other ligands can bond to transition metals in this way, for example, alkenes and phosphines, but they are not as good  $\pi$  acceptors as carbon monoxide.

### Evidence for Synergistic Bonding

Infrared spectroscopy is a useful tool for investigating the structures of carbonyl compounds. The  $\text{C}\equiv\text{O}$  bond vibrates around  $2143\text{ cm}^{-1}$  in the gaseous state. The vibration frequency in carbonyl compounds lies within the range 2150 to  $1850\text{ cm}^{-1}$ , depending on the structure and nature of other ligands present.

If the synergistic bonding model is valid, then we would expect the length and strength of the  $\text{C}\text{—}\text{O}$  bond to be affected as electrons are pushed into the  $\pi^*$  orbital. As the bond becomes weaker and longer, it should vibrate at a lower frequency. (Think about “twanging” a tight elastic band. This is like a strong bond and vibrates at a high frequency. Now compare this to what happens when you twang a less taut elastic band. This represents the “weaker” bond and will vibrate at a lower frequency.) The fact that  $\text{C}\equiv\text{O}$  bonds in carbonyl compounds do vibrate at lower frequencies than gaseous carbon monoxide does, indeed, support this model.

The  $\text{C}\text{—}\text{O}$  stretching frequency is very sensitive to the electronic environment around the metal. For example, a higher electron density on the metal will cause an increase in the extent of the back bonding as more electron density is removed. This leads to an increase in the electron density in the  $\pi^*$  orbital, a lengthening of the bond, and a decrease of the  $\text{C}\text{—}\text{O}$  stretching frequency. This effect can be seen in the isoelectronic series

$[\text{Fe}(\text{CO})_4]^{2-}$	$1790\text{ cm}^{-1}$
$[\text{Co}(\text{CO})_4]^-$	$1890\text{ cm}^{-1}$
$[\text{Ni}(\text{CO})_4]$	$2060\text{ cm}^{-1}$

All of these species have eight d electrons. However, the effective nuclear charge increases from iron to nickel (see Chapter 2, Section 2.5). This means that the *residual* negative charge of the metal is greater for iron than for nickel. As the negative charge on the complex increases, the metal has a higher electron density to be dispersed and so the back bonding is increased. Consequently, the electron density in the  $\pi^*$  will be increased, and the bond between the carbon and oxygen will become weaker and vibrate at a lower frequency.

In substituted carbonyls, the extent of back bonding can be observed by examining CO frequencies:

$[\text{Ni}(\text{CO})_3(\text{PMe}_3)]$	$2064\text{ cm}^{-1}$
$[\text{Ni}(\text{CO})_3(\text{PPh}_3)]$	$2069\text{ cm}^{-1}$
$[\text{Ni}(\text{CO})_3(\text{PF}_3)]$	$2111\text{ cm}^{-1}$

The methyl groups on  $\text{PMe}_3$  show an inductive effect. An *inductive effect* is the shifting of electrons in a bond in response to the electronegativity of nearby atoms. In other words, a highly electronegative atom will tend to pull electron density toward itself, while an electropositive group will act as an electron source. In this case, electron density will be pushed toward the metal. This leads to an increase in the extent of back bonding, stronger  $\text{M—C}$  bonds, and a weaker  $\text{C—O}$  interaction, shown by the lower infrared stretching frequency. By contrast, fluorine in  $\text{PF}_3$  is electron withdrawing and will remove electron density from the metal. This leads to a reduction in the extent of back bonding required, and so the  $\text{C—O}$  bond remains stronger and shorter, indicated by the higher stretching frequency.

### WORKED EXAMPLE 23.6

Predict which of  $[\text{Cr}(\text{CO})_5(\text{PEt}_3)]$  and  $[\text{Cr}(\text{CO})_5(\text{PPh}_3)]$  will have the lower CO stretching frequency? Which will have the shorter  $\text{Cr—C}$  bond?

#### Answer

The ethyl groups on  $\text{PEt}_3$  show more of an inductive effect than the phenyl groups on  $\text{PPh}_3$ . So there will be higher electron density on the cobalt in  $[\text{Cr}(\text{CO})_5(\text{PEt}_3)]$  and the extent of back bonding will be greater, leading to a shorter stronger  $\text{Cr—C}$  bond, a longer weaker  $\text{C—O}$  bond, and thus a lower  $\text{C—O}$  infrared stretching frequency. ■

## Symmetry in Carbonyl Compounds

As we have seen, infrared spectroscopy can be used to provide information about the electronic environment of a carbonyl ligand. Infrared spectroscopy can also be used to probe the structures of transition metal carbonyl compounds. A molecule is infrared active if a stretching mode results in a change in a dipole (see Chapter 3, Section 3.14). If we consider an octahedral carbonyl complex,  $[\text{M}(\text{CO})_6]$ , a symmetrical stretch of each  $\text{C—O}$  bond gives no overall change in dipole, so this stretching mode is not seen in the infrared spectrum of the compound.

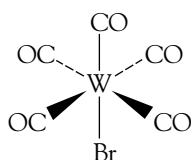
However, we have to consider all other possible stretching modes. We can use the symmetry of the molecule and group theory to calculate the expected number of infrared (and Raman) active stretching modes for a molecule. These calculations are beyond the scope of this text, so we will use a shortcut that applies the results of the group theoretical approach. To predict the expected number of  $\text{C—O}$  peaks in an infrared spectrum of a carbonyl compound, we consider the shape of the  $\text{M—CO}$  part of the molecule only and refer to Table 23.4.

For example,  $[\text{W}(\text{CO})_6]$  is octahedral with the point group  $\text{O}_h$ . Table 23.4 indicates that one stretching mode is infrared active, and, in fact, one peak is observed in the infrared spectrum of  $[\text{W}(\text{CO})_6]$ . If we substitute one CO group



**TABLE 23.4** Number of C—O stretching bands in the infrared spectrum

Residual shape	Point group	Number of bands
Linear	$D_{\infty h}$	1
Bent	$C_{2v}$	2
Planar triangle	$D_{3h}$	2
Pyramid	$C_{3v}$	2
Tetrahedral	$T_d$	1
Square planar	$D_{4h}$	1
Trigonal bipyramid	$D_{3h}$	2
Square pyramid	$C_{4v}$	2
Octahedral	$O_h$	1

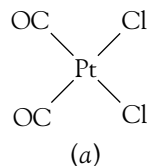
**FIGURE 23.23** Structure of  $[\text{WBr}(\text{CO})_5]$ .

by a halide (Figure 23.23), the overall molecule is still octahedral, but the shape made by the M—CO is a square pyramid with a  $C_{4v}$  point group. According to Table 23.5, there are two infrared active stretching modes, and two peaks are indeed observed in the infrared spectrum. Infrared spectroscopy can be used to distinguish between isomers. For example, consider the *cis* and *trans* isomers of the square-planar  $[\text{PtCl}_2(\text{CO})_2]$  (Figure 23.24). The *cis* isomer gives a bent arrangement of M—CO bonds, which gives rise to two infrared active stretching modes and two peaks. The *trans* isomer gives a linear arrangement of M—CO bonds, which gives rise to one infrared active stretching mode and one peak in the infrared spectrum.

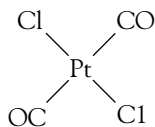
### Types of Carbonyl Bonding

As we described in Section 23.2, the carbonyl ligand may bond to transition metal centers in several ways. It may bond as a terminal ligand, as in simple complexes such as  $[\text{Mo}(\text{CO})_6]$ , Figure 23.25, in which it acts as a two-electron donor. The carbonyl infrared stretching frequency for these groups is usually in the range from 2010 to 1850  $\text{cm}^{-1}$ .

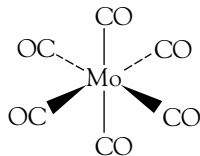
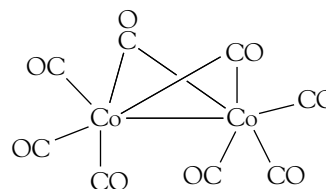
The carbonyl ligand may also bridge two or more metal centers (see Figure 23.3). In this case, the carbonyl infrared stretching frequency is in the range 1850–1750  $\text{cm}^{-1}$ . A carbonyl that bridges two metals atoms is identified by the prefix  $\mu$  or, more precisely,  $\mu^2$ , and donates one electron to each metal species. An example of a complex with bridging carbonyl groups is  $[\text{Co}_2(\text{CO})_8]$  (Figure 23.26).

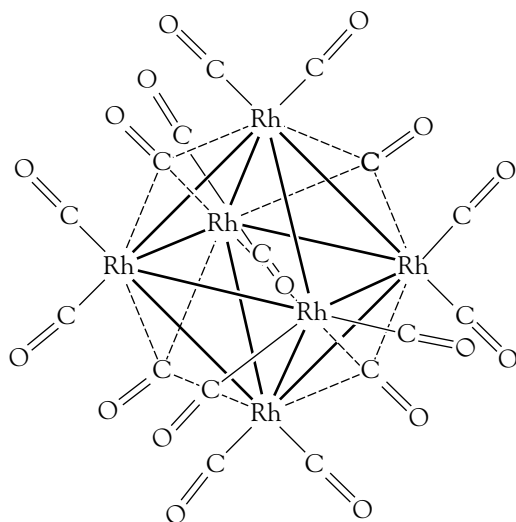


(a)



(b)

**FIGURE 23.24** Structure of (a) *cis* and (b) *trans*- $[\text{PtCl}_2(\text{CO})_2]$ .**FIGURE 23.25** Structure of  $[\text{Mo}(\text{CO})_6]$ .**FIGURE 23.26** Structure of  $[\text{Co}_2(\text{CO})_8]$ .



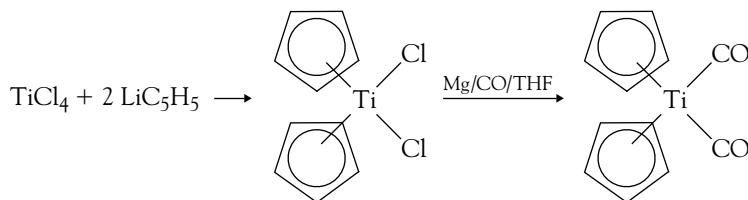
**FIGURE 23.27** Structure of  $[\text{Rh}_6(\text{CO})_{16}]$ .

When carbonyl ligands bridge three metal centers, the carbonyl infrared stretching frequencies lie in the range  $1675\text{--}1600\text{ cm}^{-1}$ . These most often occur in “cluster” compounds and are given the prefix  $\mu^3$ ; for example,  $[\text{Rh}_6(\text{CO})_{16}]$  (Figure 23.27).

## 23.8 Synthesis and Properties of Simple Metal Carbonyls

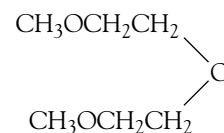
### Carbonyls of the Group 4 Elements

Titanium has a  $d^4$  electron configuration. The 18-electron rule suggests that the stable carbonyl would be  $[\text{Ti}(\text{CO})_7]$ , but titanium has insufficient electron density for this to be formed. However, substituted carbonyls are known. For example,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2]$  is a red, 18-electron compound that is prepared from titanium(IV) chloride:



### Carbonyls of the Group 5 Elements

Hexacarbonylvandium(0),  $[\text{V}(\text{CO})_6]$ , a 17-electron species, is a green-black, paramagnetic solid that decomposes at  $70^\circ\text{C}$ . It can be prepared from vanadium(III) chloride via an 18-electron anionic intermediate using 2-methoxyethyl ether, abbreviated to *diglyme* (from the common name *diethyleneglycol dimethyl ether*), as solvent (Figure 23.28):



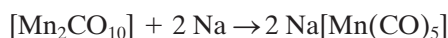
**FIGURE 23.28** Structure of diglyme.

### Carbonyls of the Group 6 Elements

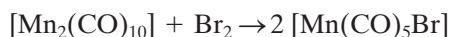
Hexacarbonylchromium(0),  $[\text{Cr}(\text{CO})_6]$ , is a stable, 18-electron, octahedral molecule that can be synthesized in the same way as  $[\text{V}(\text{CO})_6]$ . All three Group 6 hexacarbonyls,  $[\text{Cr}(\text{CO})_6]$ ,  $[\text{Mo}(\text{CO})_6]$ , and  $[\text{W}(\text{CO})_6]$ , are white crystalline solids that will sublime under vacuum. They are the most stable binary carbonyl compounds and do not react until heated.

### Carbonyls of the Group 7 Elements

Manganese forms the 17-electron pentacarbonylmanganese(0),  $[\text{Mn}(\text{CO})_5]$ . It readily dimerizes to give the 18-electron, yellow, crystalline  $[\text{Mn}_2(\text{CO})_{10}]$ , as we mentioned in Section 23.6. The Mn—Mn bond is long and weak and is easily broken. For example, the reaction with sodium amalgam leads to cleavage of the Mn—Mn bond and reduction of the manganese to manganese(−I):



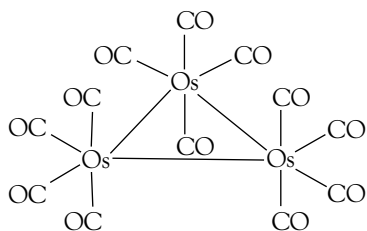
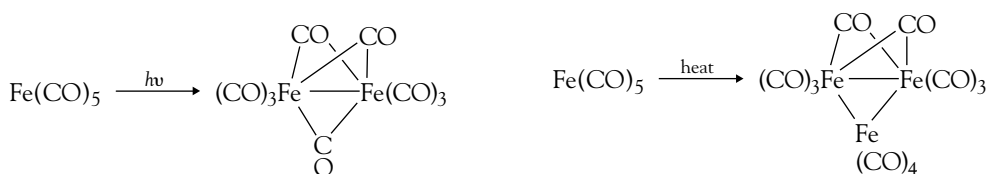
The reaction with a halogen leads to cleavage of the bond and oxidation of the manganese to manganese(I):



The corresponding carbonyls of the lower members of the group,  $[\text{Tc}_2(\text{CO})_{10}]$  and  $[\text{Re}_2(\text{CO})_{10}]$ , are both white, crystalline solids.

### Carbonyls of the Group 8 Elements

Pentacarbonyliron(0),  $[\text{Fe}(\text{CO})_5]$ , is a yellow, toxic liquid that is used for making magnets and iron films. It can be prepared by heating finely divided iron under carbon monoxide.  $[\text{Fe}(\text{CO})_5]$  reacts photochemically to give the yellow dimer  $[\text{Fe}_2(\text{CO})_9]$ . When heated, it forms the dark green solid  $[\text{Fe}_3(\text{CO})_{12}]$ :



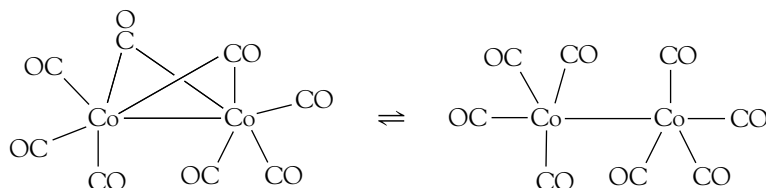
**FIGURE 23.29** Representation of  $[\text{Os}_3(\text{CO})_{12}]$ .

Ruthenium and osmium form  $[\text{Ru}(\text{CO})_5]$  and  $[\text{Os}(\text{CO})_5]$ , which are both colorless liquids. They also form corresponding cluster compounds,  $[\text{Ru}_3(\text{CO})_{12}]$  and  $[\text{Os}_3(\text{CO})_{12}]$ , although their structures are different from that of  $[\text{Fe}_3(\text{CO})_{12}]$ . The structure of  $[\text{Os}_3(\text{CO})_{12}]$  is shown in Figure 23.29.

### Carbonyls of the Group 9 Elements

Cobalt has an odd number of electrons, so the carbonyl compound,  $[\text{Co}(\text{CO})_4]$ , has 17 electrons and dimerizes to give  $[\text{Co}_2(\text{CO})_8]$ , an orange, low-melting solid. The solid contains a metal-metal bond and bridging carbonyl groups, as described in Section 23.7. However in hexane solution, the compound changes to a different isomeric form. The bridging carbonyl bands disappear from the

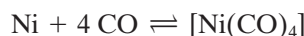
infrared spectrum and a staggered structure is formed. The energy difference between these two forms is only approximately  $5 \text{ kJ}\cdot\text{mol}^{-1}$ , so the interconversion occurs easily. Such interconversions and intramolecular rearrangements are common in organometallic chemistry.



Cobalt also forms the cluster compounds  $[\text{Co}_4(\text{CO})_{12}]$  and  $[\text{Co}_6(\text{CO})_{16}]$ , which are both black solids. Rhodium and iridium also form cluster compounds of the same formula and similar structures. The structure of  $[\text{Rh}_6(\text{CO})_6]$  was shown in Section 23.7.

### Carbonyls of the Group 10 Elements

Tetracarbonylnickel(0),  $[\text{Ni}(\text{CO})_4]$ , is a toxic, colorless liquid synthesized by direct interaction of carbon monoxide with the finely divided metal. The reaction takes place a little above room temperature and at atmospheric pressure. The reaction is the basis of the Mond process for extraction and purification of nickel (see Chapter 20, Section 20.10).

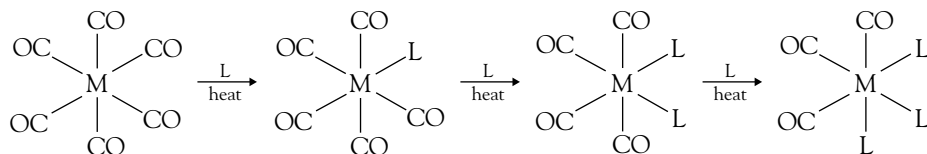


### Carbonyls of the Group 11 Elements

Copper has very high electron density and no vacant d orbitals. A few substituted carbonyl compounds are known, but they are all very unstable.

## 23.9 Reactions of Transition Metal Carbonyls

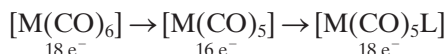
The most important reactions of metal carbonyls are substitution reactions. Carbonyl ligands can be displaced by other ligands such as phosphines and unsaturated hydrocarbons. The substitution may be activated by either heat or light, and the products usually still obey the 18-electron rule. For example, for an octahedral complex such as  $[\text{Cr}(\text{CO})_6]$ , the reaction with another ligand may lead to a trisubstituted carbonyl:



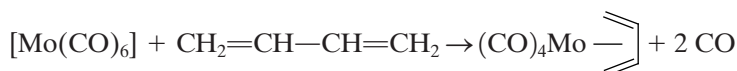
Subsequent substitutions by the incoming ligand always happen *cis* to the initial ligand. This is because the substitution of any ligand that is a better

$\sigma$  donor but poorer  $\pi$  acceptor than carbonyl will lead to an increase in the back bonding between the metal and the carbonyl ligand *trans* to the incoming ligand. The substitution reaction rarely proceeds further than  $[\text{M}(\text{CO})_3\text{L}_3]$  because the electron density on the metal would be too great.

These substitution reactions of 18-electron complexes follow a *dissociative mechanism*, which means that a species that is coordinatively unsaturated is produced as an intermediate. An associative mechanism would produce a seven-coordinate intermediate, a complex with more than 18 electrons:



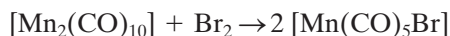
Complexes of 4d transition metals react much more quickly than those of the 5d metals. As a result, ruthenium, rhodium, and palladium are much more widely used in catalysis than osmium, iridium, and platinum, as we will see later in the chapter. Some typical substitution reactions are the following:



Another important type of reaction is the formation of carbonylate anions by reaction with reducing agents or alkali. The species that form anions most readily are odd-electron species, particularly 17-electron species, and dimers. The species formed are 18-electron complexes. For example,



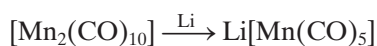
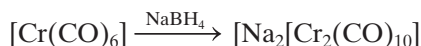
A related reaction of dimers is the formation of halides by reaction with a halogen and cleavage of the metal-metal bond:



## 23.10 Other Carbonyl Compounds

### Metal Carbonyl Anions

As we have already mentioned, the reduction of metal carbonyls gives rise to anionic species that are very reactive. These are most often prepared by reacting a carbonyl compound with an alkali metal or sodium borohydride:

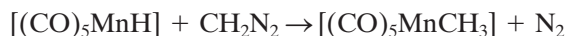
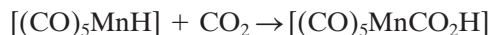


Some of these compounds form hydrides, such as  $[\text{HMn}(\text{CO})_5]$ , when acidified. Manganese, iron, and cobalt carbonyl hydrides are colorless or yellow

liquids. Studies have shown that the hydrogen is directly attached to the metal. The  $[\text{HMn}(\text{CO})_5]$  and  $[\text{H}_2\text{Fe}(\text{CO})_4]$  compounds are quite acidic in aqueous solution. The cobalt compound,  $[\text{HCo}(\text{CO})_4]$ , is insoluble in water but is a strong acid in methanol.

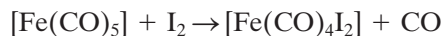
### Metal Carbonyl Hydrides

Metal carbonyl hydrides are highly reactive, and most reactions involve the insertion of another species into the  $\text{M}-\text{H}$  bond. Some typical reactions of metal hydrides are the following:

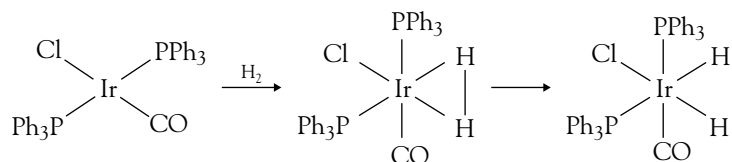


### Metal Carbonyl Halides

Most metals that form stable carbonyls also form carbonyl halides. Their structures are analogous to the carbonyl for monomeric species. Dimers are always bridged through the halide rather than through the carbonyl. They are usually white or yellow solids and are made by the reaction of a halogen with a metal carbonyl at high temperatures and pressures. For example:



Carbonyl halides are soluble in organic solvents but decompose in water. Most of the carbonyl halides obey the 18-electron rule. The most notable exception is Vaska's compound, *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ . This compound undergoes a wide range of addition reactions during which the metal atom achieves 18 electrons in the valence shell. During these reactions, the square-planar compound is converted to an octahedral one and the iridium is oxidized by two charge units. This type of reaction is known as *oxidative addition*. The scheme for the oxidative addition of Vaska's complex with hydrogen is shown in the following figure. Note the three-centered intermediate formed between the metal and the  $\text{H}_2$ .

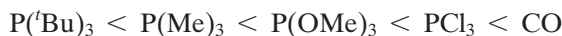


Oxidative addition is a common reaction of organometallic compounds, and it is key to many catalytic processes. For an oxidative addition reaction to occur, there must be two free sites for coordination of incoming ligands and the metal must be able to exist in stable oxidation states separated by two units. During the reaction, two ligands are associated to the metal, which is simultaneously oxidized by two units. The reverse of the reaction is, not surprisingly, called *reductive elimination*.

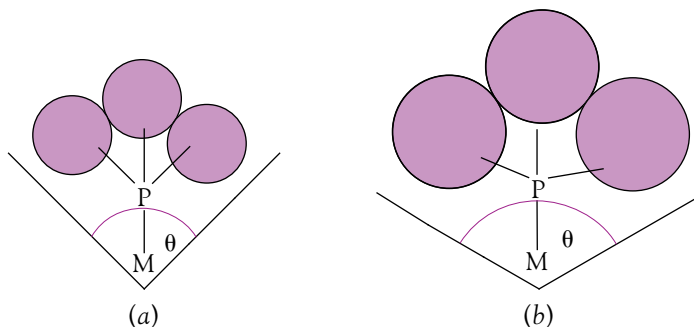
### 23.11 Complexes with Phosphine Ligands

We have already seen that metal carbonyl complexes may react with ligands such as triphenyl phosphine and phosphorus trichloride. Phosphine ligands are so important that they deserve a whole section for discussion.

Phosphines are able to accept some electron density through back bonding via the P—C (antibonding)  $\sigma^*$  orbital. The extent of this back bonding depends on the nature of the ligand. For example, alkyl phosphines, such as  $\text{P}(\text{CH}_3)_3$ , are strong electron donors but fairly weak electron acceptors due to the inductive effect of the alkyl group. Conversely, the phosphine halides are weak donors but strong electron acceptors due to the electron-withdrawing properties of the halide atoms.  $\pi$ -Acidity is the term used to describe the ability of a species to accept electron density through a  $\pi$ -type overlap of orbitals. The order of increasing  $\pi$  acidity is given by



So, the stability of a phosphine-containing species is affected by the electronic characteristics of the phosphine. A further important factor in determining the stability and structure of phosphine-containing ligands is the shape and size of the ligand, the steric bulk. The “bulkiness” of a ligand is defined by its *Tolman cone angle*. Figure 23.30 shows that a small, compact, substituted ligand gives a small Tolman cone angle, whereas a large, bulky, substituted phosphine gives a large cone angle. Some examples are given in Table 23.5.



**FIGURE 23.30** The Tolman cone angle for (a) a small and (b) a bulky phosphine ligand.

**TABLE 23.5** Tolman cone angles for phosphine ligands

Ligand	$\Theta/\text{deg}$
$\text{PH}_3$	87
$\text{PF}_3$	104
$\text{PMe}_3$	118
$\text{PMe}_2\text{Ph}$	123
$\text{PMePh}_2$	136
$\text{PPh}_3$	145
$\text{P}^i\text{Bu}_3$	183

With the crowding resulting from bulky ligands, it is not surprising that a ligand can sometimes be expelled. For example, tetrakis(triphenylphosphine) platinum(0),  $[\text{Pt}(\text{PPh}_3)_4]$ , readily loses a ligand to form tris(triphenylphosphine) platinum(0),  $[\text{Pt}(\text{PPh}_3)_3]$ . These two factors, the amount of electron density on the metal and the bulkiness of the ligand, determine the reactivity and the coordination number of the complex.

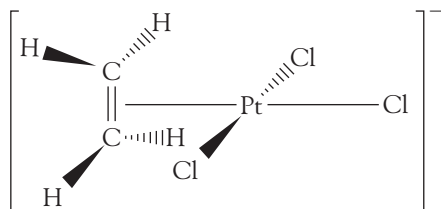
## 23.12 Complexes with Alkyl, Alkene, and Alkyne Ligands

The making and breaking of  $\text{M}-\text{C}$  bonds play an important role in organometallic chemistry and are central to its application in catalysis. Whenever alkanes, alkenes, or alkynes are generated, polymerized, or functionalized, metal alkyl intermediates are involved. About 75 percent of all products produced by the chemical industry pass through a catalytic cycle involving an organometallic catalyst at some stage.

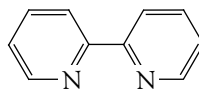
Transition metals form simple alkyls, but, with the exception of zinc and mercury, they are unstable. Most stable organometallic compounds are formed with alkenes, alkynes, and unsaturated ring systems. The first truly organometallic compound to be synthesized was the yellow, crystalline Zeise's salt,  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ , in 1830 (Figure 23.31).

Transition metal organometallic compounds with metal-alkyl bonds are known with both  $\sigma$  and  $\pi$  interactions. In general, most compounds obey the 18-electron rule with the exception of alkyl groups, which are only  $\sigma$  bonded to the metal. Some of these, such as Zeise's salt, mentioned before, have only 16 electrons. They are square planar and are said to be *coordinationally unsaturated*, which means that they can accept other ligands to give a maximum of six-coordination. Such coordinative unsaturation is an extremely important feature of transition metal homogeneous catalysis. Simple  $\sigma$ -bonding alkyls can be understood by analogy with metal halides and hydrides. So a methyl ligand will be considered to have a formal charge of  $-1$  and donate two electrons to the metal.

Alkyls that contain no other groups are very unstable. For example,  $[\text{Ti}(\text{CH}_3)_4]$  decomposes at  $-50^\circ\text{C}$ , whereas  $[\text{Ti}(\text{bipy})(\text{CH}_3)_4]$  (*bipy* is the abbreviation for bipyridine; Figure 23.32) can be warmed to  $30^\circ\text{C}$ . Alkyls are stabilized by the presence of  $\pi$ -bonding ligands such as bipyridine, carbonyl, and triphenylphosphine, which results in an increase in stability since the electron density can be removed from the metal.



**FIGURE 23.31** Structure of the anion of Zeise's salt,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ .

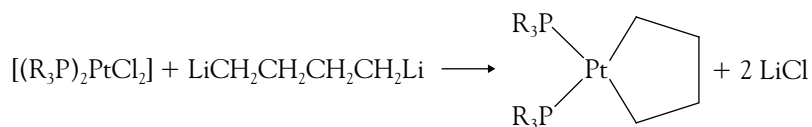
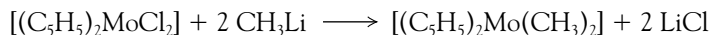


**FIGURE 23.32** Bipyridine.

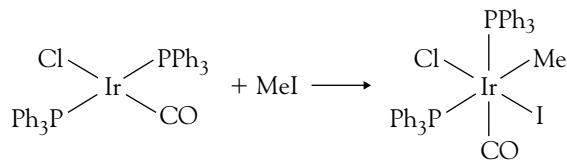


### Synthesis of Transition Metal Alkyls

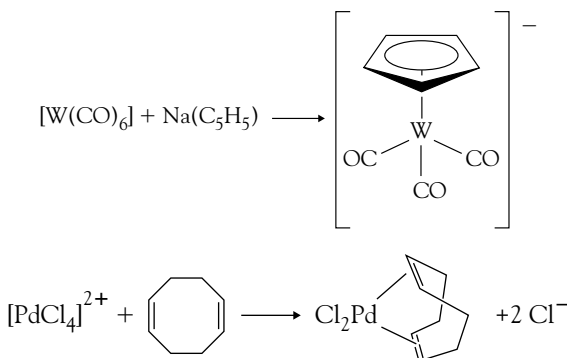
The most widely used method for preparing transition metal alkyls is *alkylation*, often using a Grignard reagent or a lithium alkyl:



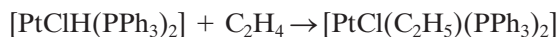
Low-valent complexes, stabilized by phosphines, can be synthesized by oxidative addition with an alkyl halide. Such stabilization is particularly important for iridium(I), nickel(0), palladium(0), and platinum(0) complexes. For these species, we have a coordinatively unsaturated, square-planar complex containing labile ligands that is simultaneously oxidized and has the coordination number expanded to 6. Whether the final product is *cis* or *trans* is influenced by the solvent. For example, for Vaska's compound, *cis*-addition occurs:



Complexes of alkenes, alkynes, and polyconjugated systems are prepared when other ligands, often carbonyl, are displaced. The 18-electron rule can be used to predict the formulas of the products since each  $\pi$  bond can replace a lone pair donated by another ligand:



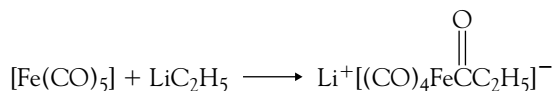
Another common method of synthesis is to insert a molecule into an M—H bond. For example:



And:



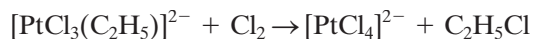
Polar, unsaturated ligands (for example, carbonyl) are susceptible to nucleophilic attack. A *nucleophile* is a reagent that is “nucleus loving,” having electron-rich sites that can form a bond by donating an electron pair to an electron-poor site. Nucleophiles are often, although not always, negatively charged. The converse is an *electrophile*, an electron-poor species that will accept an electron pair, sometimes a positively charged species. This pair of definitions might sound familiar (see Chapter 7, Section 7.5). Lewis bases are electron donors and usually behave as nucleophiles, whereas Lewis acids are electron acceptors and usually behave as electrophiles. The main difference is that the terms *nucleophile* and *electrophile* are normally used in the context of bonds to carbon. In the following reaction, the ethyl anion,  $\text{C}_2\text{H}_5^-$ , is the nucleophile, and the carbon of a carbonyl is the electrophile:



As with the carbonyl complexes, most transition metal alkyls obey the 18-electron rule (Figure 23.33) or have 16 electrons for the square-planar  $d^8$  system. On the other hand, there are numerous complexes for which the stability cannot be explained on the basis of the 18-electron rule. These species often have very low numbers of electrons and owe their stability to the kinetic stabilization provided by sterically demanding, bulky ligands. These ligands are often too bulky to allow the metal to bind to enough donor ligands in order to achieve the higher electron count but provide an effective “umbrella,” shielding the metal from incoming ligands. Examples are found mainly among early transition metals (Figure 23.34).

### Reactions of the Metal-Carbon Bond

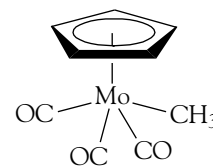
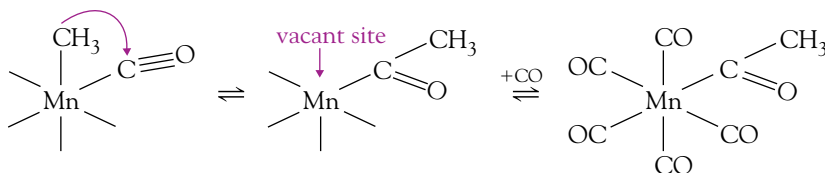
Metal alkyls, alkenes, and alkynes are highly reactive. The reactions generally involve  $\text{M}-\text{C}$  bond cleavage and insertion reactions. Simple diatomic molecules such as halogens and hydrogen promote bond cleavage reactions and lead to the formation of halides and hydride species; for example:



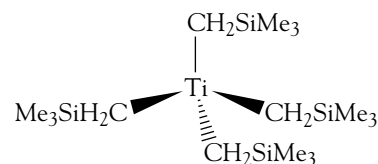
Another common reaction is the insertion of carbon monoxide into a metal-carbon bond to form a metal acyl derivative:



The mechanism of this reaction is not as straightforward as it might seem at first glance. The inserted carbonyl group is actually one of those originally coordinated to the metal center. The reaction takes place by intramolecular nucleophilic attack followed by alkyl migration:

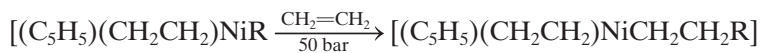


**FIGURE 23.33** Structure of the 18-electron compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CH}_3)(\text{CO})_3]$ .

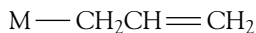


**FIGURE 23.34** Structure of the 8-electron compound  $[\text{Ti}(\text{CH}_2\text{SiMe}_3)_4]$ .

Alkenes and alkynes may also insert in a metal-carbon bond:

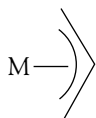


An industrially important example of this reaction uses the Ziegler-Natta catalyst for alkene polymerization (see Section 23.18).



2-electron donor

(a)



4-electron donor

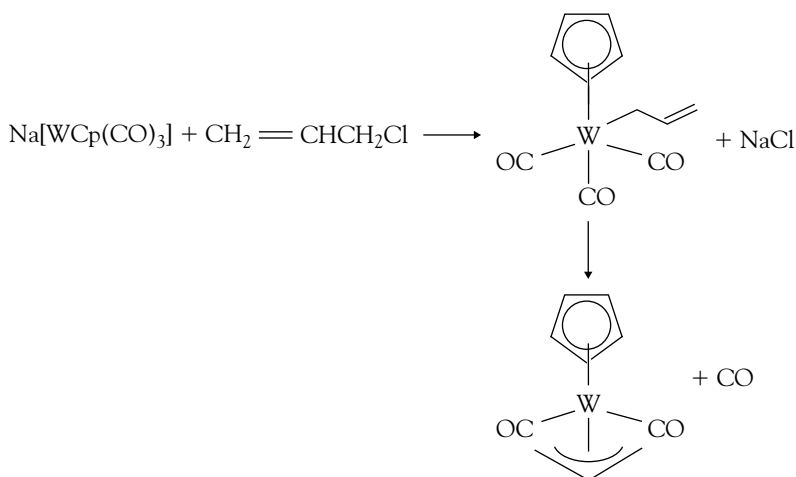
(b)

**FIGURE 23.35** A propenyl species bonding via (a) the terminal carbon atom and (b) the delocalized allyl system.

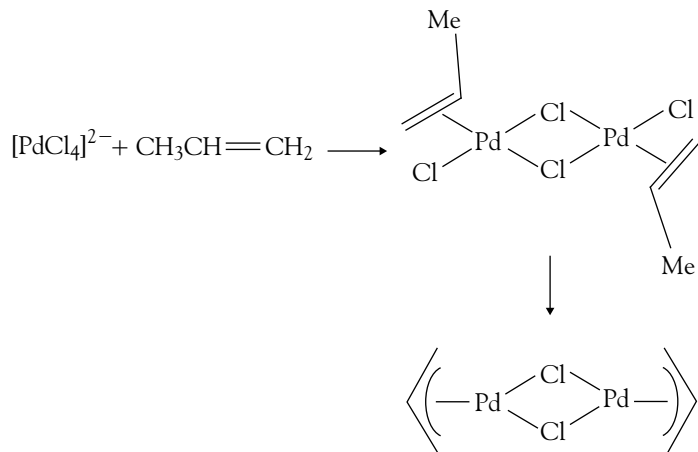
### 23.13 Complexes with Allyl and 1,3-Butadiene Ligands

Propenyl species can bond to transition metals via the terminal carbon atom (Figure 23.35a) or, more usually, through the delocalized allyl system, forming an  $\eta^3$  complex (Figure 23.35b).

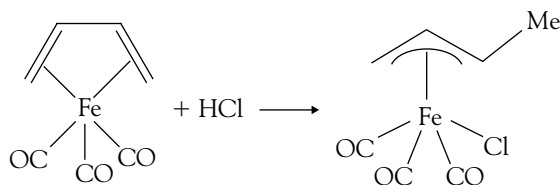
$\eta^3$ -Allyl-containing molecules can be formed via a  $\sigma$ -bonded  $\eta^1$ -intermediate followed by expulsion of another ligand, often carbon monoxide. For example,



The  $\eta^3$ -complexes may be prepared in a variety of ways, including by the deprotonation of a coordinated propene ligand, as shown for palladium:

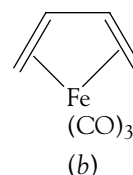
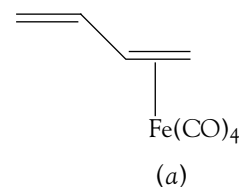
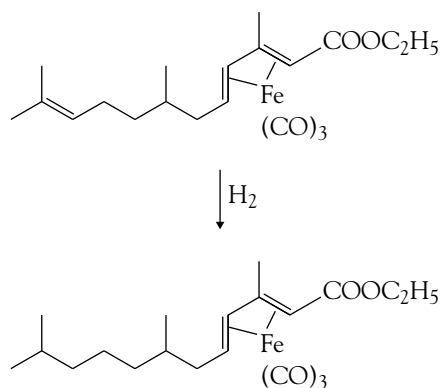


and by the protonation of a coordinated 1,3-butadiene ligand, as shown for iron:



1,3-Butadiene ligands may bond to transition metals via one or both  $\pi$  bonds, thereby donating either two or four electrons, while the number of other coordinating ligands reduces accordingly. The most important of these compounds are the two iron carbonyl derivatives shown in Figure 23.36.

The iron tricarbonyl-1,3-diene derivatives are important in organic synthesis. The coordinated diene is difficult to hydrogenate and does not undergo the classic organic *Diels-Alder reactions*, typical of 1,3-dienes. The  $\text{Fe}(\text{CO})_3$  group acts as a protecting group for the diene, preventing additions to the double bonds and allowing reactions to be carried out on other parts of the molecules. In the example shown, the iron tricarbonyl is used to protect two  $\text{C}=\text{C}$  bonds against hydrogenation while it takes place readily at the third  $\text{C}=\text{C}$  bond:



**FIGURE 23.36** Structure of (a)  $[\text{Fe}(\text{CO})_4(\eta^2\text{-CH}_2\text{CHCHCH}_2)]$  and (b)  $[\text{Fe}(\text{CO})_3(\eta^4\text{-CH}_2\text{CHCHCH}_2)]$ .

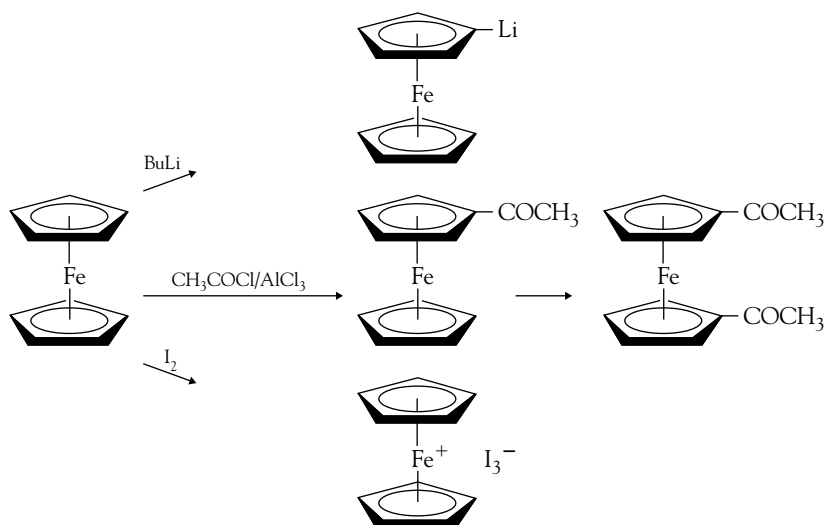
## 23.14 Metallocenes

Metallocenes are sandwich compounds in which the metal center lies between two  $\pi$ -bonded  $\eta^5$ -cyclopentadienyl rings. By far the most important of these is ferrocene  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$ , the structure of which was shown in Figure 23.4. The accidental synthesis of ferrocene in 1951 by Peter Pauson and Tom Kealy at Duquesne University and separately by Samuel Miller of the British Oxygen Company was one of the greatest chemical discoveries of the twentieth century, and it greatly stimulated interest in organometallic chemistry.

### Ferrocene

Ferrocene is a diamagnetic, orange solid with a melting point of  $174^\circ\text{C}$ . It is a very stable compound and can be heated to  $400^\circ\text{C}$  without decomposing. In

the gas phase, the two cyclopentadienyl rings are eclipsed, but at room temperature, the two rings rotate freely and all the hydrogen atoms appear equivalent. The cyclopentadiene rings are aromatic and can be derivatized in many ways (that is, substitution reactions can be performed on the rings themselves). A selection of reactions is shown in the following figure:



### Uses of Ferrocene

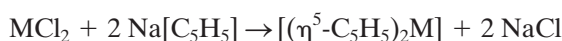
Ferrocene and its derivatives have found uses as a liquid hydrocarbon fuel additive. Its addition to diesel fuel results in reduced smoke emissions and increased fuel economy. Ferrocene is also used in the formulation of high-grade lead-free gasoline fuels, being one of the compounds that replaced tetraethyllead as an antiknock agent. The additive improves the performance of these fuels because the combustion of ferrocene produces iron ions, which react with oxygen to give iron oxides, promoters of the hydrocarbon combustion reaction.

Ferrocene compounds have been developed as electron transfer catalysts in the formation of compounds with specific magnetic and conducting properties. It is the redox properties of the ferrocene that make these applications possible. Another application arising from the redox properties is the use of ferrocene derivatives as a molecular switch.

Some biosensors also use ferrocene derivatives. One such example uses vinyl ferrocene cross-linked with an acrylamide monomer to form a conducting polymer gel. Enzymes may be trapped in the gel, and then this is used in sensors for determining amounts of the enzyme in solution.

### Other Metallocenes

Metallocenes are known for first-row transition metals: vanadium (II), chromium (II), manganese (II), cobalt (II), and nickel(II). With the exception of vanadium, where the starting compound is vanadium (III) chloride, they can all be prepared by the following reaction:



Unlike ferrocene, most of the other metallocenes are air sensitive or pyrophoric since they are not 18-electron systems:

$[(\eta^5\text{-C}_5\text{H}_5)_2\text{V}]$  is an air-sensitive violet solid.

$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}]$  is an air-sensitive red solid.

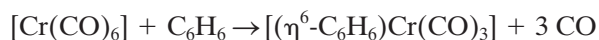
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}]$  is a pyrophoric brown solid. At room temperature, manganocene is polymeric, while at higher temperatures, its structure is related to that of ferrocene.

$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]$  is an air-sensitive, black solid that has 19 electrons and is easily oxidized to  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+$ .

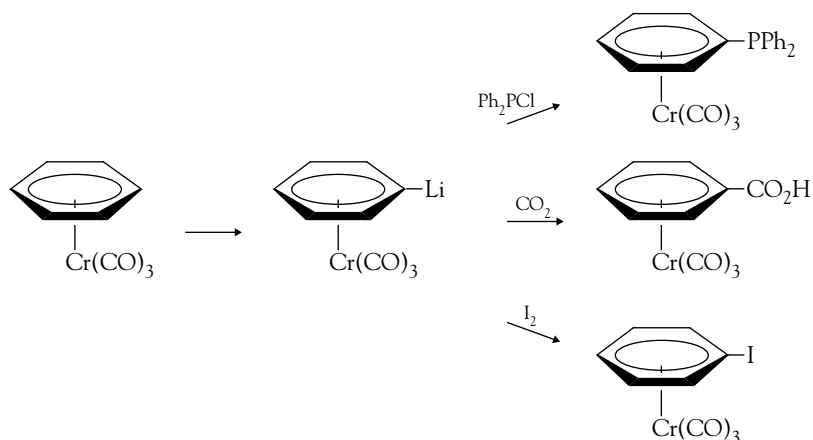
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}]$  is a green solid that has 20 electrons. The reactions of nickelocene result in 18-electron species.

## 23.15 Complexes with $\eta^6$ -Arene Ligands

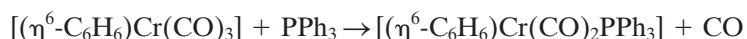
Species such as benzene or toluene can act as 6-electron donors. Complexes containing these ligands can be prepared from a carbonyl or substituted carbonyl. For example,



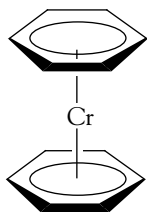
Compounds of this type, with just one ring system, are often referred to as *half-sandwich compounds*. The electron-withdrawing nature of the carbonyl groups means that the arene ring is much more reactive than it would be normally. In particular, the arene ring in these compounds can be subjected to *lithiation* (that is, the substitution of a lithium atom for a hydrogen atom) and the activated ring can undergo a wide variety of reactions (see following figure).



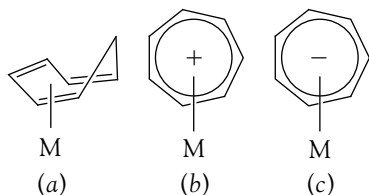
The carbonyl ligands may also be susceptible to substitution by other ligands; for example, phosphines:



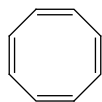
True sandwich compounds also exist. For example, chromium, molybdenum, and tungsten form air-sensitive 18-electron complexes. In the solid state,



**FIGURE 23.37** The sandwich compound dibenzenechromium(0),  $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]$ .

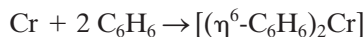


**FIGURE 23.38** The ligands (a)  $\eta^6$ -cycloheptatriene,  $\text{C}_7\text{H}_7$ , (b)  $\eta^7$ -cycloheptatrienylium,  $\text{C}_7\text{H}_7^+$ , and (c)  $\eta^7$ -cycloheptatrienyl,  $\text{C}_7\text{H}_7^-$ .



**FIGURE 23.39** Cyclooctatetraene,  $\text{C}_8\text{H}_8$ .

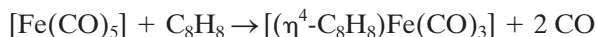
the two benzene rings are eclipsed and the C—C bond lengths are slightly longer than in benzene (Figure 23.37). They can be prepared by co-condensing the metal and arene vapors as shown in the following equation for chromium.



### 23.16 Complexes with Cycloheptatriene and Cyclooctatetraene Ligands

If cycloheptatriene,  $\text{C}_7\text{H}_8$ , is reacted with hexacarbonylchromium(0),  $[\text{Cr}(\text{CO})_6]$ , it will replace three carbonyl ligands and add to the metal as a 6-electron donor via the three  $\pi$  bonds. It forms a classic  $\eta^6$ -triene with the molecule being folded with the  $\text{CH}_2$  group directed away from the metal (Figure 23.38a). Under some conditions, an  $\text{H}^-$  can be removed from the cycloheptatriene to form the cycloheptatrienylium (tropylium) cation,  $\text{C}_7\text{H}_7^+$ , which is aromatic and bonds through all seven carbon atoms (Figure 23.38b). In this case, the ligand is planar, a 6-electron donor like cycloheptatriene but bonding as an  $\eta^7$  species. In this situation, all of the C—C bond lengths are equal, unlike cycloheptatriene. Under other conditions, an  $\text{H}^+$  may be removed from the cycloheptatriene species, giving  $\text{C}_7\text{H}_7^-$ , the cycloheptatrienyl anion, which may then act as an 8-electron donor (Figure 23.38c).

Cyclooctatetraene (Figure 23.39) is a large ligand that may bond as an  $\eta^2$ ,  $\eta^4$ ,  $\eta^6$ , or  $\eta^8$  species. In the case of  $\eta^2$ ,  $\eta^4$ , and  $\eta^6$ , the ring is puckered. In the  $\eta^8$  species, the ring is planar and is best considered to exist as the  $\text{C}_8\text{H}_8^{2-}$  group. Cyclooctatetraene complexes are best prepared from the photochemical reactions of carbonyl compounds:



### 23.17 Fluxionality

One of the remarkable features of many complexes with cyclic polyene ligands is their structural nonrigidity. For example, the two rings in ferrocene rotate rapidly relative to each other. This form of *fluxionality* is called *internal rotation*.

More interesting is the fluxionality that is observed when a polyene ligand is attached to the metal by some, but not all, of the carbon atoms. In these cases, the metal-carbon interaction may hop around the ring. This is known as *ring whizzing*.  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy provides evidence of this process. For example, at room temperature the NMR spectrum of  $[(\eta^4\text{-C}_8\text{H}_8)\text{Ru}(\text{CO})_3]$  consists of a single sharp peak, which might suggest that the ligand is attached by all eight carbons. However, when the temperature is reduced, the signal broadens to give four peaks, which would be expected from the four different hydrogen environments in the  $\eta^4$ -bonded ligand. At room temperature, the ring whizzing occurs too quickly for the NMR experiment to

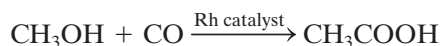
observe the individual environments, so an averaged signal is recorded. However, at low temperatures, the ring motion is slowed down, and so the NMR experiment can “see” the environment of each hydrogen atom.

## 23.18 Organometallic Compounds in Industrial Catalysis

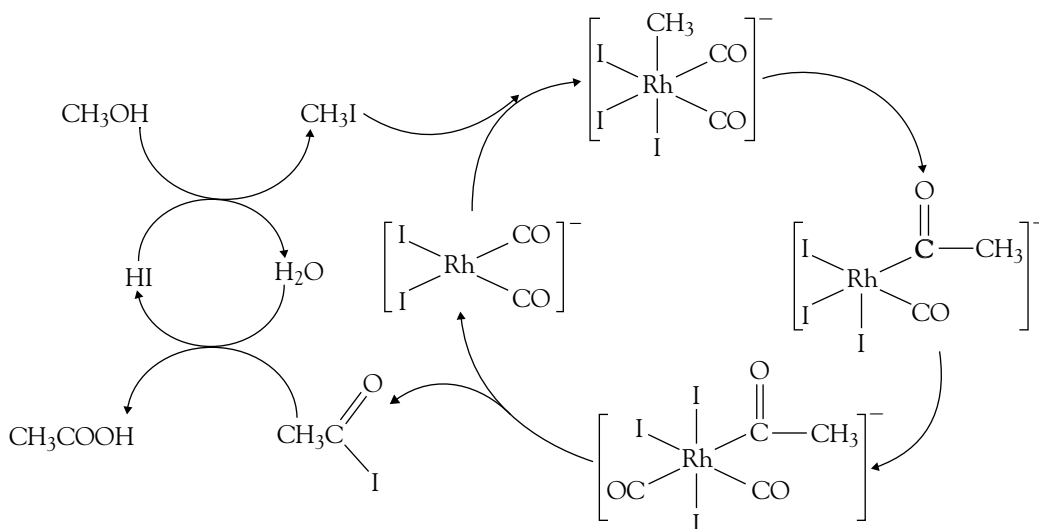
A catalyst increases the rate, and sometimes the selectivity, of a reaction without itself being consumed. Catalysts play an important role in the production of organic chemicals and petrochemical products and often provide routes to cleaner technology. In addition to playing an important economic and environmental role, catalyzed reactions are interesting because the exact reaction pathways are by no means certain, and there is still scope for much further research. Organometallic compounds are crucial to many of the more important catalytic processes. Some of these are described here.

### Acetic Acid Synthesis: The Monsanto and Cativa Processes

The age-old method for producing acetic acid is by fermentation of ethanol, which produces vinegar. However, this is an inefficient way to synthesize concentrated acetic acid for industrial applications. The Monsanto Company developed a catalytic method for the production of acetic acid by the carbonylation of methanol. Using a rhodium complex, the method is so successful that it is used throughout the world. Over 1 million tonnes of acetic acid are produced every year using this *Monsanto process*. The reaction is highly selective, goes in high yield, and is extremely fast:



The catalytic cycle for the Monsanto process is shown in Figure 23.40.

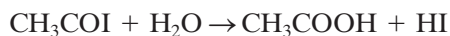


**FIGURE 23.40** The catalytic cycle for the Monsanto process.



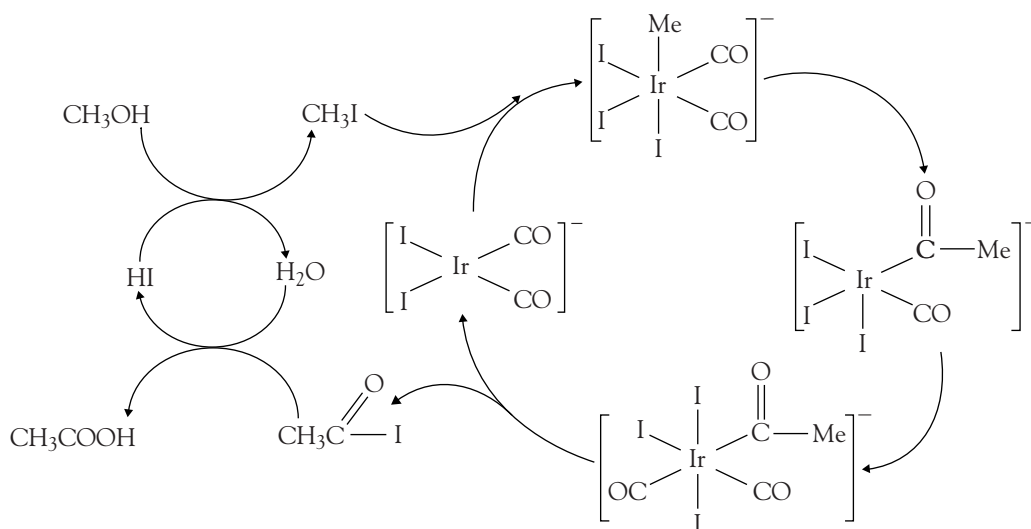
The catalyst is the four-coordinate  $cis$ - $[RhI_2(CO)_2]^-$ . This is a 16-electron species and is coordinatively unsaturated. The first step in the reaction is the oxidative addition of iodomethane to give the 18-electron, six-coordinate species. This oxidative addition to coordinatively unsaturated species is very common in catalytic cycles.

That step is followed by migration of the methyl group to the carbonyl group, resulting in another 16-electron species, which can gain a carbonyl ligand to form an 18-electron species. This species can then lose acetyl iodide,  $CH_3COI$ , by reductive elimination, another common step in catalytic cycles. This final step regenerates the catalyst, and acetic acid is formed by hydrolysis of the acetyl iodide:



There are two major concerns with the Monsanto process. First, rhodium is an expensive catalyst. Second, iodine is cheap but is extremely corrosive. Other halogens or halogen substitutes do not work as well.

In 1996, BP announced a new method for acetic acid manufacture, the *Cativa process*. The new process is based on an iridium catalyst, operates at lower water concentrations, and produces less by-products. Consequently, high-purity acetic acid is synthesized more cheaply than in the Monsanto process. The catalyst is the four-coordinate  $cis$ - $[Ir(CO)_2I_2]^-$ , and the mechanism of the catalytic process mirrors that of the Monsanto process (Figure 23.41). In the Cativa process, the rate-limiting step is the migratory insertion reaction and not the oxidative addition step as in the Monsanto process. This means that the reaction occurs at a high rate without the need for high concentrations of methyl iodide, thus reducing the amounts of propionate by-products.



**FIGURE 23.41** The catalytic cycle for the Cativa process.

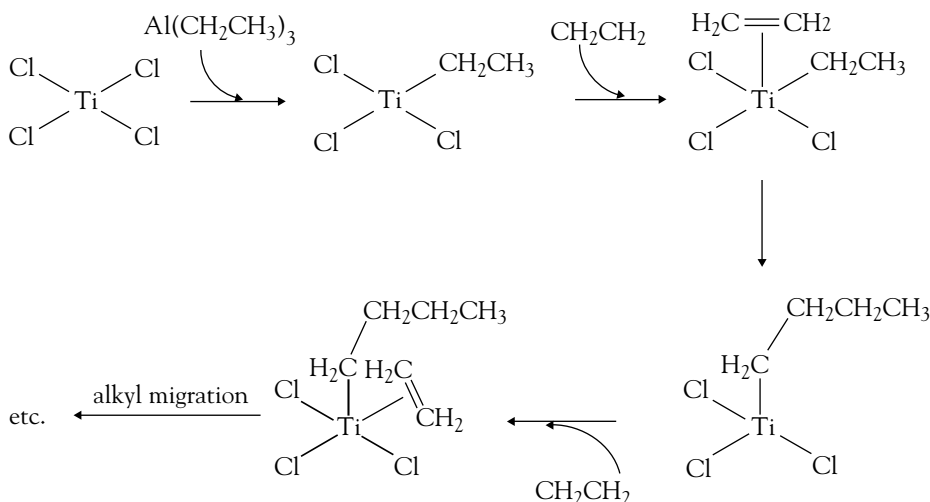
### Alkene Polymerization: The Ziegler-Natta Catalyst

The polymerization of alkenes to form polyethylenes is extremely important commercially. The most useful polyethylenes are the stiff, high-density ones that are produced via stereospecific polymerization. These polymers are described as *isotactic*, since all the branched groups lie on the same side of the polymer chain. This regularity leads to efficient packing and a highly ordered, crystalline polymer.

The German chemist Karl Ziegler found that mixing triethylaluminum with titanium(IV) chloride in a hydrocarbon solvent gave a brown suspension that caused *ethene* (old name, ethylene) to polymerize to polythene (polyethylene) at room temperature and pressure. The high-density polymer formed by this route had different uses compared to the low-density form produced by the traditional high temperature and very high pressures pathway. Ziegler and the Italian chemist Giulio Natta, who utilized this catalyst for the stereospecific polymerization of propene, were awarded a Nobel Prize in 1963 for their development of the organoaluminum catalyst (the *Ziegler-Natta catalyst*). This catalyst is now used for the production of about  $5 \times 10^7$  tonnes of polyalkenes per year.

The catalyst forms a solid mass, so the catalysis is heterogeneous. The reaction takes place at the coordinatively unsaturated titanium centers. The exact mechanism is still not entirely known, but the *Cosee-Arlmann mechanism* is widely accepted as a plausible one and is shown in Figure 23.42.

Triethylaluminum,  $\text{Al}(\text{CH}_2\text{CH}_3)_3$ , alkylates the titanium species before the incoming alkene molecule coordinates to a neighboring vacant site on the titanium. The alkene then undergoes insertion into the  $\text{Ti}-\text{C}$  bond, leaving another site vacant for coordination of another alkene molecule. The insertion process is repeated, thus building the polymer chain. The polymer can ultimately be cleaved from the catalyst by  $\beta$ -hydrogen elimination (sometimes



**FIGURE 23.42** The mechanism for the catalytic cycle for the Ziegler-Natta polymerization of ethene.

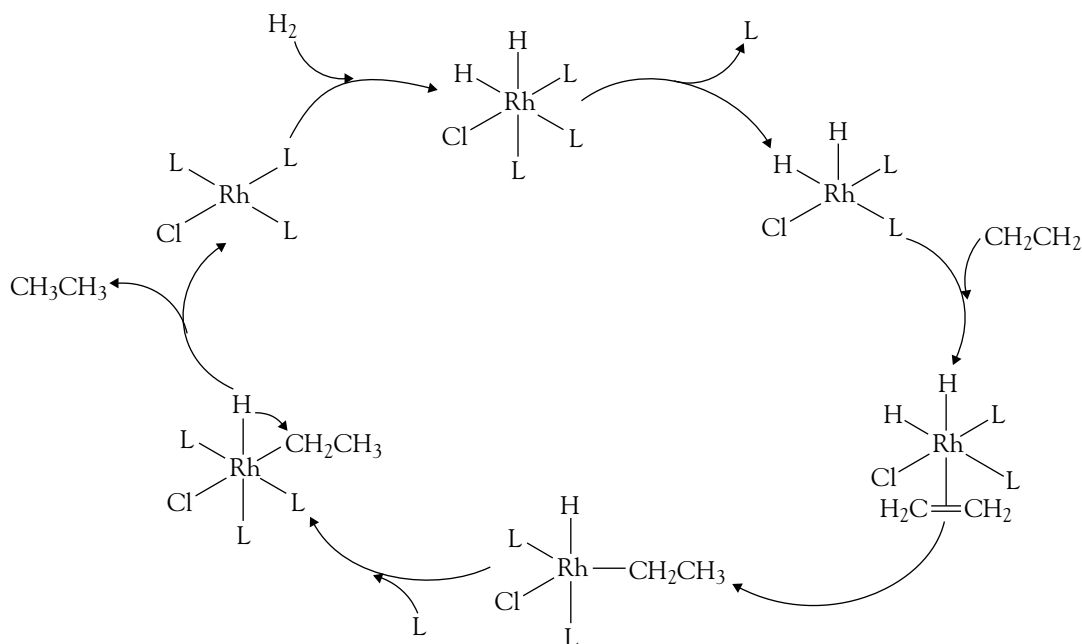
called de-insertion).  $\beta$ -Hydrogen elimination is the transfer of a  $\beta$ -hydrogen atom from the alkyl group to the metal.

### Hydrogenation of Alkenes: Wilkinson's Catalyst

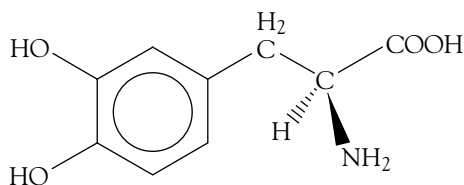
Hydrogenation of alkenes by catalytic processes is used in the manufacture of such diverse products as margarine, pharmaceuticals, and petrochemicals. The most studied catalytic system for these hydrogenation reactions is  $[\text{RhCl}(\text{PPh}_3)_3]$ , which is known as *Wilkinson's catalyst* after its discoverer, Sir Geoffrey Wilkinson, who was awarded the Nobel Prize in Chemistry in 1973.

The catalyst hydrogenates a wide range of alkenes at atmospheric or reduced pressure. The catalytic cycle involves the oxidative addition of hydrogen to the 16-electron rhodium(I) species to give an 18-electron rhodium(III) species. A phosphine ligand is then lost, giving a coordinatively unsaturated molecule that interacts with the alkene. Hydrogen transfer from the rhodium to the alkene is followed by reductive elimination of the alkane (Figure 23.43).

These catalysts can be used in *enantioselective reactions*. Enantioselective reactions produce products that are chiral. In organic chemistry, a chiral compound is a compound that has four different groups attached to a carbon atom within the molecule. Chiral compounds exist in two isomers called enantiomers and are *optically active*, which means that they rotate the plane of polarization of light. (We discussed related coordination isomers in Chapter 19, Section 19.4.) In biological chemistry it is very important to know which enantiomer is being used since one isomer may be beneficial, while the other may be inactive or harmful. An important example of this is the enantioselective



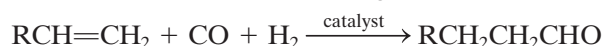
**FIGURE 23.43** The catalytic cycle for the hydrogenation of ethene using Wilkinson's catalyst, where L =  $\text{PPh}_3$ .

**FIGURE 23.44** L-Dopa.

synthesis of L-dopa by the Monsanto Company. L-dopa (Figure 23.44) is used in the treatment of Parkinson's disease.

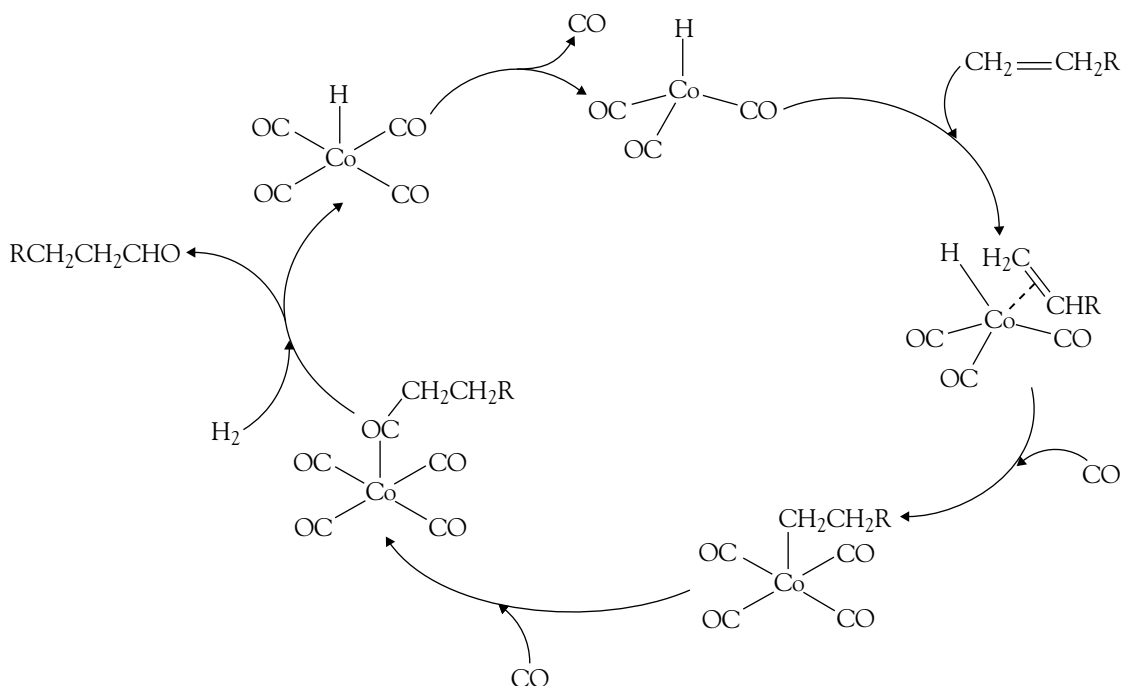
### Hydroformylation

In a *hydroformylation reaction*, an alkene reacts with carbon monoxide and hydrogen over a rhodium or cobalt catalyst to form an aldehyde containing one more carbon atom than the original alkene:

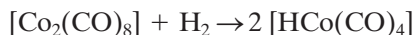


The aldehydes that are produced are usually converted to alcohols that go on to be utilized in a wide range of products, including solvents, plasticizers, and detergents. The reaction produces millions of tonnes of product per year.

The catalytic cycle for the hydroformylation reaction was first proposed by Richard F. Heck and David S. Breslow in 1961. Their cycle, shown in Figure 23.45, is still used today, but, as with many other catalytic processes, it has proven difficult to verify experimentally.

**FIGURE 23.45** The catalytic cycle for a hydroformylation reaction.

The catalyst used is of the type  $[\text{Co}_2(\text{CO})_8]$ , and this initially reacts with hydrogen to break the Co—Co bond and to form the hydride complex, as shown in the following equation:



This product then loses carbon monoxide to form  $[\text{HCo}(\text{CO})_3]$ , which can then coordinate to the alkene. The hydrogen attached to the cobalt inserts into the alkene, giving a coordinated alkyl. Under high pressures of carbon monoxide, the carbonyl inserts into the metal-alkyl bond. The aldehyde is finally formed by attack of hydrogen, which also regenerates the catalyst.

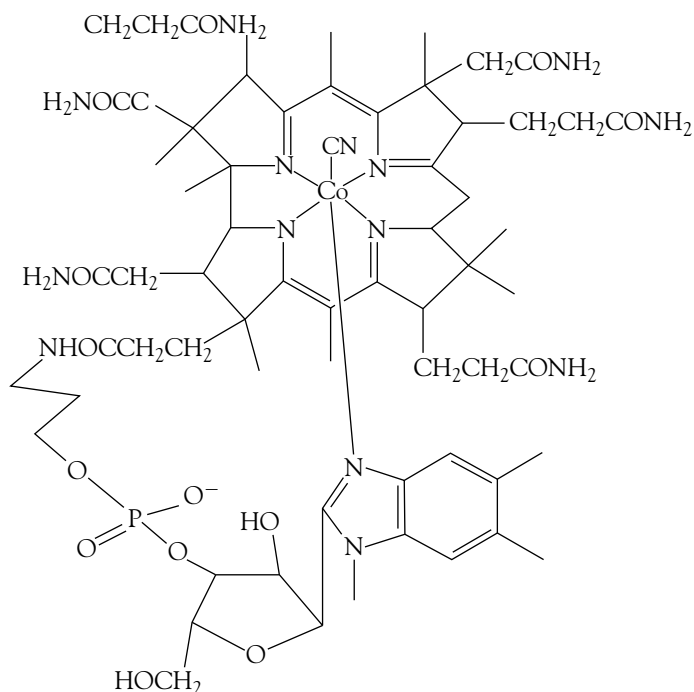
### 23.19 Biological Aspects

#### Vitamin B<sub>12</sub>: A Naturally Occurring Organometallic Compound

A deficiency of vitamin B<sub>12</sub> in the diet can result in pernicious anemia, with symptoms that can include fatigue, dizziness, palpitations, and headache. Vitamin B<sub>12</sub> is found in meat, particularly liver, and it is the only vitamin that is not produced in plants. The compound was discovered when it was observed that eating large amounts of liver was an effective treatment for pernicious anemia. Very strict vegans can suffer from vitamin B<sub>12</sub> deficiency, which has to be remedied by injections of the vitamin.

Vitamin B<sub>12</sub> is a rare example of a naturally occurring organometallic compound. It is also known as cyanocobalamin and contains an octahedral Co(III) ion at the center of a square-planar corrin ring. The fifth and sixth coordination sites are taken up by an alkyl group and cyano group (Figure 23.46). The cyano

**FIGURE 23.46** Structure of vitamin B<sub>12</sub>.



group is introduced when the vitamin is isolated. In the body, it is replaced by a hydroxide ion, water, or an organic group, such as methyl in methylcobalamin.

Methylcobalamin is important in the metabolism of methane-producing bacteria. These bacteria can cause ecological problems because they are able to transfer methyl groups to some metals, including mercury. Thus, elemental mercury and mercury compounds can be converted to the highly toxic dimethylmercury by these bacteria in lakes and rivers.

### Mercury: Inorganic vs Organometallic Toxicity

Mercury and its compounds are all very toxic to living organisms. There are several sources of mercury in the environment. Most environmental mercury is produced by volcanic eruptions. Other sources include oil, gas- and coal-fired power stations, incineration of sewage sludge, and cremations. Inorganic mercury in the form of mercury(II) chloride is used in the standard calomel electrode and is used in skin bleaching creams in some parts of the world. The mercury mineral cinnabar,  $\text{HgS}$ , is used in Chinese medicines, and elemental mercury is found in thermometers and in dental fillings, although these uses are being phased out, and in mercury vapor lamps. Although these inorganic mercury compounds are toxic, organic mercury compounds are even more so. Methyl mercury compounds,  $\text{CH}_3\text{HgX}$ , where X is a halide ion, are water soluble and pass through cell membranes much more readily than inorganic species.

Many discharges of mercury into the environment are inorganic compounds, but this does not minimize their impact. Bacteria that are found in water, soil, sediment, and the gastrointestinal tract of humans convert inorganic mercury compounds to methyl mercury compounds by enzymatic reactions that are also involved in the anaerobic evolution of methane. As the methyl mercury compounds pass through cell walls more readily than inorganic compounds, these reactions probably evolved as a way to excrete mercury from cells. An additional problem with methyl mercury compounds is that they bioaccumulate as we move up the food chain. This has been confirmed by the observation of high levels of mercury in fish high in the food chain, such as tuna and swordfish, and in consumers of fish and shellfish. Methyl mercury is fat soluble and accumulates in the internal organs and in muscle. Cells are less efficient at removing mercury than accumulating it, so the levels increase within an organism. When the organism is consumed, the levels are accumulated in the consuming species and can be 10 times higher than in the species consumed.

The effect of bioaccumulation was observed in the devastating widespread mercury poisoning in Minamata in Japan in the last century. The symptoms observed in the population of the area around Minamata Bay included muscle weakness and lack of coordination, numb hands and feet, loss of vision and hearing, insanity, paralysis, and death, and became known as *Minamata disease*. Methyl mercury in the waste water from the Chisso Corporation's chemical plant was discharged into Minamata Bay between 1932 and 1968 and was bioaccumulated into the shellfish which was consumed by the local population. Severe symptoms were reported by large numbers in the population for over

thirty years, with nothing being done. The Chisso Corporation was a successful company that contributed greatly to the local economy, and many of the victims were also loyal and dependent employees of the company. Eventually, over 2000 victims were identified, but it was too late for most of them because they had already died. To date, over 10 000 people have been compensated and the Chisso Corporation had paid out \$86 million up to 2010. The discharge into Minamata Bay contained up to 2 kg of mercury per tonne of sludge, and the Chisso Corporation even set up a subsidiary company to extract mercury from the river sediment.

## KEY IDEAS

- The electron count on organometallic species is useful in predicting stability.
- The structures of some main group organometallic compounds are analogous to those of hydrogen compounds.
- Most stable transition metal organometallic compounds are 18-electron species.
- Bonding in transition metal carbonyls involves  $\pi$  back bonding.
- Infrared spectroscopy is a useful tool for probing the structures of carbonyl compounds.
- The metallocenes are sandwich compounds in which the metal lies between two cyclopentadiene rings.
- Organometallic compounds are important catalysts in many industrial processes.

## EXERCISES

**23.1** Decide whether each of the following compounds should be described as organometallic:

- (a)  $\text{B}(\text{CH}_3)_3$       (e)  $\text{CH}_3\text{COONa}$   
 (b)  $\text{B}(\text{OCH}_3)_3$     (f)  $\text{Si}(\text{CH}_3)_4$   
 (c)  $\text{Na}_4(\text{CH}_3)_4$     (g)  $\text{SiH}(\text{C}_2\text{H}_5)_3$   
 (d)  $\text{N}(\text{CH}_3)_3$

**23.2** Name each of the compounds in Exercise 23.1.

**23.3** Write the formula for each of the following species. Where appropriate, give the alternative name based on the hydrogen compound:

- (a) methylbismuth  
 (b) tetraphenylsilicon  
 (c) potassium tetraphenylboron  
 (d) methyl lithium  
 (e) ethylmagnesium chloride

**23.4** Sketch the structures of the following compounds:

- (a)  $\text{Li}_4(\text{CH}_3)_4$       (d)  $(\text{CH}_3)_3\text{SnF}$   
 (b)  $\text{Be}(\text{CH}_3)_2$       (e)  $(\text{CH}_3)_3\text{PbCl}$   
 (c)  $\text{B}(\text{C}_2\text{H}_5)_3$

**23.5** Discuss the difference that you might expect between the structures of the two Grignard compounds  $\text{C}_2\text{H}_5\text{MgBr}$  and  $(2,4,6\text{-}(\text{CH}_3)_3\text{C}_6\text{H}_2)\text{MgBr}$ .

**23.6** Discuss how the steric features of the alkyl group affect the structures of main group organometallic compounds.

**23.7** Give an example of a transmetallation reaction.

**23.8** Give an example of a halogen exchange reaction.

**23.9** Predict the products of the following reactions:

- (a)  $\text{CH}_3\text{Br} + 2 \text{Li} \rightarrow$   
 (b)  $\text{MgCl}_2 + \text{LiC}_2\text{H}_5 \rightarrow$   
 (c)  $\text{Mg} + (\text{C}_2\text{H}_5)_2\text{Hg} \rightarrow$   
 (d)  $\text{C}_2\text{H}_5\text{Li} + \text{C}_6\text{H}_6 \rightarrow$   
 (e)  $\text{Mg} + \text{C}_2\text{H}_5\text{HgCl} \rightarrow$   
 (f)  $\text{B}_2\text{H}_6 + \text{CH}_3\text{CH}=\text{CH}_2 \rightarrow$   
 (g)  $\text{SnCl}_4 + \text{C}_2\text{H}_5\text{MgCl} \rightarrow$

**23.10** Compare the nature of the bonding in the aluminum compounds  $\text{Al}_2\text{Cl}_6$ ,  $\text{Al}_2(\text{CH}_3)_6$ , and  $\text{Al}_2(\text{CH}_3)_4(\mu\text{-Cl})_2$ .

**23.11** Name each of the following species:

- (a)  $[\text{Cr}(\text{CO})_6]$   
 (b)  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$   
 (c)  $[(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{CO})_3]$   
 (d)  $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]^-$   
 (e)  $[\text{MnBr}(\text{CO})_5]$

**23.12** For each of the following compounds, determine the formal oxidation state of the transition metal and the corresponding number of d electrons. State whether or not each one is likely to be stable enough to be characterized.

- $[\text{Re}(\text{CO})_5]$
- $[\text{HFe}(\text{CO})_4]^-$
- $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$
- $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]$
- $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}(\text{OCH}_3)]$
- $[\text{IrCl}(\text{PPh}_3)_3]$
- $[\text{Mo}(\text{CO})_3(\text{PPh}_3)_3]$
- $[\text{Fe}(\text{C}_2\text{H}_4)(\text{CO})_4]$
- $[\text{WCl}(\text{CO})_5]^-$
- $[\text{Ni}(\text{CO})_4]$

**23.13** Deduce the probable formula of the simplest carbonyl compounds of chromium, iron, and nickel. Show your calculations.

**23.14** Chromium forms two common anionic carbonyls:  $[\text{Cr}(\text{CO})_5]^{n-}$  and  $[\text{Cr}(\text{CO})_4]^{m-}$ . Deduce the probable charges,  $n$  and  $m$ , on these ions.

**23.15** Suggest why  $[\text{V}(\text{CO})_6]$  is easily reduced to  $[\text{V}(\text{CO})_6]^-$ .

**23.16** Use the 18-electron rule to predict the number of carbonyl ligands,  $n$ , in each of the following complexes:

- $[\text{Cr}(\text{CO})_n]$
- $[\text{Fe}(\text{CO})_n(\text{PPh}_3)_2]$
- $[\text{Mo}(\text{CO})_n(\text{PMe}_3)_3]$
- $[\text{W}(\text{CO})_n(\eta^6\text{-C}_6\text{H}_6)]$

**23.17** Assuming that each of the following obeys the 18-electron rule determine the number of metal-metal bonds in each complex. Sketch a possible structure in each case.

- $[\text{Mn}_2(\text{CO})_{10}]$
- $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2$
- $\mu\text{-CO}-[(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_2]_2$
- $(\mu\text{-Br})_2\text{-}[\text{Mn}(\text{CO})_4]_2$

**23.18** Consider each pair of carbonyl complexes. In each case, decide which one would have the lower infrared CO stretching frequency. Explain your choice.

- $[\text{Fe}(\text{CO})_5]$  and  $[\text{FeCl}(\text{CO})_4]$
- $[\text{Mo}(\text{CO})_6]$  and  $[\text{Mo}(\text{CO})_4(\text{PPh}_3)_2]$
- $[\text{Mo}(\text{CO})_4(\text{PPh}_3)_2]$  and  $[\text{Mo}(\text{CO})_4(\text{PMe}_3)_2]$

**23.19** Predict the products from each of the following reactions:

- $[\text{Cr}(\text{CO})_6] + \text{CH}_3\text{CN} \rightarrow$
- $[\text{Mn}_2(\text{CO})_{10}] + \text{H}_2 \rightarrow$
- $[\text{Mo}(\text{CO})_6] + (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2 \rightarrow$
- $[\text{Fe}(\text{CO})_5] + 1,3\text{-cyclohexadiene} \rightarrow$
- $\text{Na}[\text{Mn}(\text{CO})_5] + \text{CH}_2=\text{CHCH}_2\text{Cl} \rightarrow$
- $[\text{Cr}(\text{CO})_6] + \text{C}_6\text{H}_6 \rightarrow$
- $[\text{PtCl}_2(\text{PMe}_3)_2] + \text{LiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Li} \rightarrow$
- $[\text{Ni}(\text{CO})_4] + \text{PF}_3 \rightarrow$
- $[\text{Mn}_2(\text{CO})_{10}] + \text{Br}_2 \rightarrow$
- $[\text{HMn}(\text{CO})_5] + \text{CO}_2 \rightarrow$

**23.20** The compound  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ , Vaska's compound, is used for the study of oxidative addition processes. What is the formal oxidation number of iridium in this compound?

**23.21** Iridium forms a compound  $[\text{Ir}(\text{C}_5\text{H}_5)(\text{H}_3)(\text{PPh}_3)]^+$ . Two possible structures were proposed, one containing three separate hydride ions and the other containing the unusual trihydrogen ligand,  $\text{H}_3$ .

- What would be the oxidation state of the iridium if the compound contained three hydride ions?
- If the compound contained a single  $\text{H}_3$  ligand and the iridium had the same oxidation state as that in Vaska's compound (Exercise 23.20), what would be the charge on the  $\text{H}_3$  unit? By comparison with diborane, suggest why this trihydrogen ion might indeed exist.

**23.22** Predict the products from the oxidative addition reactions of

- dihydrogen
- dinitrogen
- hydrogen chloride
- dioxygen

to Vaska's compound, *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ .

## BEYOND THE BASICS

**23.23** When nickelocene,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$ , and tetracarbonylnickel(0),  $[\text{Ni}(\text{CO})_4]$ , are refluxed together in benzene in a 1:1 molar ratio, the product is a red-purple crystalline

compound. This compound has the empirical formula  $\text{C}_6\text{H}_5\text{ONi}$  and has a relative molecular mass of 302. Suggest a possible structure for the compound.



**23.24** When hexacarbonylmolybdenum(0) is reacted with an excess of acetonitrile,  $\text{CH}_3\text{CN}$ , a pale yellow product, A, is formed.

When compound A is refluxed with benzene, the pale yellow product, B, is obtained, which has the molecular formula  $\text{C}_9\text{H}_6\text{O}_3\text{Mo}$  and shows a sharp singlet at 5.5 ppm in the  $^1\text{H}$  NMR spectrum.

When compound A is refluxed with 1,3,5,7-cyclooctatetraene in hexane, compound C is produced, which has the molecular formula  $\text{C}_{11}\text{H}_8\text{O}_3\text{Mo}$ .

Use this information to identify compounds A, B, and C and suggest a name for each of them.

**23.25** Sodium tricarbonyl(pentahaptocyclopentadienyl)tungsten(0) reacts with 3-chloropropene to give a solid, A, which has the molecular formula  $(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)(\text{CO})_3\text{W}$ . This compound loses carbon monoxide on exposure to light and forms the compound B, which has the formula  $(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)(\text{CO})_2\text{W}$ . Treating compound A with hydrogen chloride and then potassium hexafluorophosphate,  $\text{K}^+[\text{PF}_6]^-$ , results in the formation of a salt, C. Compound C has the molecular formula  $[(\text{C}_3\text{H}_6)(\text{C}_5\text{H}_5)(\text{CO})_3\text{W}][\text{PF}_6]$ . When this is left to stand for some time, a hydrocarbon is produced.

Use this information and the 18-electron rule to identify the compounds A, B, and C. Show how the hydrocarbon

interacts with the metal in each case. Name each of the compounds and identify the hydrocarbon formed.

**23.26** Draw the catalytic cycle for the Ziegler-Natta polymerization of propene. What do you notice about the polymer that is formed?

**23.27** Predict what the product would be if carbon disulfide were interacted with the Ziegler-Natta titanium species. (*Hint:* Consider the structure of carbon disulfide,  $\text{S}=\text{C}=\text{S}$ .)

**23.28** The trend in the rate of hydrogenation of some alkenes by Wilkinson's catalyst is given in the following:

Cyclohexene > hexene > *cis*-4-methyl-2-pentene  
> 1-methylcyclohexene

Explain this trend and identify the step in the catalytic cycle that is most affected.

**23.29** When  $[\text{Mn}_2(\text{CO})_{10}]$  is reacted with chlorine gas, compound A is formed. When compound A is reacted with  $\text{NaC}_5\text{H}_5$ , product B is obtained. A also reacts with cyclooctatetraene to give compound C. Sketch the structure of each of the compounds A, B, and C and demonstrate that they each satisfy the 18-electron rule.

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## ADDITIONAL RESOURCES

For answers to odd-numbered questions: [www.whfreeman.com/descriptive6e](http://www.whfreeman.com/descriptive6e)

						5 B	6 C	7 N	8 O
						13 Al	14 Si	15 P	16 S
25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se
43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te
75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po
107	108	109	110	111	112	113	114	115	116

Diagram illustrating the periodic table structure, highlighting the f-block elements (lanthanides and actinides) in pink. The f-block is shown as a separate block below the main table, with lines connecting it to its positions in the main table.

Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

## 24.1 The Group 3 Elements

## 24.2 The Lanthanoids

### 24.3 The Actinoids

## 24.4 Uranium

## 24.5 Postactinoid Elements

## 24.6 Biological Aspects

Just as the chemistry of the 3d transition metals differs from that of the 4d and 5d transition metals, so the chemistry of the 4f lanthanoids is quite different from that of the 5f actinoids. In addition, the chemistry of the Group 3 elements is so similar to that of the lanthanoids that it is convenient to consider them also in this chapter. Little has been established of the chemistry of the postactinoid elements as the half-lives of all isotopes of these elements are so short.

For Chapter 24, see <http://www.whfreeman.com/descriptive6e>



# APPENDIX 1

## Thermodynamic Properties of Some Selected Inorganic Compounds

As thermodynamic data are experimental, their values differ from one source to another. A consistent set of values has been used here, summarized from G. Aylward and T. Findlay, *SI Chemical Data*, 3d ed. (New York: Wiley, 1994).

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
<b>Aluminum</b>	Al(s)	0	+28	0
	Al(g)	+330	+165	+290
	Al <sup>3+</sup> (aq)	-538	-325	-492
aluminate ion	Al(OH) <sub>4</sub> <sup>-</sup> (aq)	-1502	+103	-1305
bromide	AlBr <sub>3</sub> (s)	-511	+180	-489
carbide	Al <sub>4</sub> C <sub>3</sub> (s)	-209	+89	-196
chloride	AlCl <sub>3</sub> (s)	-704	+111	-629
chloride hexahydrate	AlCl <sub>3</sub> ·6H <sub>2</sub> O(s)	-2692	+318	-2261
fluoride	AlF <sub>3</sub> (s)	-1510	+66	-1431
iodide	AlI <sub>3</sub> (s)	-314	+159	-301
nitride	AlN(s)	-318	+20	-287
oxide	Al <sub>2</sub> O <sub>3</sub> (s)	-1676	+51	-1582
phosphate	AlPO <sub>4</sub> (s)	-1734	+91	-1618
sulfate	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s)	-3441	+239	-3100
<b>Ammonium</b>	NH <sub>4</sub> <sup>+</sup> (aq)	-133	+111	-79
bromide	NH <sub>4</sub> Br(s)	-271	+113	-175
chloride	NH <sub>4</sub> Cl(s)	-314	+95	-203
fluoride	NH <sub>4</sub> F(s)	-464	+72	-349
iodide	NH <sub>4</sub> I(s)	-201	+117	-113
nitrate	NH <sub>4</sub> NO <sub>3</sub> (s)	-366	+151	-184
sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (s)	-1181	+220	-902
vanadate	NH <sub>4</sub> VO <sub>3</sub> (s)	-1053	+141	-888
<b>Antimony</b>	Sb(s)	0	+46	0
	Sb(g)	+262	+180	+222
pentachloride	SbCl <sub>5</sub> (l)	-440	+301	-350
pentaoxide	Sb <sub>2</sub> O <sub>5</sub> (s)	-972	+125	-829
tribromide	SbBr <sub>3</sub> (s)	-259	+207	-239
trichloride	SbCl <sub>3</sub> (s)	-382	+184	-324
trihydride	SbH <sub>3</sub> (g)	+145	+233	+148
triiodide	SbI <sub>3</sub> (s)	-100	+215	-99
trioxide	Sb <sub>2</sub> O <sub>3</sub> (s)	-720	+110	-634
trisulfide	Sb <sub>2</sub> S <sub>3</sub> (s)	-175	+182	-174
<b>Arsenic</b>	As(s) (gray)	0	+35	0
	As(g)	+302	+174	+261
pentafluoride	AsF <sub>5</sub> (g)	-1237	+317	-1170

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
pentoxide	As <sub>2</sub> O <sub>5</sub> (s)	-925	+105	-782
tribromide	AsBr <sub>3</sub> (s)	-130	+364	-159
trichloride	AsCl <sub>3</sub> (l)	-305	+216	-259
trifluoride	AsF <sub>3</sub> (l)	-786	+289	-771
trihydride (arsine)	AsH <sub>3</sub> (g)	+66	+223	+69
triiodide	AsI <sub>3</sub> (s)	-58	+213	-59
trioxide	As <sub>2</sub> O <sub>3</sub> (s)	-657	+107	-576
trisulfide	As <sub>2</sub> S <sub>3</sub> (s)	-169	+164	-169
<b>Barium</b>	Ba(s)	0	+63	0
	Ba(g)	+180	+170	+146
	Ba <sup>2+</sup> (aq)	-538	+10	-561
bromide	BaBr <sub>2</sub> (s)	-757	+146	-737
carbonate	BaCO <sub>3</sub> (s)	-1216	+112	-1138
chloride	BaCl <sub>2</sub> (s)	-859	+124	-810
chloride dihydrate	BaCl <sub>2</sub> ·2H <sub>2</sub> O(s)	-1460	+203	-1296
fluoride	BaF <sub>2</sub> (s)	-1207	+96	-1157
hydroxide	Ba(OH) <sub>2</sub> (s)	-945	+101	-856
hydroxide octahydrate	Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O(s)	-3342	+427	-2793
iodide	BaI <sub>2</sub> (s)	-605	+165	-601
nitrate	Ba(NO <sub>3</sub> ) <sub>2</sub> (s)	-992	+214	-797
nitride	Ba <sub>3</sub> N <sub>2</sub> (s)	-363	+152	-292
oxide	BaO(s)	-554	+70	-525
peroxide	BaO <sub>2</sub> (s)	-634		
sulfate	BaSO <sub>4</sub> (s)	-1473	+132	-1362
sulfide	BaS(s)	-460	+78	-456
<b>Beryllium</b>	Be(s)	0	+9	0
	Be(g)	+324	+136	+287
	Be <sup>2+</sup> (aq)	-383	-130	-380
bromide	BeBr <sub>2</sub> (s)	-356	+100	-337
chloride	BeCl <sub>2</sub> (s)	-490	+83	-445
fluoride	BeF <sub>2</sub> (s)	-1027	+53	-979
hydroxide	Be(OH) <sub>2</sub> (s)	-903	+52	-815
iodide	BeI <sub>2</sub> (s)	-189	+120	-187
oxide	BeO(s)	-609	+14	-580
<b>Bismuth</b>	Bi(s)	0	+57	0
chloride	BiCl <sub>3</sub> (s)	-379	+177	-315
oxide	Bi <sub>2</sub> O <sub>3</sub> (s)	-574	+151	-494
oxide chloride	BiOCl(s)	-367	+120	-322
sulfide	Bi <sub>2</sub> S <sub>3</sub> (s)	-143	+200	-141
<b>Boron</b>	B(s)	0	0	6
	B(g)	+565	+153	+521
boric acid	H <sub>3</sub> BO <sub>3</sub> (s)	-1095	+90	-970
carbide	B <sub>4</sub> C(s)	-71	+27	-71
decaborane(14)	B <sub>10</sub> H <sub>14</sub> (g)	+32	+353	+216
diborane	B <sub>2</sub> H <sub>6</sub> (g)	+36	+232	+87
nitride	BN(s)	-254	+15	-228
pentaborane(9)	B <sub>5</sub> H <sub>9</sub> (l)	+43	+184	+172
tribromide	BBr <sub>3</sub> (l)	-240	+230	-238
trichloride	BCl <sub>3</sub> (g)	-404	+290	-389

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
trifluoride	BF <sub>3</sub> (g)	-1136	+254	-1119
trioxide (di-)	B <sub>2</sub> O <sub>3</sub> (s)	-1273	+54	-1194
trisulfide (di-)	B <sub>2</sub> S <sub>3</sub> (s)	-252	+92	-248
<b>Bromine</b>	Br <sub>2</sub> (l)	0	+152	0
	Br <sub>2</sub> (g)	+31	+245	+3
	Br(g)	+112	+175	+82
	Br <sup>-</sup> (aq)	-121	+83	-104
bromate ion	BrO <sub>3</sub> <sup>-</sup> (aq)	-67	+162	+19
hypobromite ion	BrO <sup>-</sup> (aq)	-94	+42	-33
monochloride	BrCl(g)	+15	+240	-1
monofluoride	BrF(g)	-94	+229	-109
pentafluoride	BrF <sub>5</sub> (g)	-429	+320	-351
trifluoride	BrF <sub>3</sub> (g)	-256	+293	-229
<b>Cadmium</b>	Cd(s)	0	+52	0
	Cd(g)	+112	+168	+77
	Cd <sup>2+</sup> (aq)	-76	-73	-78
bromide	CdBr <sub>2</sub> (s)	-316	+137	-296
carbonate	CdCO <sub>3</sub> (s)	-751	+92	-669
chloride	CdCl <sub>2</sub> (s)	-391	+115	-344
fluoride	CdF <sub>2</sub> (s)	-700	+77	-648
hydroxide	Cd(OH) <sub>2</sub> (s)	-561	+96	-474
iodide	CdI <sub>2</sub> (s)	-203	+161	-201
nitrate	Cd(NO <sub>3</sub> ) <sub>2</sub> (s)	-456		
oxide	CdO(s)	-258	+55	-228
sulfate	CdSO <sub>4</sub> (s)	-933	+123	-823
sulfide	CdS(s)	-162	+65	-156
<b>Calcium</b>	Ca(s)	0	+42	0
	Ca(g)	+178	+155	+144
	Ca <sup>2+</sup> (aq)	-543	-56	-553
bromide	CaBr <sub>2</sub> (s)	-683	+130	-664
carbide	CaC <sub>2</sub> (s)	-60	+70	-65
carbonate	CaCO <sub>3</sub> (s) (calcite)	-1207	+93	-1129
chloride	CaCl <sub>2</sub> (s)	-796	+105	-748
fluoride	CaF <sub>2</sub> (s)	-1220	+69	-1167
hydride	CaH <sub>2</sub> (s)	-186	+42	-147
hydroxide	Ca(OH) <sub>2</sub> (s)	-986	+83	-898
iodide	CaI <sub>2</sub> (s)	-533	+142	-529
nitrate	Ca(NO <sub>3</sub> ) <sub>2</sub> (s)	-938	+193	-743
oxide	CaO(s)	-635	+38	-603
phosphate	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (s)	-4121	+236	-3885
silicate	CaSiO <sub>3</sub> (s)	-1567	+82	-1499
sulfate	CaSO <sub>4</sub> (s)	-1434	+107	-1332
sulfate hemihydrate	CaSO <sub>4</sub> · $\frac{1}{2}$ H <sub>2</sub> O(s)	-1577	+131	-1437
sulfate dihydrate	CaSO <sub>4</sub> ·2H <sub>2</sub> O(s)	-2023	+194	-1797
sulfide	CaS(s)	-482	+56	-477
<b>Carbon</b>	C(s) (graphite)	0	+6	0
	C(s) (diamond)	+2	+2	+3
	C(g)	+717	+158	+671
carbonate ion	CO <sub>3</sub> <sup>2-</sup> (aq)	-675	-50	-528

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
chloride (-yl)				
(phosgene)	COCl <sub>2</sub> (g)	-219	+284	-205
cyanide ion	CN <sup>-</sup> (aq)	+151	+94	+172
dioxide	CO <sub>2</sub> (g)	-394	+214	-394
dioxide	CO <sub>2</sub> (aq)	-413	+119	-386
disulfide	CS <sub>2</sub> (l)	+90	+151	+65
ethane	C <sub>2</sub> H <sub>6</sub> (g)	-85	+230	-33
hydrogen				
carbonate ion	HCO <sub>3</sub> <sup>-</sup> (aq)	-690	+98	-587
methane	CH <sub>4</sub> (g)	-75	+186	-51
monoxide	CO(g)	-111	+198	-137
tetrabromide	CBr <sub>4</sub> (s)	+19	+213	+48
tetrachloride	CCl <sub>4</sub> (l)	-135	+216	-65
tetrafluoride	CF <sub>4</sub> (g)	-933	+262	-888
thiocyanate ion	NCS <sup>-</sup> (aq)	+76	+144	+93
<b>Cesium</b>				
	Cs(s)	0	+85	0
	Cs(g)	+76	+176	+49
	Cs <sup>+</sup> (aq)	-258	+132	-291
bromide	CsBr(s)	-406	+113	-391
carbonate	Cs <sub>2</sub> CO <sub>3</sub> (s)	-1140	+204	-1054
chloride	CsCl(s)	-443	+101	-415
fluoride	CsF(s)	-554	+93	-526
iodide	CsI(s)	-347	+123	-341
nitrate	CsNO <sub>3</sub> (s)	-506	+155	-407
sulfate	Cs <sub>2</sub> SO <sub>4</sub> (s)	-1443	+212	-1324
<b>Chlorine</b>				
	Cl <sub>2</sub> (g)	0	+223	0
	Cl <sub>2</sub> (aq)	-23	+121	+7
	Cl(g)	+121	+165	+105
	Cl <sup>-</sup> (aq)	-167	+57	-131
chlorate ion	ClO <sub>3</sub> <sup>-</sup> (aq)	-104	+162	-8
dioxide	ClO <sub>2</sub> (g)	+102	+257	+120
hypochlorite ion	ClO <sup>-</sup> (aq)	-107	+42	-37
monofluoride	ClF(g)	-54	+218	-56
oxide (di-)	Cl <sub>2</sub> O(g)	+80	+266	+98
perchlorate ion	ClO <sub>4</sub> <sup>-</sup> (aq)	-128	+184	-8
trifluoride	ClF <sub>3</sub> (g)	-163	+282	-123
<b>Chromium</b>				
	Cr(s)	0	+24	0
	Cr(g)	+397	+175	+352
	Cr <sup>2+</sup> (aq)	-139		-165
	Cr <sup>3+</sup> (aq)	-256		-205
(II) chloride	CrCl <sub>2</sub> (s)	-395	+115	-356
(III) chloride	CrCl <sub>3</sub> (s)	-556	+123	-486
chromate ion	CrO <sub>4</sub> <sup>-</sup> (aq)	-881	+50	-728
dichromate ion	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (aq)	-1490	+262	-1301
(III) oxide	Cr <sub>2</sub> O <sub>3</sub> (s)	-1140	+81	-1058
(VI) oxide	CrO <sub>3</sub> (s)	-580	+72	-513
(III) sulfate	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s)	-2911	+259	-2578
<b>Cobalt</b>				
	Co(s)	0	+30	0
	Co(g)	+425	+180	+380

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
	Co <sup>2+</sup> (aq)	-58	-113	-54
	Co <sup>3+</sup> (aq)	+92	-305	+134
(II) carbonate	CoCO <sub>3</sub> (s)	-713	+89	-637
(II) chloride	CoCl <sub>2</sub> (s)	-313	+109	-270
(II) chloride hexahydrate	CoCl <sub>2</sub> ·6H <sub>2</sub> O(s)	-2115	+343	-1725
(II) hydroxide	Co(OH) <sub>2</sub> (s) (pink)	-540	+79	-454
(II) oxide	CoO(s)	-238	+53	-214
(II) sulfate	CoSO <sub>4</sub> (s)	-888	+118	-782
(II) sulfate heptahydrate	CoSO <sub>4</sub> ·7H <sub>2</sub> O(s)	-2980	+406	-2474
<b>Copper</b>	Cu(s)	0	+33	0
	Cu(g)	+337	+166	+298
	Cu <sup>+</sup> (aq)	+72	+41	+50
	Cu <sup>2+</sup> (aq)	+65	-98	+65
(I) chloride	CuCl(s)	-137	+86	-120
(II) chloride	CuCl <sub>2</sub> (s)	-220	+108	-176
(II) chloride dihydrate	CuCl <sub>2</sub> ·2H <sub>2</sub> O(s)	-821	+167	-656
(II) hydroxide	Cu(OH) <sub>2</sub> (s)	-450	+108	-373
(I) oxide	Cu <sub>2</sub> O(s)	-169	+93	-146
(II) oxide	CuO(s)	-157	+43	-130
(II) sulfate	CuSO <sub>4</sub> (s)	-771	+109	-662
(II) sulfate pentahydrate	CuSO <sub>4</sub> ·5H <sub>2</sub> O(s)	-2280	+300	-1880
(I) sulfide	Cu <sub>2</sub> S(s)	-80	+121	-86
(II) sulfide	CuS(s)	-53	+67	-54
<b>Fluorine</b>	F <sub>2</sub> (g)	0	+203	0
	F(g)	+79	+159	+62
	F <sup>-</sup> (aq)	-335	-14	-281
<b>Gallium</b>	Ga(s)	0	+41	0
	Ga(g)	+277	+169	+239
	Ga <sup>3+</sup> (aq)	-212	-331	-159
bromide	GaBr <sub>3</sub> (s)	-387	+180	-360
chloride	GaCl <sub>3</sub> (s)	-525	+142	-455
fluoride	GaF <sub>3</sub> (s)	-1163	+84	-1085
iodide	GaI <sub>3</sub> (s)	-239	+204	-236
oxide	Ga <sub>2</sub> O <sub>3</sub> (s)	-1089	+85	-998
<b>Germanium</b>	Ge(s)	0	+31	0
	Ge(g)	+372	+168	+331
dioxide	GeO(s)	-262	+50	-237
tetrachloride	GeCl <sub>4</sub> (g)	-496	+348	-457
tetroxide	GeO <sub>2</sub> (s)	-580	+40	-521
<b>Hydrogen</b>	H <sub>2</sub> (g)	0	+131	0
	H(g)	+218	+115	+203
	H <sup>+</sup> (aq)	0	0	0
bromide	HBr(g)	-36	+199	-53
chloride	HCl(g)	-92	+187	-95
fluoride	HF(g)	-273	+174	-275



Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
hydrobromic acid	HBr(aq)	-122	+82	-104
hydrochloric acid	HCl(aq)	-167	+56	-131
hydrofluoric acid	HF(aq)	-333	-14	-279
hydroiodic acid	HI(aq)	-55	+111	-52
iodide	HI(g)	+26	+207	+2
oxide (water)	H <sub>2</sub> O(l)	-286	+70	-237
	H <sub>2</sub> O(g)	-242	+189	-229
hydroxide ion	OH <sup>-</sup> (aq)	-230	-11	-157
peroxide	H <sub>2</sub> O <sub>2</sub> (l)	-188	+110	-120
selenide	H <sub>2</sub> Se(g)	+30	+219	+16
sulfide	H <sub>2</sub> S(g)	-21	+206	-34
telluride	H <sub>2</sub> Te(g)	+100	+229	+85
<b>Indium</b>	In(s)	0	+58	0
	In(g)	+243	+174	+209
	In <sup>3+</sup> (aq)	-105	-151	-98
(I) chloride	InCl(s)	-186	+95	-164
(III) chloride	InCl <sub>3</sub> (s)	-537	+141	-462
oxide	In <sub>2</sub> O <sub>3</sub> (s)	-926	+104	-831
<b>Iodine</b>	I <sub>2</sub> (s)	0	+116	0
	I <sub>2</sub> (g)	+62	+261	+19
	I(g)	+107	+181	+70
	I <sup>-</sup> (aq)	-55	+106	-52
iodate ion	IO <sub>3</sub> <sup>-</sup> (aq)	-221	+118	-128
heptafluoride	IF <sub>7</sub> (g)	-944	+346	-818
monochloride	ICl(g)	+18	+248	-5
triiodide ion	I <sub>3</sub> <sup>-</sup> (aq)	-51	+239	-51
<b>Iron</b>	Fe(s)	0	+27	0
	Fe(g)	+416	+180	+371
	Fe <sup>2+</sup> (aq)	-89	-138	-79
	Fe <sup>3+</sup> (aq)	-49	-316	-5
(II) carbonate	FeCO <sub>3</sub> (s)	-741	+93	-667
(II) chloride	FeCl <sub>2</sub> (s)	-342	+118	-302
(III) chloride	FeCl <sub>3</sub> (s)	-399	+142	-334
(II) disulfide	FeS <sub>2</sub> (s) (pyrite)	-178	+53	-167
(II) hydroxide	Fe(OH) <sub>2</sub> (s)	-569	+88	-487
(III) hydroxide	Fe(OH) <sub>3</sub> (s)	-823	+107	-697
(II) oxide	FeO(s)	-272	+61	-251
(II)(III) oxide	Fe <sub>3</sub> O <sub>4</sub> (s)	-1118	+146	-1015
(III) oxide	Fe <sub>2</sub> O <sub>3</sub> (s)	-824	+87	-742
(II) sulfate	FeSO <sub>4</sub> (s)	-928	+108	-821
(II) sulfate heptahydrate	FeSO <sub>4</sub> ·7H <sub>2</sub> O(s)	-3015	+409	-2510
(III) sulfate	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s)	-2582	+308	-2262
(II) sulfide	FeS(s)	-100	+60	-100
<b>Lead</b>	Pb(s)	0	+65	0
	Pb(g)	+196		
	Pb <sup>2+</sup> (aq)	+1	+18	-24
(II) carbonate	PbCO <sub>3</sub> (s)	-699	+131	-626
(II) chloride	PbCl <sub>2</sub> (s)	-359	+136	-314

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
(IV) chloride	PbCl <sub>4</sub> (g)	-552	+382	-492
(II) oxide	PbO(s)	-217	+69	-188
(IV) oxide	PbO <sub>2</sub> (s)	-277	+69	+217
(II) sulfate	PbSO <sub>4</sub> (s)	-920	+149	-813
(II) sulfide	PbS(s)	-100	+91	-99
<b>Lithium</b>	Li(s)	0	+29	0
	Li(g)	+159	+139	+127
	Li <sup>+</sup> (aq)	-278	+12	-293
bromide	LiBr(s)	-351	+74	-342
carbonate	Li <sub>2</sub> CO <sub>3</sub> (s)	-1216	+90	-1132
chloride	LiCl(s)	-409	+59	-384
fluoride	LiF(s)	-616	+36	-588
hydride	LiH(s)	-91	+20	-68
hydroxide	LiOH(s)	-479	+43	-439
iodide	LiI(s)	-270	+87	-270
nitrate	LiNO <sub>3</sub> (s)	-483	+90	-381
nitride	Li <sub>3</sub> N(s)	-164	+63	-128
oxide	Li <sub>2</sub> O(s)	-598	+38	-561
sulfate	Li <sub>2</sub> SO <sub>4</sub> (s)	-1436	+115	-1322
sulfide	Li <sub>2</sub> S(s)	-441	+61	-433
tetrahydridoaluminate	LiAlH <sub>4</sub> (s)	-116	+79	-45
<b>Magnesium</b>	Mg(s)	0	+33	0
	Mg(g)	+147	+149	+112
	Mg <sup>2+</sup> (aq)	-467	-137	-455
bromide	MgBr <sub>2</sub> (s)	-524	+117	-504
carbonate	MgCO <sub>3</sub> (s)	-1096	+66	-1012
chloride	MgCl <sub>2</sub> (s)	-641	+90	-592
chloride hexahydrate	MgCl <sub>2</sub> ·6H <sub>2</sub> O(s)	-2499	+366	-2115
fluoride	MgF <sub>2</sub> (s)	-1124	+57	-1071
hydride	MgH <sub>2</sub> (s)	-75	+31	-36
hydroxide	Mg(OH) <sub>2</sub> (s)	-925	+63	-834
iodide	MgI <sub>2</sub> (s)	-364	+130	-358
nitrate	Mg(NO <sub>3</sub> ) <sub>2</sub> (s)	-791	+164	-589
nitrate hexahydrate	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O(s)	-2613	+452	-2080
nitride	Mg <sub>3</sub> N <sub>2</sub> (s)	-461	+88	-401
oxide	MgO(s)	-602	+27	-569
sulfate	MgSO <sub>4</sub> (s)	-1285	+92	-1171
sulfate heptahydrate	MgSO <sub>4</sub> ·7H <sub>2</sub> O(s)	-3389	+372	-2872
sulfide	MgS(s)	-346	+50	-342
<b>Manganese</b>	Mn(s)	0	+32	0
	Mn(g)	+281	+174	+238
	Mn <sup>2+</sup> (aq)	-221	-74	-228
(II) carbonate	MnCO <sub>3</sub> (s)	-894	+86	-817
(II) chloride	MnCl <sub>2</sub> (s)	-481	+118	-441
(II) fluoride	MnF <sub>2</sub> (s)	-803	+92	-761
(III) fluoride	MnF <sub>3</sub> (s)	-1004	+105	-935
(II) hydroxide	Mn(OH) <sub>2</sub> (s)	-695	+99	-615
(II) oxide	MnO(s)	-385	+60	-363
(III) oxide	Mn <sub>2</sub> O <sub>3</sub> (s)	-959	+110	-881
(IV) oxide	MnO <sub>2</sub> (s)	-520	+53	-465

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
permanganate ion	MnO <sub>4</sub> <sup>-</sup> (aq)	-541	+191	-447
(II) sulfate	MnSO <sub>4</sub> (s)	-1065	+112	-957
(II) sulfide	MnS(s)	-214	+78	-218
<b>Mercury</b>	Hg(l)	0	+76	0
	Hg(g)	+61	+175	+32
	Hg <sub>2</sub> <sup>2+</sup> (aq)	+167	+66	+154
	Hg <sub>2</sub> <sup>2+</sup> (aq)	+170	-36	+165
(I) chloride	Hg <sub>2</sub> Cl <sub>2</sub> (s)	-265	+192	-211
(II) chloride	HgCl <sub>2</sub> (s)	-224	+146	-179
(II) oxide	HgO(s)	-91	+70	-59
(I) sulfate	Hg <sub>2</sub> SO <sub>4</sub> (s)	-743	+201	-626
(II) sulfate	HgSO <sub>4</sub> (s)	-708	+140	-595
<b>Nickel</b>	Ni(s)	0	+30	0
	Ni(g)	+430	+182	+385
	Ni <sup>2+</sup> (aq)	-54	-129	-46
(II) bromide	NiBr <sub>2</sub> (s)	-212	+136	-198
(II) carbonate	NiCO <sub>3</sub> (s)	-681	+118	-613
(II) chloride	NiCl <sub>2</sub> (s)	-305	+98	-259
(II) chloride hexahydrate	NiCl <sub>2</sub> ·6H <sub>2</sub> O(s)	-2103	+344	-1714
(II) fluoride	NiF <sub>2</sub> (s)	-651	+74	-604
(II) hydroxide	Ni(OH) <sub>2</sub> (s)	-530	+88	-447
(II) iodide	NiI <sub>2</sub> (s)	-78	+154	-81
(II) oxide	NiO(s)	-240	+38	-212
(II) sulfate	NiSO <sub>4</sub> (s)	-873	+92	-760
(II) sulfate heptahydrate	NiSO <sub>4</sub> ·7H <sub>2</sub> O(s)	-2976	+379	-2462
(II) sulfide	NiS(s)	-82	+53	-80
tetracarbonyl(0)	Ni(CO) <sub>4</sub> (l)	-633	+313	-588
<b>Nitrogen</b>	N <sub>2</sub> (g)	0	+192	0
	N(g)	+473	+153	+456
ammonia	NH <sub>3</sub> (g)	-46	+193	-16
azide ion	N <sub>3</sub> <sup>-</sup> (aq)	+275	+108	+348
dinitrogen oxide	N <sub>2</sub> O(g)	+82	+220	+104
dinitrogen pentoxide	N <sub>2</sub> O <sub>5</sub> (g)	+11	+356	+115
dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub> (g)	+9	+304	+98
dinitrogen trioxide	N <sub>2</sub> O <sub>3</sub> (g)	+84	+312	+139
hydrazine	N <sub>2</sub> H <sub>4</sub> (l)	+51	+121	+149
hydrogen azide	HN <sub>3</sub> (l)	+264	+141	+327
hydrogen nitrate	HNO <sub>3</sub> (l)	-174	+156	-81
nitrate ion	NO <sub>3</sub> <sup>-</sup> (aq)	-207	+147	-111
nitrite ion	NO <sub>2</sub> <sup>-</sup> (aq)	-105	+123	-32
nitrogen dioxide	NO <sub>2</sub> (g)	+33	+240	+51
nitrogen monoxide	NO(g)	+90	+211	+87
<b>Oxygen</b>	O <sub>2</sub> (g)	0	+205	0
	O <sub>3</sub> (g)	+143	+239	+163
	O(g)	+249	+161	+232
	O <sup>-</sup> (g)	+102	+158	+92
difluoride	OF <sub>2</sub> (g)	+25	+247	+42

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
<b>Phosphorus</b>	P <sub>4</sub> (s) (white)	0	+41	0
	P(s) (red)	-18	+23	-12
	P <sub>4</sub> (g)	+59	+280	+24
	P(g)	+317	+163	+278
hydrogen phosphate	H <sub>3</sub> PO <sub>4</sub> (s)	-1279	+110	-1119
pentachloride	PCl <sub>5</sub> (g)	-375	+365	-305
pentafluoride	PF <sub>5</sub> (g)	-1594	+301	-1521
phosphate ion	PO <sub>4</sub> <sup>3-</sup> (aq)	-1277	-220	-1019
phosphoryl chloride	POCl <sub>3</sub> (l)	-597	+222	-521
tetraphosphorus				
decaoxide	P <sub>4</sub> O <sub>10</sub> (s)	-2984	+229	-2700
trichloride	PCl <sub>3</sub> (l)	-320	+217	-272
trifluoride	PF <sub>3</sub> (g)	-919	+273	-898
trihydride (phosphine)	PH <sub>3</sub> (g)	+5	+210	+13
<b>Potassium</b>	K(s)	0	+65	0
	K(g)	+89	+160	+61
	K <sup>+</sup> (aq)	-252	+101	-284
bromide	KBr(s)	-394	+96	-381
carbonate	K <sub>2</sub> CO <sub>3</sub> (s)	-1151	+156	-1064
chlorate	KClO <sub>3</sub> (s)	-398	+143	-296
chloride	KCl(s)	-437	+83	-409
chromate	K <sub>2</sub> CrO <sub>4</sub> (s)	-1404	+200	-1296
cyanide	KCN(s)	-113	+128	-102
dichromate	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (s)	-2062	+291	-1882
dioxide(2-) (peroxide)	K <sub>2</sub> O <sub>2</sub> (s)	-494	+102	-425
dioxide(1-)				
(superoxide)	KO <sub>2</sub> (s)	-285	+117	-239
fluoride	KF(s)	-567	+67	-538
hydride	KH(s)	-58	+50	-53
hydrogen carbonate	KHCO <sub>3</sub> (s)	-963	+116	-864
hydrogen sulfate	KHSO <sub>4</sub> (s)	-1161	+138	-1031
hydroxide	KOH(s)	-425	+79	-379
iodide	KI(s)	-328	+106	-325
nitrate	KNO <sub>3</sub> (s)	-495	+133	-395
nitrite	KNO <sub>2</sub> (s)	-370	+152	-307
oxide	K <sub>2</sub> O(s)	-363	+94	-322
perchlorate	KClO <sub>4</sub> (s)	-433	+151	-303
permanganate	KMnO <sub>4</sub> (s)	-837	+172	-738
peroxodisulfate	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (s)	-1916	+279	-1697
pyrosulfate	K <sub>2</sub> S <sub>2</sub> O <sub>7</sub> (s)	-1987	+225	-1792
sulfate	K <sub>2</sub> SO <sub>4</sub> (s)	-1438	+176	-1321
sulfide	K <sub>2</sub> S(s)	-376	+115	-363
tetrafluoroborate	KBF <sub>4</sub> (s)	-1882	+152	-1786
<b>Rubidium</b>	Rb(s)	0	+77	0
	Rb(g)	+81	+170	+53
	Rb <sup>+</sup> (aq)	-251	+122	-284
bromide	RbBr(s)	-395	+110	-382
carbonate	Rb <sub>2</sub> CO <sub>3</sub> (s)	-1179	+186	-1096
chloride	RbCl(s)	-435	+96	-408
fluoride	RbF(s)	-558	+75	-521
iodide	RbI(s)	-334	+118	-329

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
nitrate	RbNO <sub>3</sub> (s)	-495	+147	-396
sulfate	Rb <sub>2</sub> SO <sub>4</sub> (s)	-1436	+197	-1317
<b>Selenium</b>	Se(s) (gray)	0	+42	0
	Se(g)	+227	+177	+187
hexafluoride	SeF <sub>6</sub> (g)	-1117	+314	-1017
selenate ion	SeO <sub>4</sub> <sup>2-</sup> (aq)	-599	+54	-441
tetrachloride	SeCl <sub>4</sub> (s)	-183	+195	-95
<b>Silicon</b>	Si(s)	0	+19	0
	Si(g)	+450	+168	+406
carbide	SiC(s)	-65	+17	-63
dioxide (quartz)	SiO <sub>2</sub> (s)	-911	+41	-856
tetrachloride	SiCl <sub>4</sub> (l)	-687	+240	-620
tetrafluoride	SiF <sub>4</sub> (g)	-1615	+283	-1573
tetrahydride (silane)	SiH <sub>4</sub> (g)	+34	+205	+57
<b>Silver</b>	Ag(s)	0	+43	0
	Ag(g)	+285	+173	+246
	Ag <sup>+</sup> (aq)	+106	+73	+77
bromide	AgBr(s)	-100	+107	-97
carbonate	Ag <sub>2</sub> CO <sub>3</sub> (s)	-506	+167	-437
chloride	AgCl(s)	-127	+96	-110
chromate	Ag <sub>2</sub> CrO <sub>4</sub> (s)	-732	+218	-642
cyanide	AgCN(s)	+146	+107	+157
fluoride	AgF(s)	-205	+84	-187
iodide	AgI(s)	-62	+115	-66
nitrate	AgNO <sub>3</sub> (s)	-124	+141	-33
oxide	Ag <sub>2</sub> O(s)	-31	+121	-11
sulfate	Ag <sub>2</sub> SO <sub>4</sub> (s)	-716	+200	-618
sulfide	Ag <sub>2</sub> S(s)	-33	+144	-41
<b>Sodium</b>	Na(s)	0	+51	0
	Na(g)	+107	+154	+77
	Na <sup>+</sup> (aq)	-240	+58	-262
azide	NaN <sub>3</sub> (s)	+22	+97	+94
bromide	NaBr(s)	-361	+87	-349
carbonate	Na <sub>2</sub> CO <sub>3</sub> (s)	-1131	+135	-1044
carbonate				
monohydrate	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O(s)	-1431	+168	-1285
carbonate decahydrate	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O(s)	-4081	+563	-3428
chlorate	NaClO <sub>3</sub> (s)	-366	+123	-262
chloride	NaCl(s)	-411	+72	-384
cyanide	NaCN(s)	-87	+116	-76
dihydrogen phosphate	NaH <sub>2</sub> PO <sub>4</sub> (s)	-1537	+127	-1386
dioxide(2-) (peroxide)	Na <sub>2</sub> O <sub>2</sub> (s)	-511	+95	-448
fluoride	NaF(s)	-574	+51	-544
hydride	NaH(s)	-56	+40	-33
hydrogen carbonate	NaHCO <sub>3</sub> (s)	-951	+102	-851
hydrogen phosphate	Na <sub>2</sub> HPO <sub>4</sub> (s)	-1748	+150	-1608
hydrogen sulfate	NaHSO <sub>4</sub> (s)	-1126	+113	-993
hydroxide	NaOH(s)	-425	+64	-379
iodide	NaI(s)	-288	+99	-286

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
nitrate	NaNO <sub>3</sub> (s)	-468	+117	-367
nitrite	NaNO <sub>2</sub> (s)	-359	+104	-285
oxide	Na <sub>2</sub> O(s)	-414	+75	-375
perchlorate	NaClO <sub>4</sub> (s)	-383	+142	-255
phosphate	Na <sub>3</sub> PO <sub>4</sub> (s)	-1917	+174	-1789
silicate	Na <sub>2</sub> SiO <sub>3</sub> (s)	-1555	+114	-1463
sulfate	Na <sub>2</sub> SO <sub>4</sub> (s)	-1387	+150	-1270
sulfide	Na <sub>2</sub> S(s)	-365	+84	-350
sulfite	Na <sub>2</sub> SO <sub>3</sub> (s)	-1101	+146	-1012
tetrahydroborate	NaBH <sub>4</sub> (s)	-189	+101	-124
thiosulfate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (s)	-1123	+155	-1028
thiosulfate pentahydrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O(s)	-2608	+372	-2230
<b>Strontium</b>	Sr(s)	0	+52	0
	Sr(g)	+164	+165	+131
	Sr <sup>2+</sup> (aq)	-546	-33	-559
carbonate	SrCO <sub>3</sub> (s)	-1220	+97	-1140
chloride	SrCl <sub>2</sub> (s)	-829	+115	-781
oxide	SrO(s)	-592	+54	-562
sulfate	SrSO <sub>4</sub> (s)	-1453	+117	-1341
<b>Sulfur</b>	S <sub>8</sub> (s) (rhombic)	0	+32	0
	S <sub>8</sub> (s) (monoclinic)	+0.3	+33	+0.1
	S <sub>8</sub> (g)	+102	+431	+50
	S(g)	+227	+168	+236
dichloride	SCl <sub>2</sub> (l)	-50	+184	-28
dichloride (disulfur)	S <sub>2</sub> Cl <sub>2</sub> (l)	-58	+224	-39
dioxide	SO <sub>2</sub> (g)	-297	+248	-300
hexafluoride	SF <sub>6</sub> (g)	-1209	+292	-1105
hydrogen sulfate	H <sub>2</sub> SO <sub>4</sub> (l)	-814	+157	-690
hydrogen sulfide ion	HS <sup>-</sup> (aq)	-16	+67	+12
peroxodisulfate ion	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> (aq)	-1345	+244	-1115
sulfate ion	SO <sub>4</sub> <sup>2-</sup> (aq)	-909	+19	-744
sulfide ion	S <sup>2-</sup> (aq)	+33	-15	+86
sulfite ion	SO <sub>3</sub> <sup>2-</sup> (aq)	-635	-29	-487
thiosulfate ion	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (aq)	-652	+67	-522
trioxide	SO <sub>3</sub> (g)	-396	+257	-371
<b>Thallium</b>	Tl(s)	0	+64	0
	Tl(g)	+182	+181	+147
	Tl <sup>+</sup> (aq)	+5	+125	-32
	Tl <sup>3+</sup> (aq)	+197	-192	+215
(I) chloride	TlCl(s)	-204	+111	-185
(III) chloride	TlCl <sub>3</sub> (s)	-315	+152	-242
<b>Tin</b>	Sn(s) (white)	0	+51	0
	Sn(s) (gray)	-2	+44	+0.1
	Sn(g)	+301	+168	+266
(II) chloride	SnCl <sub>2</sub> (s)	-331	+132	-289
(IV) chloride	SnCl <sub>4</sub> (l)	-551	+259	-440
hydride	SnH <sub>4</sub> (g)	+163	+228	+188
(II) hydroxide	Sn(OH) <sub>2</sub> (s)	-561	+155	-492

Compound name	Formula	$\Delta H^\ominus$ (kJ·mol <sup>-1</sup> )	$S^\ominus$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta G^\ominus$ (kJ·mol <sup>-1</sup> )
(II) oxide	SnO( <i>s</i> )	-281	+57	-252
(IV) oxide	SnO <sub>2</sub> ( <i>s</i> )	-578	+49	-516
(II) sulfide	SnS( <i>s</i> )	-100	+77	-98
(IV) sulfide	SnS <sub>2</sub> ( <i>s</i> )	-154	+87	-145
<b>Titanium</b>	Ti( <i>s</i> )	0	+31	0
	Ti( <i>g</i> )	+473	+180	+428
(II) chloride	TiCl <sub>2</sub> ( <i>s</i> )	-514	+87	-464
(III) chloride	TiCl <sub>3</sub> ( <i>s</i> )	-721	+140	-654
(IV) chloride	TiCl <sub>4</sub> ( <i>l</i> )	-804	+252	-737
(IV) oxide	TiO <sub>2</sub> ( <i>s</i> ) (rutile)	-944	+51	-890
<b>Vanadium</b>	V( <i>s</i> )	0	+29	0
	V( <i>g</i> )	+514	+182	+469
(II) chloride	VCl <sub>2</sub> ( <i>s</i> )	-452	+97	-406
(III) chloride	VCl <sub>3</sub> ( <i>s</i> )	-581	+131	-511
(IV) chloride	VCl <sub>4</sub> ( <i>l</i> )	-569	+255	-504
(II) oxide	VO( <i>s</i> )	-432	+39	-404
(III) oxide	V <sub>2</sub> O <sub>3</sub> ( <i>s</i> )	-1219	+98	-1139
(IV) oxide	VO <sub>2</sub> ( <i>s</i> )	-713	+51	-659
(V) oxide	V <sub>2</sub> O <sub>5</sub> ( <i>s</i> )	-1551	+131	-1420
<b>Xenon</b>	Xe( <i>g</i> )	0	+170	0
difluoride	XeF <sub>2</sub> ( <i>g</i> )	-130	+260	-96
tetrafluoride	XeF <sub>4</sub> ( <i>g</i> )	-215	+316	-138
trioxide	XeO <sub>3</sub> ( <i>g</i> )	+502	+287	+561
<b>Zinc</b>	Zn( <i>s</i> )	0	+42	0
	Zn( <i>g</i> )	+130	+161	+94
	Zn <sup>2+</sup> ( <i>aq</i> )	-153	-110	-147
carbonate	ZnCO <sub>3</sub> ( <i>s</i> )	-813	+82	-732
chloride	ZnCl <sub>2</sub> ( <i>s</i> )	-415	+111	-369
hydroxide	Zn(OH) <sub>2</sub> ( <i>s</i> )	-642	+81	-554
nitride	Zn <sub>3</sub> N <sub>2</sub> ( <i>s</i> )	-23	+140	+30
oxide	ZnO( <i>s</i> )	-350	+44	-320
sulfate	ZnSO <sub>4</sub> ( <i>s</i> )	-983	+110	-872
sulfate heptahydrate	ZnSO <sub>4</sub> ·7H <sub>2</sub> O( <i>s</i> )	-3078	+389	-2563
sulfide	ZnS( <i>s</i> ) (wurtzite)	-193	+68	-191
sulfide	ZnS( <i>s</i> ) (sphalerite)	-206	+58	-201

## APPENDIX 2

### Charge Densities of Selected Ions

Charge densities ( $\text{C mm}^{-3}$ ) are calculated according to the formula

$$\frac{ne}{(4/3)\pi r^3}$$

where the ionic radii  $r$  are the Shannon-Prewitt values in millimeters (*Acta Cryst.*, 1976, A32, 751),  $e$  is the electron charge ( $1.60 \times 10^{-19}$  C), and  $n$  represents the ion charge. The radii used are the values for six-coordinate ions except where noted by (T) for four-coordinate tetrahedral ions; (HS) and (LS) designate the high-spin and low-spin radii for the transition metal ions.

Cation	Charge density	Cation	Charge density	Cation	Charge density
Ac <sup>3+</sup>	57	B <sup>3+</sup>	1663	Cl <sup>7+</sup>	3880
Ag <sup>+</sup>	15	Ba <sup>2+</sup>	23	Cm <sup>3+</sup>	84
Ag <sup>2+</sup>	60	Be <sup>2+</sup>	1108 (T)	Co <sup>2+</sup>	155 (LS)
Ag <sup>3+</sup>	163	Bi <sup>3+</sup>	72	Co <sup>2+</sup>	108 (HS)
Al <sup>3+</sup>	770 (T)	Bi <sup>5+</sup>	262	Co <sup>3+</sup>	349 (LS)
Al <sup>3+</sup>	364	Bk <sup>3+</sup>	86	Co <sup>3+</sup>	272 (HS)
Am <sup>3+</sup>	82	Br <sup>7+</sup>	1796	Co <sup>4+</sup>	508 (HS)
As <sup>3+</sup>	307	C <sup>4+</sup>	6265 (T)	Cr <sup>2+</sup>	116 (LS)
As <sup>5+</sup>	884	Ca <sup>2+</sup>	52	Cr <sup>2+</sup>	92 (HS)
At <sup>7+</sup>	609	Cd <sup>2+</sup>	59	Cr <sup>3+</sup>	261
Au <sup>+</sup>	11	Ce <sup>3+</sup>	75	Cr <sup>4+</sup>	465
Au <sup>3+</sup>	118	Ce <sup>4+</sup>	148	Cr <sup>5+</sup>	764
B <sup>3+</sup>	7334 (T)	Cl <sup>3+</sup>	88	Cr <sup>6+</sup>	1175
Cs <sup>+</sup>	6	Mn <sup>4+</sup>	508	Sb <sup>3+</sup>	157
Cu <sup>+</sup>	51	Mn <sup>7+</sup>	1238	Sb <sup>5+</sup>	471
Cu <sup>2+</sup>	116	Mo <sup>3+</sup>	200	Se <sup>3+</sup>	163
Dy <sup>2+</sup>	43	Mo <sup>6+</sup>	589	Se <sup>4+</sup>	583
Dy <sup>3+</sup>	99	NH <sub>4</sub> <sup>+</sup>	11	Se <sup>6+</sup>	1305
Er <sup>3+</sup>	105	Na <sup>+</sup>	24	Si <sup>4+</sup>	970
Eu <sup>2+</sup>	34	Nb <sup>3+</sup>	180	Sm <sup>3+</sup>	86
Eu <sup>3+</sup>	88	Nb <sup>5+</sup>	402	Sn <sup>2+</sup>	54

HS, high spin; LS, low spin; T, four-coordinate tetrahedral ions.



Cation	Charge density	Cation	Charge density	Cation	Charge density
$\text{F}^{7+}$	25 110	$\text{Nd}^{3+}$	82	$\text{Sn}^{4+}$	267
$\text{Fe}^{2+}$	181 (LS)	$\text{Ni}^{2+}$	134	$\text{Sr}^{2+}$	33
$\text{Fe}^{2+}$	98 (HS)	$\text{No}^{2+}$	40	$\text{Ta}^{3+}$	180
$\text{Fe}^{3+}$	349 (LS)	$\text{Np}^{5+}$	271	$\text{Ta}^{5+}$	402
$\text{Fe}^{3+}$	232 (HS)	$\text{Os}^{4+}$	335	$\text{Tb}^{3+}$	96
$\text{Fe}^{6+}$	3864	$\text{Os}^{6+}$	698	$\text{Tc}^{4+}$	310
$\text{Fr}^{+}$	5	$\text{Os}^{8+}$	2053	$\text{Tc}^{7+}$	780
$\text{Ga}^{3+}$	261	$\text{P}^{3+}$	587	$\text{Te}^{4+}$	112
$\text{Gd}^{3+}$	91	$\text{P}^{5+}$	1358	$\text{Te}^{6+}$	668
$\text{Ge}^{2+}$	116	$\text{Pa}^{5+}$	245	$\text{Th}^{4+}$	121
$\text{Ge}^{4+}$	508	$\text{Pb}^{2+}$	32	$\text{Ti}^{2+}$	76
$\text{Hf}^{4+}$	409	$\text{Pb}^{4+}$	196	$\text{Ti}^{3+}$	216
$\text{Hg}^{+}$	16	$\text{Pd}^{2+}$	76	$\text{Ti}^{4+}$	362
$\text{Hg}^{2+}$	49	$\text{Pd}^{4+}$	348	$\text{Ti}^{+}$	9
$\text{Ho}^{3+}$	102	$\text{Pm}^{3+}$	84	$\text{Tl}^{3+}$	105
$\text{I}^{7+}$	889	$\text{Po}^{4+}$	121	$\text{Tm}^{2+}$	48
$\text{In}^{3+}$	138	$\text{Po}^{6+}$	431	$\text{Tm}^{3+}$	108
$\text{Ir}^{3+}$	208	$\text{Pr}^{3+}$	79	$\text{U}^{4+}$	140
$\text{Ir}^{5+}$	534	$\text{Pr}^{4+}$	157	$\text{U}^{6+}$	348
$\text{K}^{+}$	11	$\text{Pt}^{2+}$	92	$\text{V}^{2+}$	95
$\text{La}^{3+}$	72	$\text{Pt}^{4+}$	335	$\text{V}^{3+}$	241
$\text{Li}^{+}$	98 (T)	$\text{Pu}^{4+}$	153	$\text{V}^{4+}$	409
$\text{Li}^{+}$	52	$\text{Ra}^{2+}$	18	$\text{V}^{5+}$	607
$\text{Lu}^{3+}$	115	$\text{Rb}^{+}$	8	$\text{W}^{4+}$	298
$\text{Mg}^{2+}$	120	$\text{Re}^{7+}$	889	$\text{W}^{6+}$	566
$\text{Mn}^{2+}$	114 (LS)	$\text{Rh}^{3+}$	224	$\text{Y}^{3+}$	102
$\text{Mn}^{2+}$	84 (HS)	$\text{Ru}^{3+}$	208	$\text{Yb}^{3+}$	111
$\text{MN}^{3+}$	307 (LS)	$\text{S}^{4+}$	1152	$\text{Zn}^{2+}$	112
$\text{Mn}^{3+}$	232 (HS)	$\text{S}^{6+}$	2883	$\text{Zr}^{4+}$	240

Anion	Charge density	Anion	Charge density	Anion	Charge density
As <sup>3-</sup>	12	I <sup>-</sup>	4	O <sub>2</sub> <sup>2-</sup>	19
Br <sup>-</sup>	6	MnO <sub>4</sub> <sup>-</sup>	4	OH <sup>-</sup>	23
CN <sup>-</sup>	7	N <sup>3-</sup>	50	P <sup>3-</sup>	14
CO <sub>3</sub> <sup>2-</sup>	17	N <sub>3</sub> <sup>-</sup>	6	S <sup>2-</sup>	16
Cl <sup>-</sup>	8	NO <sub>3</sub> <sup>-</sup>	9	SO <sub>4</sub> <sup>2-</sup>	5
ClO <sub>4</sub> <sup>-</sup>	3	O <sup>2-</sup>	40	Se <sup>2-</sup>	12
F <sup>-</sup>	24	O <sub>2</sub> <sup>-</sup>	13	Te <sup>2-</sup>	9

## APPENDIX 3

### Selected Bond Energies

For homonuclear diatomic molecules, such as dihydrogen, precise measured values of bond energies are listed. For most of the heteronuclear bonds, only average values are given, and these tend to differ among literature sources. (All values here are in units of  $\text{kJ}\cdot\text{mol}^{-1}$ .)

#### Hydrogen

H—H	432	H—S	363
H—B	389	H—F	565
H—C	411	H—Cl	428
H—N	386	H—Br	362
H—O	459	H—I	295

#### Group 13

##### Boron

B—C	372	B—F	613
B—O	536	B—Cl	456
B=O	636	B—Br	377

#### Group 14

##### Carbon

C—C	346	C—O	358
C=C	602	C=O	799
C≡C	835	C≡O	1072
C—N	305	C—F	485
C=N	615	C—Cl	327
C≡N	887	C—Br	310
C—P	264	C—I	213

##### Silicon

Si—Si	222	Si—F	565
Si—O	452	Si—Cl	381
Si=O	642	Si—Br	310
		Si—I	234

#### Group 15

##### Nitrogen

N—N	247	N—O	201
N=N	418	N=O	607
N≡N	942	N—F	278
		N—Cl	192

##### Phosphorus

P—P	200	P—F	490
P≡P	481	P—Cl	326
P—O	335	P—Br	264
		P—I	184

**Group 16**

## Oxygen

O—O	142	O—F	190
O=O	494	O—Cl	218
O=S	523	O—Br	201
O—Xe	84	O—I	201

## Sulfur

S—S	268	S—F	327
S=S	425	S—Cl	271

**Group 17**

## Fluorine

F—F	155	F—Cl	249
F—Kr	50	F—Br	250
F—Xe	133	F—I	278

## Chlorine

Cl—Cl	240	Cl—Br	216
		Cl—I	208

## Bromine

Br—Br	190	Br—I	175
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## Iodine

I—I	149
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## APPENDIX 4

### Ionization Energies of Selected Metals

These ionization energies are in units of  $\text{MJ}\cdot\text{mol}^{-1}$ , and they have been summarized from G. Aylward and T. Findlay, *SI Chemical Data*, 3d ed. (New York: Wiley, 1994). Only selected ionization energies for outer (valence) electrons are listed.

The 1st ionization energy represents the energy required for the process:



while that of the 2nd ionization process represents that for:



and successive ionization energies are defined similarly as one-electron processes.

Element	Ionization energy				
	1st	2nd	3rd	4th	5th
Lithium	0.526				
Beryllium	0.906	1.763			
Sodium	0.502				
Magnesium	0.744	1.457			
Aluminum	0.584	1.823	2.751		
Potassium	0.425				
Calcium	0.596	1.152			
Scandium	0.637	1.241	2.395		
Titanium	0.664	1.316	2.659	4.181	
Vanadium	0.656	1.420	2.834	4.513	6.300
Chromium	0.659	1.598	2.993		
Manganese	0.724	1.515	3.255		

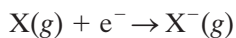
Element	Ionization energy				
	1st	2nd	3rd	4th	5th
Iron	0.766	1.567	2.964		
Cobalt	0.765	1.652	3.238		
Nickel	0.743	1.759			
Copper	0.752	1.964			
Zinc	0.913	1.740			
Lead	0.722	1.457			

## APPENDIX 5

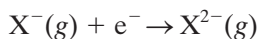
### Electron Affinities of Selected Nonmetals

These electron affinities are in units of  $\text{kJ}\cdot\text{mol}^{-1}$ , and they have been summarized from J. E. Huuhey et al., *Inorganic Chemistry*, 4th ed. (New York: HarperCollins, 1993).

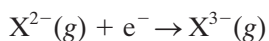
The 1st electron affinity represents the energy required for the process:



while that of the 2nd electron affinity represents that for:



and that of the 3rd electron affinity represents that for:



Element	Electron Affinity		
	1st	2nd	3rd
Nitrogen	−7	+673	+1070
Oxygen	−141	+744	
Fluorine	−328		
Phosphorus	−72	+468	+886
Sulfur	−200	+456	
Chlorine	−349		
Hydrogen	−79		
Bromine	−331		
Iodine	−301		

## APPENDIX 6

### Selected Lattice Energies

These lattice energies are in units of  $\text{kJ}\cdot\text{mol}^{-1}$ , and they have been calculated from Born-Haber cycles. The values are summarized from G. Aylward and T. Findlay, *SI Chemical Data*, 3d ed. (New York: Wiley, 1994).

Ion	Fluoride	Chloride	Bromide	Iodide	Oxide	Sulfide
Lithium	1047	862	818	759	2806	2471
Sodium	928	788	751	700	2488	2199
Potassium	826	718	689	645	2245	1986
Rubidium	793	693	666	627	2170	1936
Cesium	756	668	645	608	—	1899
Magnesium	2961	2523	2434	2318	3800	3323
Calcium	2634	2255	2170	2065	3419	3043
Strontium	2496	2153	2070	1955	3222	2879
Barium	2357	2053	1980	1869	3034	2716



## APPENDIX 7

### Selected Hydration Enthalpies

These hydration enthalpies are in units of  $\text{kJ}\cdot\text{mol}^{-1}$ , and the values were obtained from J. G. Stark and H. G. Wallace, *Chemistry Data Book* (London: John Murray, 1990).

Element	$\Delta_f H^\ominus$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
Lithium	−519
Sodium	−406
Potassium	−322
Rubidium	−301
Cesium	−276
Magnesium	−1920
Calcium	−1650
Strontium	−1480

Element	$\Delta_f H^\ominus$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
Barium	−1360
Aluminum	−4690
Silver	−464
Fluorine	−506
Chlorine	−364
Bromine	−335
Iodine	−293

## APPENDIX 8

### Selected Ionic Radii

These values of ionic radii are the Shannon–Prewitt values in pm (*Acta Cryst.*, 1976, A32, 751) for six-coordinate ions except where noted by (T) for four-coordinate tetrahedral ions; (HS) and (LS) designate the high-spin and low-spin radii for the transition metal ions. The values for polyatomic ions are adapted from Jenkins and Thakur (*J. Chem. Educ.*, 1979, 56, 576).

Ion	Ionic radii
Li <sup>+</sup> (T)	73
Na <sup>+</sup>	116
K <sup>+</sup>	152
Rb <sup>+</sup>	166
Cs <sup>+</sup>	181
Mg <sup>2+</sup>	86
Ca <sup>2+</sup>	114
Sr <sup>2+</sup>	132
Ba <sup>2+</sup>	149
Al <sup>3+</sup>	68
Fe <sup>2+</sup>	92
Fe <sup>3+</sup> (HS)	78
Fe <sup>3+</sup> (LS)	69
Co <sup>2+</sup> (HS)	88
Co <sup>3+</sup> (LS)	68
Ni <sup>2+</sup>	83

Ion	Ionic radii
Cu <sup>+</sup>	91
Cu <sup>2+</sup>	87
Zn <sup>2+</sup>	88
F <sup>-</sup> (T)	117
Cl <sup>-</sup>	167
Br <sup>-</sup>	182
I <sup>-</sup>	206
NH <sub>4</sub> <sup>+</sup>	151
CO <sub>3</sub> <sup>2-</sup>	164
NO <sub>3</sub> <sup>-</sup>	165
OH <sup>-</sup>	119
SO <sub>4</sub> <sup>2-</sup>	244
O <sup>2-</sup>	126
S <sup>2-</sup>	170



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# THE ELEMENTS

Atomic Average molar mass (g·mol <sup>-1</sup> )*			Atomic Average molar mass (g·mol <sup>-1</sup> )*			Atomic Average molar mass (g·mol <sup>-1</sup> )*		
Element	Symbol	number	Element	Symbol	number	Element	Symbol	number
Actinium	Ac	89	Gold	Au	79	Promethium	Pm	61
Aluminum	Al	13	Hafnium	Hf	72	Protactinium	Pa	91
Americium	Am	95	Hassium	Rs	108	Radium	Ra	88
Antimony	Sb	51	Helium	He	2	Radon	Rn	86
Argon	Ar	18	Holmium	Ho	67	Rhenium	Re	75
Arsenic	As	33	Hydrogen	H	1	Rhodium	Rh	45
Astatine	At	85	Indium	In	49	Roentgenium	Rg	111
Barium	Ba	56	Iodine	I	53	Rubidium	Rb	37
Berkelium	Bk	97	Iridium	Ir	77	Ruthenium	Ru	44
Beryllium	Be	4	Iron	Fe	26	Rutherfordium	Rf	104
Bismuth	Bi	83	Krypton	Kr	36	Samarium	Sm	62
Bohrium	Bh	107	Lanthanum	La	57	Scandium	Sc	21
Boron	B	5	Lawrencium	Lr	103	Seaborgium	Sg	106
Bromine	Br	35	Lead	Pb	82	Selenium	Se	34
Cadmium	Cd	48	Lithium	Li	3	Silicon	Si	14
Calcium	Ca	20	Livermorium	Lv	116	Silver	Ag	47
Californium	Cf	98	Lutetium	Lu	71	Sodium	Na	11
Carbon	C	6	Magnesium	Mg	12	Strontium	Sr	38
Cerium	Ce	58	Manganese	Mn	25	Sulfur	S	16
Cesium	Cs	55	Meitnerium	Mt	109	Tantalum	Ta	73
Chlorine	Cl	17	Mendelevium	Md	101	Technetium	Tc	43
Chromium	Cr	24	Mercury	Hg	80	Tellurium	Te	52
Cobalt	Co	27	Molybdenum	Mo	42	Terbium	Tb	65
Copernicium	Cn	112	Neodymium	Nd	60	Thallium	Tl	81
Copper	Cu	29	Neon	Ne	10	Thorium	Th	90
Curium	Cm	96	Neptunium	Np	93	Thulium	Tm	69
Darmstadtium	Ds	110	Nickel	Ni	28	Tin	Sn	50
Dubnium	Db	105	Niobium	Nb	41	Titanium	Ti	22
Dysprosium	Dy	66	Nitrogen	N	7	Tungsten	W	74
Einsteinium	Es	99	Nobelium	No	102	Ununoctium	Uuo	118
Erbium	Er	68	Osmium	Os	76	Ununpentium	Uup	115
Europium	Eu	63	Oxygen	O	8	Ununseptium	Uus	117
Fermium	Fm	100	Palladium	Pd	46	Ununtrium	Uut	113
Flerovium	Fl	114	Phosphorus	P	15	Uranium	U	92
Fluorine	F	9	Platinum	Pt	78	Vanadium	V	23
Francium	Fr	87	Plutonium	Pu	94	Xenon	Xe	54
Gadolinium	Gd	64	Polonium	Po	84	Ytterbium	Yb	70
Gallium	Ga	31	Potassium	K	19	Yttrium	Y	39
Germanium	Ge	32	Praseodymium	Pr	59	Zinc	Zn	30
						Zirconium	Zr	40

\*Average molar masses can be provided for only naturally occurring elements.