Descriptive Inorganic Chemistry
Chemistry 241
SUNY College at Oneonta

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CHAPTER 1

Origins: the Chemical Elements and the Earth

Concepts and ideas, on the origin of the universe range over the fields of science, philosophy and religion, and also in the realm of fanciful guess work. More and more evidence is being obtained which supports the contention that the chemical elements are formed by stellar nuclear synthesis, and that the earth's formation can be explained by chemical processes. In this chapter we will discuss both of these aspects.

THE ORIGIN OF THE CHEMICAL ELEMENTS

The Chemical Elements

Chemistry, which is the study of matter, and how it may be modified by physical and chemical processes, is concerned with the chemical elements. There are 90 naturally occurring elements on the earth, 81 of these (from H to Bi, excluding Tc and Pm) have at least one, or more, stable isotope, while the 9 other elements exist as unstable radioactive isotopes (Po to U). The remaining elements of those listed in Table 1.1 (Tc, Pm, and Np to element 106) do not occur naturally on earth today, but have been synthesised by man. However, it is probable that some of these elements did exist in the past, but owing to short half-lives have since decayed. Recent evidence, still being debated, indicates that some elements with atomic numbers in the region 116 to 126 may have existed on the earth in minute amounts. This group of elements are predicted to have relatively stable nuclei compared with their neighbours.

Origin of the Elements

Both the developments in nuclear chemistry over recent years, and the results of space exploration, make it possible to answer questions on the origin and distribution of the chemical elements. The elemental composition of various parts of the universe differ, as indicated by the data in Table 1.2. The relative abundance of the elements, for the universe as a whole, is depicted in Fig. 1.1. Certain features in the table and the figure lead one to raise questions such as; why the variation throughout the universe?

2

TABLE 1.1   The Occurrence of Elements in Nature

1	2	3															6
H																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
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*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	(At)	(Rn)
Fr	Ra	Ac	Th	Pa	U	Np**											
1	2	3			4								5				6

1   Soluble simple salts (Na, K, Rb chlorides, sulphates); cationic constituents in aluminosilicates (Li, Be, Cs).

2   Insoluble carbonates, sulphates.

3   Oxides.

4   Occur as free elements.

5   Sulphides

6   Atmosphere.

◯   Does not occur naturally on the earth

*   Lanthanides La to Lu

**   Actinides   Ac to Lr

why does iron feature so prominently? why are elements Li, Be and B of such
low abundance relative to their neighbours?

Before pursuing these questions it is necessary to consider, briefly, the
structure of the nucleus.

TABLE 1.2   Elemental Composition (% of total atoms) for
             Selected Systems in the Universe

Universe		Sun (% by vol.)		Bulk Earth (% by mass)		Earth's Crust		Human Body	
H	91	H	92.5	Fe	35.4	O	46.6	H	63
He	9.1	He	7.3	O	27.8	Si	27.2	O	25.5
O	0.057	O	0.068	Mg	17.0	Al	8.13	C	9.5
N	0.042	C	0.037	Si	12.6	Fe	5.00	N	1.4
C	0.021	N	0.0093	S	2.7	Ca	3.63	Ca	0.31
Ne	0.003	Ne	0.0074	Ni	2.7	Na	2.83	P	0.22
Si	0.003	Mg	0.0044	Ca	0.6	K	2.59	K	0.06
Mg	0.002	Si	0.0029	Al	0.44	Mg	2.09	Cl	0.03
Fe	0.002	Fe	0.00185	Co>Na>Mn>K >Ti>P>Cr		Ti>H>C		S>Na>Mg	

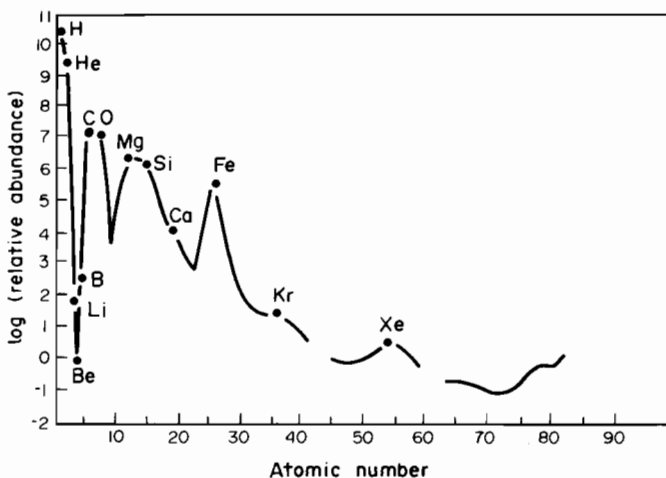(Source: Selbin, J., *J. Chem. Ed.*, 1973, 50, 306.)

Fig. 1.1.   Relative abundances of the elements in the
            universe, smoothed curve (based on
            log(abundance of Si) = 6).

Structure of the Nucleus

In broad detail an atom consists of two principal parts, the nucleus and the electron shell or cloud. The nucleus is very small relative to the size of an atom, being about 10^{-12}cm in diameter, whereas an atom, such as sodium, has a diameter of 3.80×10^{-8}cm. The fundamental difference between atoms of one element with those of another, as well as different atoms of the same element lies in the composition of the nucleus.

The two principal particles in a nucleus, the proton and the neutron, account for most of the mass of an atom (Table 1.3). An atom is characterised by its nucleus and by two quantities, the atomic number Z (number of protons) and the atomic weight A (number of protons and neutrons). The symbol $^A_Z M$ is used where M is the chemical symbol for the element. For any one element Z is constant (e.g. 6 for carbon, 8 for oxygen) but the element may have a number

TABLE 1.3   Atomic Particles

	Electron	Proton	Neutron
Charge	-1	+1	0
Absolute Value	1.6021×10^{-19} coulomb	1.6021×10^{-19} coulomb	0
Mass	9.11×10^{-31}kg	1.67×10^{-27}kg	1.67×10^{-27}kg
Relative Mass	1/1840	1	1

of values of A. The different atoms of an element are called isotopes, which are either stable or radioactive, some occur naturally, others do not.

The two particles in the nucleus are closely inter-related and may inter-convert. This can happen in atoms in order to increase nuclear stability.

$$p^+ \rightarrow n + e^+ + \nu^{(+)} \tag{1.1}$$
$$n \rightarrow p^+ + e^- + \nu^{(-)} \tag{1.2}$$

where e^+ is a positron (+ve electron), e^- is the electron, p^+ is the proton, n is the neutron and ν is a neutrino, (+) and (-) refer to the spin alignment of the neutrino.

Protons and neutrons, called neucleons, are held together by cohesive forces which cannot be just electrostatic, as proton-proton repulsions would de-stabilize the nucleus. The very strong attractive forces between nucleons are operative over distances less than 1.4×10^{-13}cm. At greater distances the attraction falls rapidly to zero, and the coulomb repulsive force dominates. The intense short range forces are said to be due to a messenger, called a pion, with finite rest mass (274 x mass of the electron). Nucleons are not tightly packed, but occupy approximately four times the volume of a close-packed arrangement.
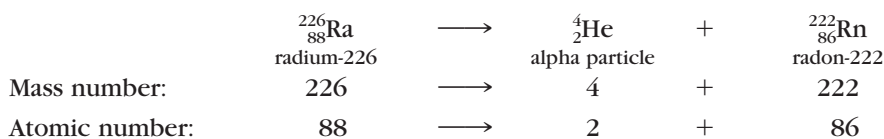
20.2 Nuclear Reactions

Equations for Nuclear Reactions

Ernest Rutherford found that radium not only emits alpha particles but also produces the radioactive gas radon in the process. Such observations led Rutherford and Frederick Soddy, in 1902, to propose the revolutionary theory that *radioactivity is the result of a natural change of a radioactive isotope of one element into an isotope of a* different *element.* In such changes, called **nuclear reactions** or *transmutations,* an unstable nucleus (the *parent nucleus*) spontaneously emits radiation and is converted (decays) into a more stable nucleus of a different element (the *daughter product*). Thus, a nuclear reaction results in a change in atomic number and, in some cases, a change in mass number as well. For example, the reaction of radium studied by Rutherford can be written as

$$^{226}_{88}\text{Ra} \longrightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$
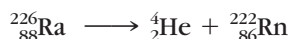
In this representation, the subscripts are the atomic numbers and the superscripts are the mass numbers *(⬅ p. 54).*

In a chemical change, the atoms in molecules and ions are rearranged, but atoms are neither created nor destroyed; the number of atoms remains the same. Similarly, in nuclear reactions the total number of nuclear particles, or **nucleons** (protons and neutrons), remains the same. The essence of nuclear reactions, however, is that one nucleon can change into a different nucleon along with the release of energy. A proton can change to a neutron or a neutron can change to a proton, but the total number of nucleons remains the same. Therefore, ***the sum of the mass numbers of reacting nuclei must equal the sum of the mass numbers of the nuclei produced.*** Furthermore, because electrical charge cannot be created or destroyed, ***the sum of the atomic numbers of the products must equal the sum of the atomic numbers of the reactants.*** These principles can be verified for the preceding nuclear equation.

> When a radioactive atom decays, the emission of a charged particle leaves behind a charged atom. Thus, when radium-226 decays, it gives a helium-4 cation ($^{4}_{2}\text{He}^{2+}$) and a radon-222 anion ($^{222}_{86}\text{Rn}^{2-}$). By convention, the ion charges are not shown in balanced nuclear equations.

> Recall that the atomic number is the number of protons in an atom's nucleus (that is, the total positive charge on the nucleus), and the mass number is the sum of protons and neutrons in a nucleus.

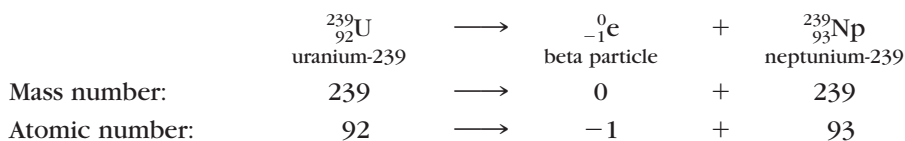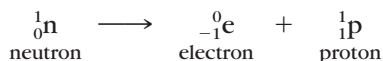|	$^{226}_{88}\text{Ra}$		$^{4}_{2}\text{He}$	+	$^{222}_{86}\text{Rn}$
	radium-226		alpha particle		radon-222
Mass number:	226	$\longrightarrow$	4	+	222
Atomic number:	88	$\longrightarrow$	2	+	86

Alpha and Beta Particle Emission

One way a radioactive isotope can decay is to eject an alpha particle from the nucleus. This is illustrated by the radium-226 reaction above and by the conversion of uranium-234 to thorium-230 by alpha emission.

	$^{234}_{92}\text{U}$		$^{4}_{2}\text{He}$	+	$^{230}_{90}\text{Th}$
	uranium-234		alpha particle		thorium-230
	(parent nucleus)				(daughter product)
Mass number:	234	$\longrightarrow$	4	+	230
Atomic number:	92	$\longrightarrow$	2	+	90
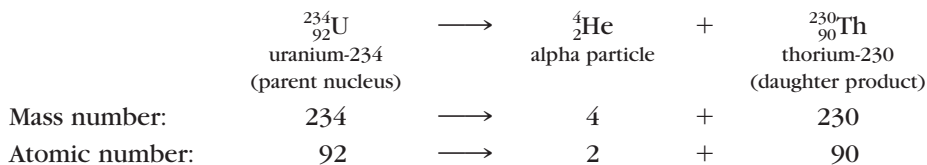
In alpha emission, *the atomic number of the parent nucleus decreases by two units and the mass number decreases by four units for each alpha particle emitted.*

> Note that in beta decay the mass number is uncharged.

Emission of a beta particle is another way for a radioactive isotope to decay. For example, loss of a beta particle by uranium-239 (parent nucleus) to form neptunium-239 (daughter product) is represented by

	$^{239}_{92}\text{U}$		$^{0}_{-1}\text{e}$	+	$^{239}_{93}\text{Np}$
	uranium-239		beta particle		neptunium-239
Mass number:	239	$\longrightarrow$	0	+	239
Atomic number:	92	$\longrightarrow$	−1	+	93

How does a nucleus, composed only of protons and neutrons, increase its number of protons by ejecting an electron during beta emission? It is generally accepted that a series of reactions is involved, but the net process is

$$\underset{\text{neutron}}{{}^{1}_{0}\text{n}} \longrightarrow \underset{\text{electron}}{{}^{0}_{-1}\text{e}} + \underset{\text{proton}}{{}^{1}_{1}\text{p}}$$

where we use the symbol p for a proton and n for a neutron. In this process, a neutron is converted to a proton and a beta particle is released. Therefore, *the ejection of a beta particle always means that a different element is formed because a neutron has been converted into a proton. The new element (daughter product) has an atomic number one unit greater than that of the decaying (parent) nucleus.* The mass number does not change, however, because no proton or neutron has been emitted.

In many cases, the emission of an alpha or beta particle results in the formation of a product nucleus that is also unstable and therefore radioactive. The new radioactive product may undergo a number of successive transformations until a stable, nonradioactive nucleus is finally produced. Such a series of reactions is called a **radioactive series.** One such series begins with uranium-238 and ends with lead-206, as illustrated in Figure 20.1. The first step in the series is

$$^{238}_{92}\text{U} \longrightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th}$$
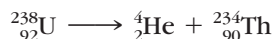
The final step, the conversion of polonium-210 to lead-206, is

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{206}_{82}\text{Pb}$$
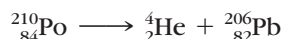
> If a neutron changes to a proton, conservation of charge requires that a negative particle (a beta particle) be created.

> A nucleus formed as a result of alpha or beta emission is often in an excited state and therefore emits a gamma ray.

PROBLEM-SOLVING EXAMPLE 20.1   Radioactive Series

An intermediate species in the uranium-238 decay series shown in Figure 20.1 is polonium-218. It emits an alpha particle, followed by emission of a beta particle, followed by the emission of a beta particle. Write the nuclear equations for these three reactions.
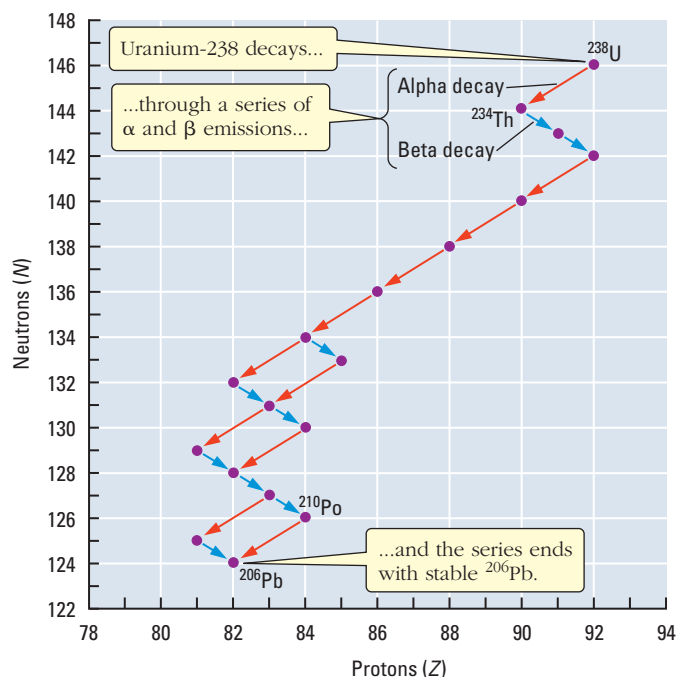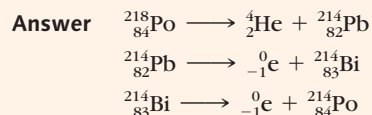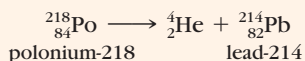

Figure 20.1 The ²³⁸U decay series.

Answer $^{218}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{214}_{82}\text{Pb}$

$^{214}_{82}\text{Pb} \longrightarrow {}^{0}_{-1}\text{e} + {}^{214}_{83}\text{Bi}$

$^{214}_{83}\text{Bi} \longrightarrow {}^{0}_{-1}\text{e} + {}^{214}_{84}\text{Po}$

Strategy and Explanation   The starting point of these linked reactions is polonium-218. When it emits an alpha particle, the atomic number decreases by two and the mass number decreases by four to produce lead-214.

$$^{218}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{214}_{82}\text{Pb}$$
polonium-218   lead-214

The second of these linked reactions begins with lead-214. When it emits a beta particle, the atomic number increases by one and the mass number remains constant to produce bismuth-214.

$$^{214}_{82}\text{Pb} \longrightarrow {}^{0}_{-1}\text{e} + {}^{214}_{83}\text{Bi}$$
lead-214   bismuth-214
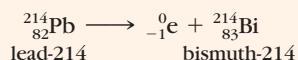
In the third reaction, bismuth-214 emits a beta particle, so the atomic number increases by one and the mass number remains constant to produce polonium-214.

$$^{214}_{83}\text{Bi} \longrightarrow {}^{0}_{-1}\text{e} + {}^{214}_{84}\text{Po}$$
bismuth-214   polonium-214
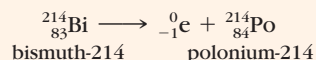
✓ **Reasonable Answer Check**   An alpha emission decreases the atomic number by two and decreases the mass number by four. Each beta emission increases the atomic number by one and leaves the mass number unchanged. Therefore, one alpha and two beta emissions would leave the atomic number unchanged and decrease the mass number by four, which is what our systematic analysis found.

PROBLEM-SOLVING PRACTICE 20.1

(a) Write an equation showing the emission of an alpha particle by an isotope of neptunium, $^{237}_{93}\text{Np}$, to produce an isotope of protactinium.
(b) Write an equation showing the emission of a beta particle by sulfur-35, $^{35}_{16}\text{S}$, to produce an isotope of chlorine.

EXERCISE   **20.1** Radioactive Decay Series

The actinium decay series begins with uranium-235, $^{235}_{92}\text{U}$, and ends with lead-207, $^{207}_{82}\text{Pb}$. The first five steps involve the successive emission of α, β, α, α, and β particles. Identify the radioactive isotope produced in each of the steps, beginning with uranium-235.

Other Types of Radioactive Decay

The positron was discovered by Carl Anderson in 1932. It is sometimes called an "antielectron," one of a group of particles that have become known as "antimatter." Contact between an electron and a positron leads to mutual annihilation of both particles with production of two high-energy photons (gamma rays). This process is the basis of positron emission tomography (PET) scanning to detect tumors (Section 20.9).

In addition to radioactive decay by emission of alpha, beta, or gamma radiation, other nuclear decay processes are known. Some nuclei decay, for example, by emission of a **positron,** $^{0}_{+1}\text{e}$ or β^{+}, which is effectively a positively charged electron. For example, positron emission by polonium-207 leads to the formation of bismuth-207.
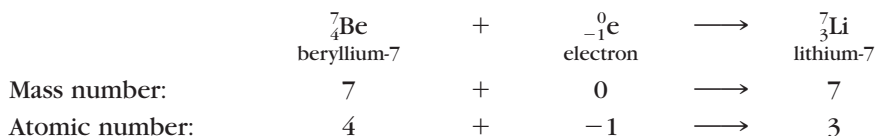
$$^{207}_{84}\text{Po} \longrightarrow {}^{0}_{+1}\text{e} + {}^{207}_{83}\text{Bi}$$
polonium-207   positron   bismuth-207
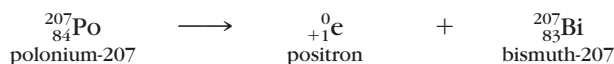
Mass number:	207	$\longrightarrow$	0	+	207
Atomic number:	84	$\longrightarrow$	+1	+	83

Notice that this process is the opposite of beta decay, because positron decay leads to a *decrease* in the atomic number. Like beta decay, positron decay does not change the mass number because no proton or neutron is ejected.

Another nuclear process is **electron capture,** in which the atomic number is reduced by one but the mass number remains unchanged. In this process an inner-shell electron (for example, a $1s$ electron) is captured by the nucleus.
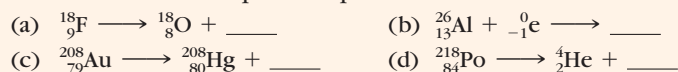
$$^{7}_{4}\text{Be} \quad + \quad ^{0}_{-1}\text{e} \quad \longrightarrow \quad ^{7}_{3}\text{Li}$$

	beryllium-7		electron		lithium-7
Mass number:	7	+	0	$\longrightarrow$	7
Atomic number:	4	+	-1	$\longrightarrow$	3

In the old nomenclature of atomic physics, the innermost shell ($n = 1$ principal quantum number) was called the K-shell, so the electron capture mechanism is sometimes called *K-capture.*

In summary, radioactive nuclei can decay in four ways, as summarized in the figure at right.

Effects of four radioactive decay processes. The chart shows the changes in the number of protons and neutrons during alpha decay, beta decay, positron emission, and electron capture.

PROBLEM-SOLVING EXAMPLE 20.2   Nuclear Equations

Complete these nuclear equations by filling in the missing symbol, mass number, and atomic number of the product species.

(a) $^{18}_{9}\text{F} \longrightarrow ^{18}_{8}\text{O} + $ _____

(b) $^{26}_{13}\text{Al} + ^{0}_{-1}\text{e} \longrightarrow$ _____

(c) $^{208}_{79}\text{Au} \longrightarrow ^{208}_{80}\text{Hg} + $ _____

(d) $^{218}_{84}\text{Po} \longrightarrow ^{4}_{2}\text{He} + $ _____

Answer

(a) $^{0}_{+1}\text{e}$ (b) $^{26}_{12}\text{Mg}$ (c) $^{0}_{-1}\text{e}$ (d) $^{214}_{82}\text{Pb}$

Strategy and Explanation

In each case we deduce the missing species by comparing the atomic numbers and mass numbers before and after the reaction.

(a) The missing particle has a mass number of zero and a charge of $+1$, so it must be a positron, $^{0}_{+1}\text{e}$. When the positron is included in the equation, the atomic mass is 18 on each side, and the atomic numbers sum to 9 on each side.

(b) The missing nucleus must have a mass number of $26 + 0 = 26$ and an atomic number of $13 - 1 = 12$, so it is $^{26}_{12}\text{Mg}$.

(c) The missing particle has a mass number of zero and a charge of -1, so it must be a beta particle, $^{0}_{-1}\text{e}$.

(d) The missing nucleus has a mass number of $218 - 4 = 214$ and an atomic number of $84 - 2 = 82$, so it is $^{214}_{82}\text{Pb}$.

PROBLEM-SOLVING PRACTICE 20.2

Complete these nuclear equations by filling in the missing symbol, mass number, and atomic number of the product species.

(a) $^{11}_{6}\text{C} \longrightarrow ^{11}_{5}\text{B} + ?$

(b) $^{35}_{16}\text{S} \longrightarrow ^{35}_{17}\text{Cl} + ?$

(c) $^{30}_{15}\text{P} \longrightarrow ^{0}_{+1}\text{e} + ?$

(d) $^{22}_{11}\text{Na} \longrightarrow ^{0}_{-1}\text{e} + ?$

EXERCISE   20.2 Nuclear Reactions

Aluminum-26 can undergo either positron emission or electron capture. Write the balanced nuclear equation for each case.

20.3 Stability of Atomic Nuclei

The naturally occurring isotopes of elements from hydrogen to bismuth are shown in Figure 20.2, where the radioactive isotopes are represented by orange circles and
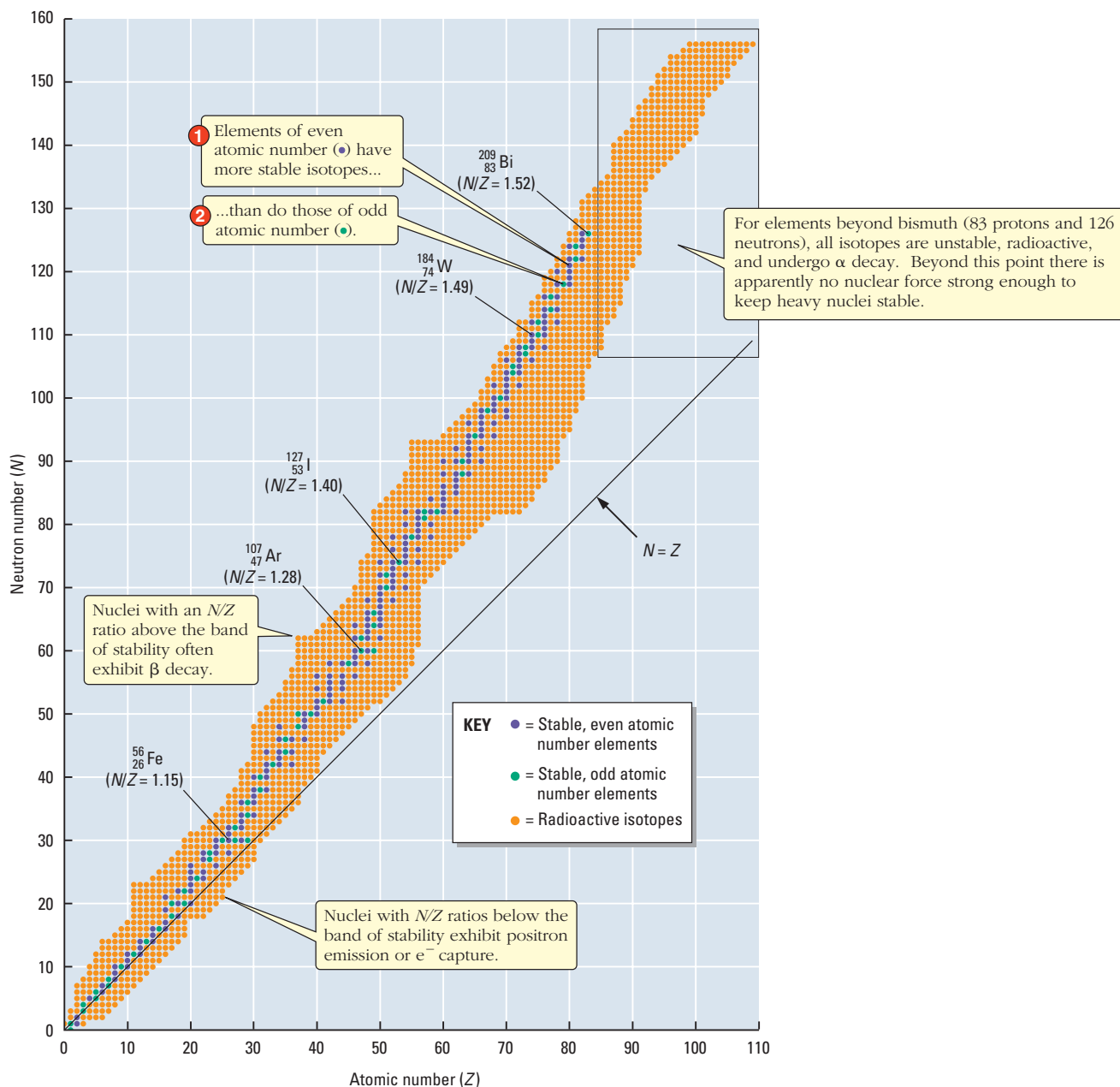
Figure 20.2   A plot of neutrons versus protons for the nuclei from hydrogen ($Z = 1$) through bismuth ($Z = 83$). A narrow band of stability is apparent. The N/Z values for some example stable nuclei are shown.

the stable (nonradioactive) isotopes are represented by purple and green circles. It is surprising that so few stable isotopes exist. Why are there not hundreds more? To investigate this question, we will systematically examine the elements, starting with hydrogen.

In its simplest and most abundant form, hydrogen has only one nuclear particle, a single proton. In addition, the element has two other well-known isotopes: nonradioactive deuterium, with one proton and one neutron, $^2_1H = D$, and radioactive tritium, with one proton and two neutrons, $^3_1H = T$. Helium, the next element, has two protons and two neutrons in its most stable isotope. At the end of the actinide series is element 103, lawrencium, one isotope of which has 154 neutrons and a mass number of 257. From hydrogen to lawrencium, except for ^1_1H and ^3_2He,

the mass numbers of stable isotopes are always at least twice as large as the atomic number. In other words, except for $_1^1H$ and $_2^3He$, every isotope of every element has a nucleus containing *at least* one neutron for every proton. Apparently the tremendous *repulsive* forces between the positively charged protons in the nucleus are moderated by the presence of neutrons, which have no electrical charge. Figure 20.2 illustrates a number of principles:

1. For light elements up to Ca ($Z = 20$), the stable isotopes usually have equal numbers of protons and neutrons, or perhaps one more neutron than protons. Examples include $_3^7Li$, $_6^{12}C$, $_8^{16}O$, and $_{16}^{32}S$.
2. Beyond calcium the neutron/proton ratio becomes increasingly greater than 1. The band of stable isotopes deviates more and more from the line $N = Z$ (number of neutrons = number of protons). It is evident that more neutrons are needed for nuclear stability in the heavier elements. For example, whereas one stable isotope of Fe has 26 protons and 30 neutrons ($N/Z = 1.15$), one stable isotope of platinum has 78 protons and 117 neutrons ($N/Z = 1.50$).
3. For elements beyond bismuth-209 (83 protons and 126 neutrons), all nuclei are unstable and radioactive. Furthermore, the rate of disintegration becomes greater the heavier the nucleus. For example, half of a sample of $_{92}^{238}U$ disintegrates in 4.5 billion years, whereas half of a sample of $_{103}^{256}Lr$ decays in only 28 seconds.
4. A careful analysis of Figure 20.2 reveals additional interesting features. First, elements with an even atomic number have a greater number of stable isotopes than do those with an odd atomic number. Second, stable isotopes usually have an even number of neutrons. For elements with an odd atomic number, the most stable isotope has an even number of neutrons. In fact, of the nearly 300 stable isotopes represented in Figure 20.2, roughly 200 have an even number of neutrons *and* an even number of protons. Only about 120 have an odd number of either protons or neutrons. Only four isotopes ($_1^2H$, $_3^6Li$, $_5^{10}B$, and $_7^{14}N$) have odd numbers of *both* protons and neutrons.

The Band of Stability and Type of Radioactive Decay

The narrow band of stable isotopes in Figure 20.2 (the purple and green circles) is sometimes called the *peninsula of stability* in a "sea of instability." Any nucleus (the orange circles) not on this peninsula will decay in such a way that the nucleus can come ashore on the peninsula. The chart can help us predict what type of decay will be observed.

The nuclei of all elements beyond Bi ($Z = 83$) are unstable—that is, radioactive—and most decay by *alpha particle emission.* For example, americium, the radioactive element used in smoke alarms, decays in this manner.

$$_{95}^{243}Am \longrightarrow {}_2^4He + {}_{93}^{239}Np$$
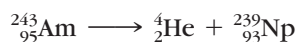
Beta emission occurs in isotopes that have too many neutrons to be stable—that is, isotopes above the peninsula of stability in Figure 20.2. When beta decay converts a neutron to a proton and an electron (beta particle), which is then ejected, the atomic number increases by one, and the mass number remains constant.

$$_{27}^{60}Co \longrightarrow {}_{-1}^{0}e + {}_{28}^{60}Ni$$
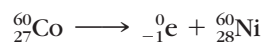
Conversely, lighter nuclei—below the peninsula of stability—that have too few neutrons attain stability by *positron emission* or by *electron capture,* because these processes convert a proton to a neutron in one step.

$$_7^{13}N \longrightarrow {}_{+1}^{0}e + {}_6^{13}C$$

$$_{20}^{41}Ca + {}_{-1}^{0}e \longrightarrow {}_{19}^{41}K$$
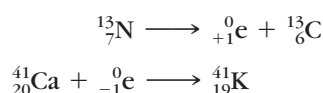
Decay by these two routes is observed for elements with atomic numbers ranging from 4 to greater than 100; as Z increases, electron capture becomes more likely than positron emission.

PROBLEM-SOLVING EXAMPLE 20.3 **Nuclear Stability**

For each of these unstable isotopes, write a nuclear equation for its probable mode of decay.

(a) Silicon-32, $^{32}_{14}Si$

(b) Titanium-43, $^{43}_{22}Ti$

(c) Plutonium-239, $^{239}_{94}Pu$

(d) Manganese-56, $^{56}_{25}Mn$

Answer

(a) $^{32}_{14}Si \longrightarrow {}^{0}_{-1}e + {}^{32}_{15}P$

(b) $^{43}_{22}Ti \longrightarrow {}^{0}_{+1}e + {}^{43}_{21}Sc$ or $^{43}_{22}Ti + {}^{0}_{-1}e \longrightarrow {}^{43}_{21}Sc$

(c) $^{239}_{94}Pu \longrightarrow {}^{4}_{2}He + {}^{235}_{92}U$

(d) $^{56}_{25}Mn \longrightarrow {}^{0}_{-1}e + {}^{56}_{26}Fe$

Strategy and Explanation Note the ratio of protons to neutrons. If there are excess neutrons, beta emission is probable. If there are excess protons, either electron capture or positron emission is probable. If the atomic number is greater than 83, then alpha emission is probable.

(a) Silicon-32 has excess neutrons, so beta decay is expected.

(b) Titanium-43 has excess protons, so either positron emission or electron capture is probable.

(c) Plutonium-239 has an atomic number greater than 83, so alpha decay is probable.

(d) Manganese-56 has excess neutrons, so beta decay is expected.

PROBLEM-SOLVING PRACTICE 20.3

For each of these unstable isotopes, write a nuclear equation for its probable mode of decay.

(a) $^{42}_{19}K$

(b) $^{234}_{92}U$

(c) $^{20}_{9}F$

The nuclear binding energy is similar to the bond energy for a chemical bond (⇐ *p. 349*) in that the binding energy is the energy that must be supplied to separate all of the particles (protons and neutrons) that make up the atomic nucleus and the bond energy is the energy that must be supplied to separate two bonded atoms. In both cases the energy change is positive, because work must be done to separate the particles.

Binding Energy

As demonstrated by Ernest Rutherford's alpha particle scattering experiment (⇐ *p. 45*), the nucleus of the atom is extremely small. Yet the nucleus can contain up to 83 protons before becoming unstable, suggesting that there must be a very strong short-range binding force that can overcome the electrostatic repulsive force of a number of protons packed into such a tiny volume. A measure of the force holding the nucleus together is the nuclear **binding energy.** This energy (E_b) is defined as the negative of the energy change (ΔE) that would occur if a nucleus were formed directly from its component protons and neutrons. For example, if a mole of protons and a mole of neutrons directly formed a mole of deuterium nuclei, the energy change would be more than 200 million kJ, the equivalent of exploding 73 tons of TNT.

$$^{1}_{1}H + {}^{1}_{0}n \longrightarrow {}^{2}_{1}H \qquad \Delta E = -2.15 \times 10^{8} \text{ kJ}$$

$$\text{Binding energy} = E_b = -\Delta E = 2.15 \times 10^{8} \text{kJ}$$

This nuclear synthesis reaction is highly exothermic (so E_b is very positive), an indication of the strong attractive forces holding the nucleus together. The deuterium nucleus is more stable than an isolated proton and an isolated neutron.

To understand the enormous energy released during the formation of atomic nuclei, we turn to an experimental observation and a theory. The experimental observation is that the mass of a nucleus is always slightly less than the sum of the masses of its constituent protons and neutrons.

$$\begin{array}{ccc} ^{1}_{1}H & + & {}^{1}_{0}n \longrightarrow {}^{2}_{1}H \\ 1.007825 \text{ g/mol} & & 1.008665 \text{ g/mol} \qquad 2.01410 \text{ g/mol} \end{array}$$
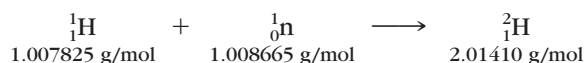
Change in mass $= \Delta m =$ mass of product $-$ sum of masses of reactants

$$\Delta m = 2.01410 \text{ g/mol} - 1.008665 \text{ g/mol} - 1.007825 \text{ g/mol}$$

$$\Delta m = 2.01410 \text{ g/mol} - 2.016490 \text{ g/mol}$$

$$\Delta m = -0.00239 \text{ g/mol} = -2.39 \times 10^{-6} \text{ kg/mol}$$

The theory is that the missing mass, Δm, is released as energy, which we describe as the binding energy.

The relationship between mass and energy is contained in Albert Einstein's 1905 theory of special relativity, which holds that mass and energy are simply different manifestations of the same quantity. Einstein stated that the energy of a body is equivalent to its mass times the square of the speed of light, $E = mc^2$. To calculate the energy change in a process in which the mass has changed, the equation becomes

$$\Delta E = (\Delta m)c^2$$

We can calculate ΔE in joules if the change in mass is given in kilograms and the velocity of light is given in meters per second (because $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$). For the formation of 1 mol deuterium nuclei from 1 mol protons and 1 mol neutrons, we have

$$\Delta E = (-2.39 \times 10^{-6} \text{ kg})(3.00 \times 10^8 \text{ m/s})^2$$

$$= -2.15 \times 10^{11} \text{ J} = -2.15 \times 10^8 \text{ kJ}$$

This is the value of ΔE given at the beginning of this section for the change in energy when a mole of protons and a mole of neutrons form a mole of deuterium nuclei.

Consider another example, the formation of a helium-4 nucleus from two protons and two neutrons.

$$2\,{}_1^1\text{H} + 2\,{}_0^1\text{n} \longrightarrow {}_2^4\text{He} \qquad\qquad E_b = +2.73 \times 10^9 \text{ kJ/mol } {}_2^4\text{He nuclei}$$

This binding energy, E_b, is very large, even larger than that for deuterium. To compare nuclear stabilities more directly, nuclear scientists generally calculate the **binding energy per nucleon.** Each ${}^4\text{He}$ nucleus contains four nucleons—two protons and two neutrons. Therefore, 1 mol ${}^4\text{He}$ atoms contains 4 mol nucleons.

$$E_b \text{ per mol nucleons} = \frac{2.73 \times 10^9 \text{ kJ}}{\text{mol } {}_2^4\text{He nuclei}} \times \frac{1 \text{ mol } {}_2^4\text{He nuclei}}{4 \text{ mol nucleons}}$$

$$= 6.83 \times 10^8 \text{ kJ/mol nucleons}$$

The greater the binding energy per nucleon, the greater the stability of the nucleus. The binding energies per nucleon are known for a great number of nuclei and are plotted as a function of mass number in Figure 20.3. It is very interesting and important that the point of maximum stability occurs in the vicinity of iron-56, ${}_{26}^{56}\text{Fe}$. This means that *all nuclei are thermodynamically unstable with respect to iron-56.* That is, very heavy nuclei can split, or *fission,* to form smaller, more stable nuclei with atomic numbers nearer to that of iron, while simultaneously releasing enormous quantities of energy (Section 20.6). In contrast, two very light nuclei can come together and undergo *nuclear fusion* exothermically to form heavier nuclei (Section 20.7). Because of its high nuclear stability, *iron is the most abundant of the heavier elements in the universe.*

EXERCISE   20.3 Binding Energy

Calculate the binding energy, in kJ/mol, for the formation of lithium-6.

$$3\,{}_1^1\text{H} + 3\,{}_0^1\text{n} \longrightarrow {}_3^6\text{Li}$$
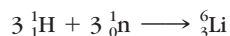
The necessary masses are ${}_1^1\text{H} = 1.00783$ g/mol, ${}_0^1\text{n} = 1.00867$ g/mol, and ${}_3^6\text{Li} = 6.015125$ g/mol. Is the binding energy greater than or less than that for helium-4? Compare the binding energy per nucleon of lithium-6 and helium-4. Which nucleus is more stable?
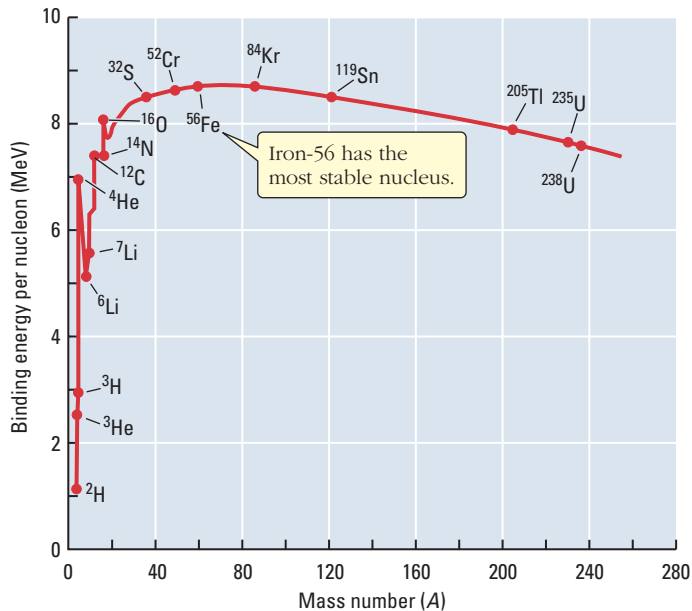
Figure 20.3 Binding energy per nucleon. The values plotted were derived by calculating the binding energy per nucleon in million electron volts (MeV) for the most abundant isotope of each element from hydrogen to uranium (1 MeV = 1.602×10^{-13} J). The nuclei at the top of the curve are most stable.

CONCEPTUAL EXERCISE **20.4** Binding Energy

By interpreting the shape of the curve in Figure 20.3, determine which is more exothermic per gram—fission or fusion. Explain your answer.

Origin of the Universe

A question, which many people at some time in their lives ponder, is "how did it all begin?". One fact is that the Universe is expanding, the evidence being that light from the furthermost galaxies is of longer wavelength (red end) than light from nearer galaxies. This is explained by the Doppler effect, i.e. the galaxies are moving outwards, away from each other, and so the light appears to the observer, who is behind the moving object, to be of longer wavelength. If the Universe is expanding it suggests there may have been a starting point.

It is proposed in the *steady state theory* of the origin of the Universe that matter, viz. hydrogen, is being created continuously to fill in the gaps created by the expanding Universe, and all other elements come from the hydrogen by nuclear reactions. The more favoured theory, the *big bang theory* states that at some definite time the Universe came into being, and that the extremely densely packed matter (elementary particles) as a result of high pressure and temperatures eventually "exploded" dispersing matter through space. The material then regrouped under gravitational influences into stars and other bodies as we know them today. An extension of this theory called the *oscillating theory* suggests that at some time in the future the expansion of the Universe will stop and contraction will then occur until a dense mass is reformed, followed by another "big bang".

During the big bang, temperatures in the region of 10^9K would have been produced and a number of nuclear reactions occur, such as:

$$\ce{^1_1H + ^1_0n -> ^2_1H} \tag{1.3}$$

$$\ce{^2_1H + ^1_1H -> ^3_2He} \tag{1.4}$$

$$\ce{^3_2He + ^1_0n -> ^4_2He} \quad (\alpha \text{ particle}) \tag{1.5}$$

$$\ce{^4_2He + ^1_0n -> ^5_2He} \tag{1.6}$$

All this would have happened in the first 30 to 60 minutes, as beyond that time the temperature would have dropped so no further reactions could occur. Also the "chain-type" reaction stops at $^5_2$He, which has a half-life of 2×10^{-21}s, and decays to $^4_2$He. Heavier chemical elements are produced in subsequent reactions in the stars.

Nuclear Synthesis

Irrespective of the origin of the Universe it is generally accepted that synthesis of the elements that go to make up our world have been, and still are, carried out in the stars. We will turn our attention to this, after first discussing in more detail nuclear stability.

Nuclear stability. A number of impirical rules concerning the stability of nuclei, and their relative abundance have been formulated. For example, nuclei with even atomic numbers (Z) are more abundant than those with odd atomic numbers. Nuclei containing even numbers of protons and neutrons (even-even nuclei) are both more abundant and more stable than odd-odd nuclei, while even-odd nuclei are of intermediate stability. Often the most abundant and stable nuclei, up to atomic number 20, have a 1:1

neutron:proton ratio, e.g. $^4_2$He (99.99%), $^{14}_7$N (99.63%), $^{24}_{12}$Mg (78.70%) and $^{40}_{20}$Ca (96.97%). However, some light isotopes with odd atomic numbers, and which do not possess the 1:1 n:p ratio, are the most stable and abundant for the particular element, eg. $^{20}_9$F, $^{23}_{11}$Na, $^{27}_{13}$Al. They possess odd-even nuclei which is more stable than odd-odd nuclei (even with a 1:1 n:p ratio). Nuclei with atomic numbers 2, 8, 20, 50, 82, 126 have a special stability, and their atomic numbers are termed "magic numbers". Explanations for the above observations are in terms of inter-nuclear like-like pairing forces and like-unlike interactions and will not be discussed here.

When light nuclei are formed energy is emitted, and the nuclear mass becomes less than the sum of the masses of the component neutrons and protons. The mass of $^{16}_8$O is 15.9949 atomic mass units (amu) whereas the sum of 8 protons and 8 neutrons (8 x 1.0078 + 8 x 1.0087) is 16.1320 amu. The difference, 0.1371 amu, is the mass loss on forming the oxygen nucleus, which corresponds to 128 MeV (using $E = mc^2$). The energy per nucleon (128/16 = 8.0 MeV) is termed the binding energy of the nucleus and this varies with mass number as shown in Fig. 1.2. Since the binding energy is proportional to the number of nucleons, one could expect a regular increase. However, for mass number >56 proton-proton repulsions become more significant destabilizing the
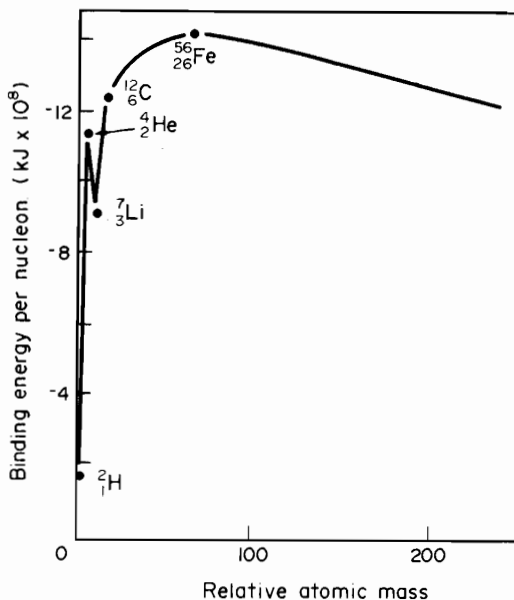
Fig. 1.2. Stabilities of atomic nuclei relative to
separated protons and neutrons.

nucleus, which is offset somewhat, by dilution with more neutrons. Therefore heavier nuclei have more neutrons than protons. A plot of atomic number against number of neutrons (Fig. 1.3) indicates this. Nuclei that lie off the stability area undergo radioactive decay in order to achieve stability.
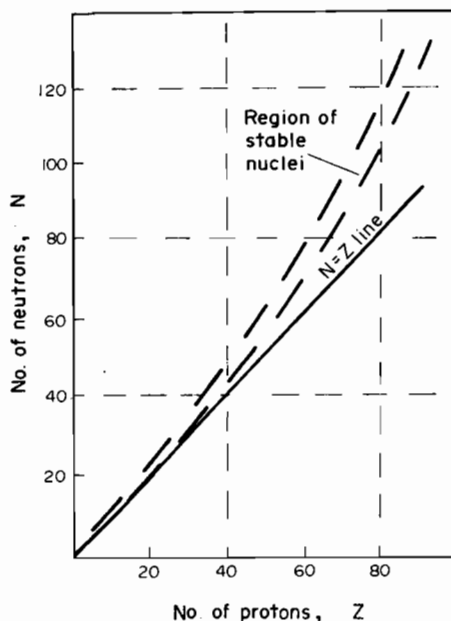
Fig. 1.3.   Neutrons versus protons for stable nuclei.

Hydrogen burning. The initial process in stellar nuclear synthesis is
hydrogen burning, producing helium. Gravitational forces acting upon
hydrogen produce a density around 10^5kg m^{-3} and the gravitational energy,
converted into heat, raises the temperature to around $1-3 \times 10^7$K. At this
temperature the kinetic energy of the hydrogen nuclei is sufficient to over-
come the strong barrier to two positively charged nuclei undergoing nuclear
fusion.

$$^1_1\text{H} + {}^1_1\text{H} \rightarrow {}^2_1\text{H} + \beta^+ + \nu^{(+)} \text{(neutrino)} \tag{1.7}$$

$$^2_1\text{H} + {}^1_1\text{H} \rightarrow {}^3_2\text{He} + \gamma \tag{1.8}$$

$$^3_2\text{He} + {}^3_2\text{He} \rightarrow {}^4_2\text{He} + 2^1_1\text{H} \tag{1.9}$$

$$\overline{4^1_1\text{H} \rightarrow {}^4_2\text{He} + 2\beta^+ + 2\gamma + 2\nu^{(+)}} \tag{1.10}$$
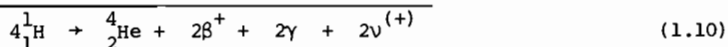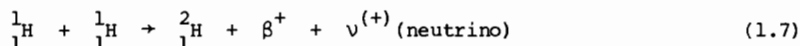
The process is exothermic (or exoergic) since more stable nuclei are
produced. This corresponds to moving down the binding energy curve (Fig. 1.2).
The time scale for hydrogen burning is greater than 5 billion years, as our
sun, which is around 5 billion years old, is in the early stages of hydrogen
burning (around 90% hydrogen remains).

Helium burning. As hydrogen is used up and helium produced, the temperature
of the core drops, and the star exterior expands to conserve heat. The star,
with a larger surface area and a lower temperature, becomes reddish in colour
and is call a *red giant*. However, the core, now mainly helium, continues to

collapse under the gravitational forces driving the temperatures up to $1-3 \times 10^8$K with a density of around 10^8kg m^{-3}. The shell at this stage becomes hotter and hydrogen in it begins to burn, while helium burning begins in the core. The higher temperatures are now sufficient to overcome the even greater energy barrier to the fusion of helium nuclei together. The first product of helium burning is $^8_4$Be which has a half-life of 2×10^{-16}s.

$$2\,^4_2\text{He} \rightarrow \,^8_4\text{Be} + \gamma. \tag{1.11}$$

However, sufficient $^8_4$Be accumulates for further reactions to occur.

$$^8_4\text{Be} + \,^4_2\text{He} \rightarrow \,^{12}_6\text{C} + \gamma. \tag{1.12}$$

Neutrons and protons can also take part in reactions during $^4_2$He burning, e.g.

$$^{12}_6\text{C} + \,^1_1\text{H} \rightarrow \,^{13}_7\text{N} \rightarrow \,^{13}_6\text{C} + \beta^+ + \nu. \tag{1.13}$$
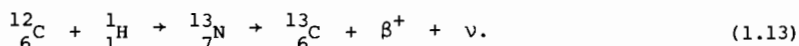
Small stars. When much of the hydrogen and helium is spent in small stars, with a mass less than $1.4 \times$ mass of our sun, gravity produces further contraction to give a *white dwarf*. Eventually both nuclear reactions and gravitational collapse stops and the body cools to an inert dense mass.

Big stars. In stars with a mass greater than 1.4 times the mass of our sun, higher temperatures are produced and when 6×10^8K is reached an alternative hydrogen burning process, the *carbon-nitrogen cycle*, takes place, provided some $^{12}_6$C, which acts as a catalyst, is available.

$$^{12}_6\text{C} + \,^1_1\text{H} \rightarrow \,^{13}_7\text{N} + \gamma \tag{1.14}$$

$$^{13}_7\text{N} \rightarrow \,^{13}_6\text{C} + \beta^+ + \nu \tag{1.15}$$

$$^{13}_6\text{C} + \,^1_1\text{H} \rightarrow \,^{14}_7\text{N} + \gamma \tag{1.16}$$

$$^{14}_7\text{N} + \,^1_1\text{H} \rightarrow \,^{15}_8\text{O} + \gamma \tag{1.17}$$

$$^{15}_8\text{O} \rightarrow \,^{15}_7\text{N} + \beta^+ + \nu \tag{1.18}$$

$$^{15}_7\text{N} + \,^1_1\text{H} \rightarrow \,^4_2\text{He} + \,^{12}_6\text{C} \tag{1.19}$$

This adds up to

$$4\,^1_1\text{H} \rightarrow \,^4_2\text{He} + 3\gamma + 2\beta^+ + 2\nu \tag{1.20}$$
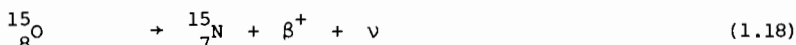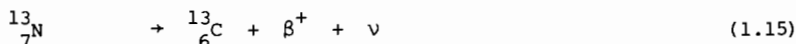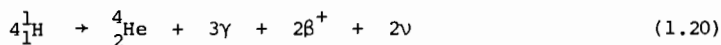
Carbon and oxygen burning also occurs at these temperatures and produce nuclei in the region of $^{28}_{14}$Si, for example,

$$^{12}_6\text{C} + \,^{12}_6\text{C} \rightarrow \,^{20}_{10}\text{Ne} + \,^4_2\text{He} \tag{1.21}$$

$$^{16}_8\text{O} + \,^{16}_8\text{O} \rightarrow \,^{28}_{14}\text{Si} + \,^4_2\text{He} \tag{1.22}$$

$$^{16}_8\text{O} + \,^{16}_8\text{O} \rightarrow \,^{31}_{16}\text{S} + \,^1_0\text{n} \tag{1.23}$$

Gamma radiation produced in many of these exoergic reactions can cause disintegration of nuclei, for example $^{20}_{10}Ne$ gives protons, neutrons and particles, which are available for further reactions. The most abundant element produced from $^{16}_{8}O$ burning in $^{28}_{14}Si$, but at higher temperatures ($\sim 3 \times 10^9$K) γ-radiation can lead to the breakdown of $^{28}_{14}Si$ opening the way for synthesis of even heavier nuclei. This is called silicon burning,

$$\gamma + {}^{28}_{14}Si \rightleftharpoons {}^{24}_{12}Mg + {}^{4}_{2}He \tag{1.24}$$

$$^{28}_{14}Si + {}^{4}_{2}He \rightleftharpoons {}^{32}_{16}S + \gamma \tag{1.25}$$

$$^{32}_{16}S + {}^{4}_{2}He \rightleftharpoons {}^{36}_{18}Ar + \gamma \tag{1.26}$$

By this stage an equilibrium between nuclei formation and disintegration occurs, with a continuing tendency towards the formation of heavier elements. The fusion process is still exoergic up to the formation of $^{56}_{26}Fe$ but then stops at $^{56}_{26}Fe$, which is the nucleus with maximum stability (Fig. 1.2). One could expect an accumulation of $^{56}_{26}Fe$ in the Universe compared with other elements. Iron is in fact a relatively abundant element, but there are lighter elements, which are more abundant, indicating that the processes described above are still in progress. The above description helps explain why in the relative abundance curve (Fig. 1.1) there are elements such as $^{12}_{6}C$, $^{16}_{8}O$, $^{20}_{10}Ne$ which are more abundant than their neighbours. We note that each of these abundant nuclei differ from the next one by a $^{4}_{2}He$ nucleus.

Eventually the temperature of big stars may reach 7-8 x 10^9K at which point many endoergic reactions will occur, such as the breakdown of nuclei giving neutrons, protons and α particles, which can be used in further reactions. Neutrinos are also produced (e.g. $e^+ + e^- \rightarrow \nu^{(+)} + \nu^{(-)}$) which carry energy away from the stars. While this is in progress considerable contraction of the core occurs up to a density of around 10^{14}kg m^{-3}. Finally an implosion of the core and explosion of the shell will result. This corresponds to a *supernova*, which flings material out into space.

Heavy elements. Since $^{56}_{26}Fe$ is the most stable nucleus any heavier nuclei can only be produced with an expenditure of energy (endoergic). Also, it becomes increasingly more difficult for highly charged nuclei to get close enough for fusion to occur. It is therefore perhaps surprising that any elements heavier than iron exist. However, one nuclear reaction that circumvents these problems is neutron capture, since the neutron has little difficulty penetrating a positively charged nucleus. Heavy elements are obtained by neutron capture beginning with the "seed" nucleus $^{56}_{26}Fe$.

Neutrons are produced in stars either as part of the normal stellar nuclear evolutionary processes in "red giants" and second generation stars (e.g. $^{13}_{6}C$ + $^{4}_{2}He \rightarrow {}^{16}_{8}O + {}^{1}_{0}n$), or in considerable quantities just prior to, and during a supernova period. Stars which emit periodic bursts of radio waves (pulsars) are mainly composed of neutrons (neutron stars). The different sources of neutrons give rise to two distinct neutron capture processes.

(a) "s" process. In the "s" process, or slow neutron capture, one neutron is captured by a nucleus which becomes, in most cases, unstable and decays usually with β^- emission in order to increase the p/n ratio before a second neutron is captured.

$$\begin{array}{l}{}^{58}_{26}Fe + {}^{1}_{0}n \rightarrow {}^{59}_{26}Fe \rightarrow {}^{59}_{27}Co + {}^{0}_{-1}e + \nu^{(-)}\end{array} \qquad (1.27)$$

(i.e. in the ${}^{59}_{26}Fe$ nucleus reaction (1.2) has occurred.) Single neutron capture occurs in periods from 1 to 10^5 years which generally gives sufficient time for β^- decay to occur. The "s" process tends to produce the lighter isotopes of elements, i.e. the "proton-rich" isotopes. The heaviest element produced by the "s" process is ${}^{209}_{83}Bi$. The range of isotopes of tin (see below) and the existence of technetium (longest ½ life 2.6 x 10^6 yrs) in the stars are evidence for the "s" process.

(b) "r" process. Rapid neutron capture occurs in environments of high neutron density, many neutrons may be captured by a nucleus in a period 10^{-2} to 10 seconds before decay occurs. The "r" process gives "neutron-rich" isotopes,

$$\begin{array}{l}{}^{56}_{26}Fe + 13{}^{1}_{0}n \rightarrow {}^{69}_{26}Fe \rightarrow {}^{69}_{27}Co + {}^{0}_{-1}e\end{array} \qquad (1.28)$$
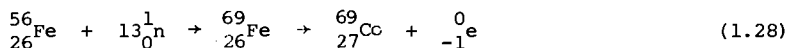
and the heavy elements. For example ${}^{254}Cf$ is produced in nuclear explosions and is present in stars.

A summary of the "r" and "s" processes which lead to the isotopes of tin is given in Fig. 1.4. The method by which the isotopes are produced is indicated by the letters "r" and "s" and b (bypassed). The black line corresponds to the "s" process path and clearly the progress from ${}^{114}_{48}Cd$ to ${}^{115}_{49}In$ to ${}^{116}_{50}Sn$
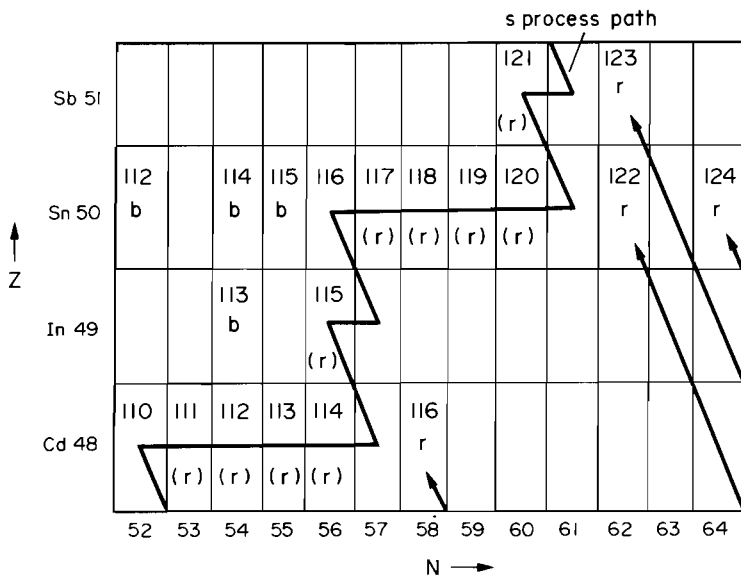
Fig. 1.4. Neutron capture process in the neighbourhood
           of tin. Isotopes marked by r are produced by
           the "r" process, (r) by both the "r" and "s"
           processes, b if they are bypassed, and those
           unmarked by the "s" process.

is by single neutron captures followed by β^- emission. The three isotopes ^{112}Sn, ^{114}Sn and ^{115}Sn are not produced by the "s" or "r" processes, and it is suggested that they are obtained by rapid proton capture. Isotopes obtained this way are rich in protons and have very low abundance, as proton capture is less favourable than neutron capture.

<u>Deuterium, Lithium, Beryllium and Boron</u>. The nuclei ^2D, ^6Li, ^7Li, ^9Be, ^{10}B and ^{11}B are not end products in any of the processes mentioned. The small amounts produced during hydrogen and helium burning are removed as they burn at lower temperatures giving helium, i.e.

$$^2_1D + ^1_1H \rightarrow ^3_2He + \gamma \tag{1.29}$$

$$^6_3Li + ^1_1H \rightarrow ^3_2He + ^4_2He \tag{1.30}$$

$$^7_3Li + ^1_1H \rightarrow \gamma + ^8_4Be \rightarrow 2^4_2He \tag{1.31}$$

$$^9_4Be + ^1_1H \rightarrow ^4_2He + ^6_3Li \overset{^1_1H}{\rightarrow} ^3_2He + 2^4_2He \tag{1.32}$$

$$^{10}_5B + ^1_1H \rightarrow ^4_2He + ^7_4Be \tag{1.33}$$

$$^{11}_5B + ^1_1H \rightarrow 3^4_2He + \gamma \tag{1.34}$$
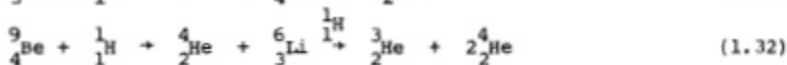
However, the nuclei do exist, but in low abundance, and are probably produced by *spallation* nuclear reactions, when heavy cosmic ray particles collide with elements, such as carbon, nitrogen and oxygen, and cause them to break up to give lighter nuclei.

The details of the above processes will be modified as more data comes to light, but the details given in Fig. 1.5 summarises the present state of our knowledge.

20.4 Rates of Disintegration Reactions

Cobalt-60 is radioactive and is used as a source of β particles and γ rays to treat malignancies in the human body. One-half of a sample of cobalt-60 will change via beta decay into nickel-60 in a little more than five years (Table 20.2). On the other

Table 20.2 Half-Lives of Some Common Radioactive Isotopes

Isotope	Decay Process	Half-Life
$^{238}_{92}U$	$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He$	4.15×10^9 yr
$^{3}_{1}H$ (tritium)	$^{3}_{1}H \longrightarrow {}^{3}_{2}He + {}^{0}_{-1}e$	12.3 yr
$^{14}_{6}C$ (carbon-14)	$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e$	5730 yr
$^{131}_{53}I$	$^{131}_{53}I \longrightarrow {}^{131}_{54}Xe + {}^{0}_{-1}e$	8.04 d
$^{123}_{53}I$	$^{123}_{53}I + {}^{0}_{-1}e \longrightarrow {}^{123}_{52}Te$	13.2 h
$^{57}_{24}Cr$	$^{57}_{24}Cr \longrightarrow {}^{57}_{25}Mn + {}^{0}_{-1}e$	21 s
$^{28}_{15}P$	$^{28}_{15}P \longrightarrow {}^{28}_{14}Si + {}^{0}_{+1}e$	0.270 s
$^{90}_{38}Sr$	$^{90}_{38}Sr \longrightarrow {}^{90}_{39}Y + {}^{0}_{-1}e$	28.8 yr
$^{60}_{27}Co$	$^{60}_{27}Co \longrightarrow {}^{60}_{28}Ni + {}^{0}_{-1}e$	5.26 yr

hand, copper-64, which is used in the form of copper acetate to detect brain tumors, decays much more rapidly; half of the radioactive copper decays in slightly less than 13 hours. These two radioactive isotopes are clearly different in their rates of decay.

Half-Life

The relative instability of a radioactive isotope is expressed as its **half-life,** the time required for one half of a given quantity of the isotope to undergo radioactive decay. In terms of reaction kinetics *(◁ p. 619),* radioactive decay is a first-order reaction. Therefore, the rate of decay is given by the first-order rate law equation

$$\ln[A]_t = -kt + \ln[A]_0$$

where $[A]_0$ is the initial concentration of isotope A, $[A]_t$ is the concentration of A after time t has passed, and k is the first-order rate constant. Because radioactive decay is first-order, the half-life $(t_{1/2})$ of an isotope is the same no matter what the initial concentration. It is given by

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

The relationship $t_{1/2} = \frac{0.693}{k}$ was introduced in the context of kinetics of reactions *(◁ p. 624).*

As illustrated by Table 20.2, isotopes have widely varying half-lives. Some take years, even millennia, for half of the sample to decay (^{238}U, ^{14}C), whereas others decay to half the original number of atoms in fractions of seconds (^{28}P). The unit of half-life is whatever time unit is most appropriate—anything from years to seconds.

As an example of the concept of half-life, consider the decay of plutonium-239, an alpha-emitting isotope formed in nuclear reactors.

$$^{239}_{94}\text{Pu} \longrightarrow {}^{4}_{2}\text{He} + {}^{235}_{92}\text{U}$$
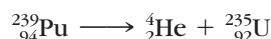
The half-life of plutonium-239 is 24,400 years. Thus, half of the quantity of $^{239}_{94}$Pu present at any given time will disintegrate every 24,400 years. For example, if we begin with 1.00 g $^{239}_{94}$Pu, 0.500 g of the isotope will remain after 24,400 years. After 48,800 years (two half-lives), only half of the 0.500 g, or 0.250 g, will remain. After 73,200 years (three half-lives), only half of the 0.250 g will still be present, or 0.125 g. The amounts of $^{239}_{94}$Pu present at various times are illustrated in Figure 20.4. All radioactive isotopes follow this type of decay curve.
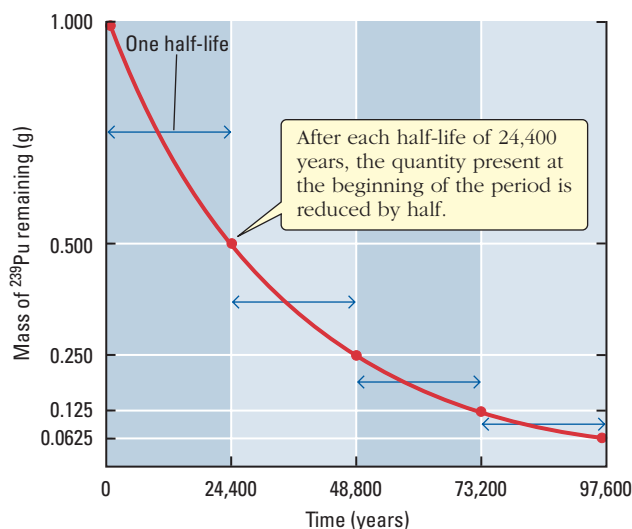
Figure 20.4   **The decay of 1.00 g plutonium-239.**

PROBLEM-SOLVING EXAMPLE **20.4** **Half-Life**

Iodine-131, used to treat hyperthyroidism, has a half-life of 8.04 days.

$$^{131}_{53}I \longrightarrow \; ^{131}_{52}Te + \; ^{0}_{-1}e \qquad t_{1/2} = 8.04 \text{ days}$$
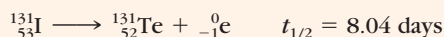
If you have a sample containing 10.0 μg of iodine-131, what mass of the isotope will remain after 32.2 days?

Answer 0.0625 μg

Strategy and Explanation First, we find the number of half-lives in the given 32.2-day time period. Since the half-life is 8.04 days, the number of half-lives is

$$32.2 \text{ days} \times \frac{1 \text{ half-life}}{8.04 \text{ days}} = 4.00 \text{ half-lives}$$

This means that the initial quantity of 10.0 μg is reduced by half four times.

$$10.0 \text{ μg} \times 1/2 \times 1/2 \times 1/2 \times 1/2 = 10.0 \text{ μg} \times 1/16 = 0.0625 \text{ μg}$$

After 32.2 days, only one sixteenth of the original ^{131}I remains.

✓ **Reasonable Answer Check** After the passage of four half-lives, the remaining ^{131}I should be a small fraction of the starting amount, and it is.

PROBLEM-SOLVING PRACTICE **20.4**

Strontium-90 is a radioisotope ($t_{1/2}$ = 29 years) produced in atomic bomb explosions. Its long half-life and tendency to concentrate in bone marrow by replacing calcium make it particularly dangerous to people and animals.
(a) The isotope decays with loss of a β particle. Write a balanced equation showing the other product of decay.
(b) A sample of the isotope emits 2000 β particles per minute. How many half-lives and how many years are necessary to reduce the emission to 125 β particles per minute?

EXERCISE **20.5** **Half-Lives**

The radioactivity of formerly highly radioactive isotopes is essentially negligible after ten half-lives. What percentage of the original radioisotope remains after this amount of time (ten half-lives)?

Rate of Radioactive Decay

To determine the half-life of a radioactive element, its *rate of decay,* that is, the number of atoms that disintegrate in a given time—per second, per hour, per year—must be measured.

Radioactive decay is a first-order process (⬅ *p. 619),* with a rate that is directly proportional to the number of radioactive atoms present (N). This proportionality is expressed as a rate law (Equation 20.1) in which A is the **activity** of the sample—the number of disintegrations observed per unit time—and k is the first-order rate constant or *decay constant* characteristic of that radioisotope.

$$A = kN \qquad\qquad [20.1]$$

Suppose the activity of a sample is measured at some time t_0 and then measured again after a few minutes, hours, or days. If the initial activity is A_0 at t_0, then a second measurement at a later time t will detect a smaller activity A. Using Equation 20.1, the ratio of the activity A at some time t to the activity at the beginning of the

experiment (A_0) must be equal to the ratio of the number of radioactive atoms N that are present at time t to the number present at the beginning of the experiment (N_0).

$$\frac{A}{A_0} = \frac{kN}{kN_0} \qquad \text{or} \qquad \frac{A}{A_0} = \frac{N}{N_0}$$

Thus, either A/A_0 or N/N_0 expresses the fraction of radioactive atoms remaining in a sample after some time has elapsed.

The activity of a sample can be measured with a device such as a Geiger counter (Figure 20.5). It detects radioactive emissions as they ionize a gas to form free electrons and cations that can be attracted to a pair of electrodes. In the Geiger counter, a metal tube is filled with low-pressure argon gas. The inside of the tube acts as the cathode. A thin wire running through the center of the tube acts as the anode. When radioactive emissions enter the tube through the thin window at the end, they collide with argon atoms; these collisions produce free electrons and argon cations. As the free electrons accelerate toward the anode, they collide with other argon atoms to generate more free electrons. The free electrons all go to the anode, and they constitute a pulse of current. This current pulse is counted, and the rate of pulses per unit time is the output of the Geiger counter.

The **curie (Ci)** is commonly used as a unit of activity. One curie represents a decay rate of 3.7×10^{10} disintegrations per second (s^{-1}), which is the decay rate of 1 g radium. One millicurie (mCi) $= 10^{-3}$ Ci $= 3.7 \times 10^7$ s^{-1}. Another unit of radioactivity is the **becquerel (Bq)**; 1 becquerel is equal to one nuclear disintegration per second (1 Bq $= 1$ s^{-1}).

The change in activity of a radioactive sample over a period of time, or the fraction of radioactive atoms still present in a sample after some time has elapsed, can be calculated using the integrated rate equation for a first-order reaction

$$\ln A = -kt + \ln A_0$$

which can be rearranged to

$$\ln \frac{A}{A_0} = -kt \qquad\qquad [20.2]$$

The curie *was named for Pierre Curie by his wife, Marie; the* becquerel *honors Henri Becquerel.*

The unit for curie and becquerel is s^{-1} because each is a number (of disintegrations) per second.

Equation 20.2 can be derived from Equation 20.1 using calculus.

1 Ionizing radiation passes through the thin window…

2 …momentarily ionizing the argon gas.

3 The ions complete a circuit between the anode and cathode.

4 The signal is amplified…

5 …to produce clicking from a speaker. The frequency of clicks indicates the radiation intensity.

Cathode ⊖   Anode ⊕

Thin window   Argon gas   Voltage source   Amplifier   Speaker

Radioactive sample (e.g., uranium ore)

Geiger counter hand piece

Active Figure 20.5   A Geiger counter. Go to the Active Figures menu at ThomsonNOW to test your understanding of the concepts in this figure.

where A/A_0 is the ratio of activities at time t. Equation 20.2 can also be stated in terms of the fraction of radioactive atoms present in the sample after some time, t, has passed.

$$\ln \frac{N}{N_0} = -kt \qquad [20.3]$$

In words, Equation 20.3 says

$$\text{Natural logarithm}\left(\frac{\text{number of radioactive atoms at time } t}{\text{number of radioactive atoms at start of experiment}}\right)$$
$$= \text{natural logarithm(fraction of radioactive atoms remaining at time } t)$$
$$= -(\text{decay constant})(\text{time})$$

As radioactive atoms decay, N becomes a smaller and smaller fraction of N_0.

Notice the negative sign in Equation 20.3. The ratio N/N_0 is less than 1 because N is always less than N_0. This means that the logarithm of N/N_0 is negative, and the other side of the equation has a compensating negative sign because k and t are always positive.

As we have seen, the half-life of an isotope is inversely proportional to the first-order rate constant k:

$$t_{1/2} = \frac{0.693}{k}$$

Thus, the half-life can be found by calculating k from Equation 20.3 using N and N_0 from laboratory measurements over the time period t, as illustrated in Problem-Solving Example 20.5.

PROBLEM-SOLVING EXAMPLE 20.5   Half-Life

A sample of ^{24}Na initially undergoes 3.50×10^4 disintegrations per second (s^{-1}). After 24 h, its disintegration rate has fallen to $1.16 \times 10^4 \ s^{-1}$. What is the half-life of ^{24}Na?

Answer   15.0 h

Strategy and Explanation   We use Equation 20.2 relating activity (disintegration rate) at time zero and time t with the decay constant k. The experiment provided us with A, A_0, and the time.

$$\ln\left(\frac{1.16 \times 10^4 \ s^{-1}}{3.50 \times 10^4 \ s^{-1}}\right) = \ln(0.331) = -k(24 \text{ h})$$

$$k = -\frac{\ln(0.331)}{24 \text{ h}} = -\left(\frac{-1.104}{24 \text{ h}}\right) = 0.0460 \text{ h}^{-1}$$

From k we can determine $t_{1/2}$.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0460 \text{ h}^{-1}} = 15.0 \text{ h}$$

✓ **Reasonable Answer Check**   The activity (disintegration rate) fell to between one half and one quarter of its initial value in 24 h, so the half-life must be less than 24 h, and this agrees with our more accurate calculation.

PROBLEM-SOLVING PRACTICE 20.5

The decay of iridium-192, a radioisotope used in cancer radiation therapy, has a rate constant of $9.3 \times 10^{-3} \ d^{-1}$.
(a)   What is the half-life of ^{192}Ir?
(b)   What fraction of an ^{192}Ir sample remains after 100 days?

PROBLEM-SOLVING EXAMPLE 20.6   Time and Radioactivity

A 1.00-mg sample of ^{131}I ($t_{1/2}$ = 8.04 days) has an initial disintegration rate of 4.7×10^{12} s^{-1} (disintegrations per second). How long will it take for the disintegration rate of the sample to fall to 2.9×10^{11} s^{-1}?

Answer   776 h

Strategy and Explanation   We use the half-life of ^{131}I to find the decay constant, k. We convert the known half-life from days to hours.

$$t_{1/2} = 8.04 \text{ days} \times \frac{24 \text{ h}}{1 \text{ day}} = 193 \text{ h}$$

Then we calculate the decay constant, k.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{193 \text{ h}} = 3.59 \times 10^{-3} \text{ h}^{-1}$$

We then use this value of k in the equation relating disintegration rate to time. The initial disintegration rate is $A_0 = 4.7 \times 10^{12}$ s^{-1}, and the disintegration rate after the elapsed time is $A = 2.9 \times 10^{11}$ s^{-1}. We can use Equation 20.2 to calculate the elapsed time t. Both disintegration rates are given in disintegrations per second, but they appear as a ratio in Equation 20.2, so we can use them as provided. If we converted them both to disintegrations per hour, we would get the same numerical result for the ratio.

$$\ln\left(\frac{2.9 \times 10^{11} \text{ s}^{-1}}{4.7 \times 10^{12} \text{ s}^{-1}}\right) = -kt = -(3.59 \times 10^{-3} \text{ h}^{-1})t$$

$$t = \frac{-2.785}{3.59 \times 10^{-3} \text{ h}^{-1}} = 776 \text{ h}$$

✓ **Reasonable Answer Check**   The disintegration rate has fallen by approximately a factor of sixteen (4.7/0.29 = 16.2), so the elapsed time must be approximately four half-lives of ^{131}I, and it is.

PROBLEM-SOLVING PRACTICE 20.6

In 1921 the women of America honored Marie Curie by giving her a gift of 1.00 g of pure radium, which is now in Paris at the Curie Institute of France. The principal isotope, ^{226}Ra, has a half-life of 1.60×10^3 years. How many grams of radium-226 remain?

Carbon-14 Dating

In 1946 Willard Libby developed a technique for measuring the age of archaeological objects using radioactive carbon-14. Carbon is an important building block of all living systems, and all organisms contain the three isotopes of carbon: ^{12}C, ^{13}C, and ^{14}C. The first two isotopes are stable (nonradioactive) and have been present for billions of years. Carbon-14, however, is radioactive and decays to nitrogen-14 by beta emission.

$$^{14}_{6}C \longrightarrow \ ^{0}_{-1}e + \ ^{14}_{7}N$$
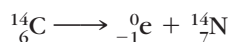
The half-life of ^{14}C is known by experiment to be 5.73×10^3 years. The number of carbon-14 atoms (N) in a carbon-containing sample can be measured from the activity of a sample (A). If the number of carbon-14 atoms originally in the sample (N_0) can be determined, or if the initial activity (A_0) can be determined, the age of the sample can be found from Equation 20.2 or 20.3.

This method of age determination clearly depends on knowing how much ^{14}C was originally in the sample. The answer to this question comes from work by physicist Serge Korff, who discovered in 1929 that ^{14}C is continually generated in the upper atmosphere. High-energy cosmic rays collide with gas molecules in the upper atmosphere and cause them to eject neutrons. These free neutrons collide with nitrogen atoms to produce carbon-14.

Willard Libby won the 1960 Nobel Prize in chemistry for his discovery of radiocarbon dating.

© Bettmann/Corbis

Willard Libby and his apparatus for carbon-14 dating.

Reuters New Media, Inc./Corbis

The Ice Man. This human mummy was found in 1991 in glacial ice high in the Alps. Carbon-14 dating determined that he lived about 5300 years ago. The mummy is exhibited at the South Tyrol Archaeological Museum in Bolzano, Italy.

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

Throughout the *entire* atmosphere, only about 7.5 kg ^{14}C is produced per year. However, this relatively small quantity of radioactive carbon is incorporated into CO_2 and other carbon compounds and then distributed worldwide as part of the carbon cycle. The continual formation of ^{14}C, transfer of the isotope within the oceans, atmosphere, and biosphere, and decay of living matter keep the supply of ^{14}C constant.

Plants absorb carbon dioxide from the atmosphere and convert it into food via photosynthesis (◁ *p. 899*). In this way, the ^{14}C becomes incorporated into living tissue, where radioactive ^{14}C atoms and nonradioactive ^{12}C atoms in CO_2 chemically react in the same way. The beta decay activity of carbon-14 in *living* plants and in the air is constant at 15.3 disintegrations per minute per gram (min^{-1} g^{-1}) of carbon. When a plant dies, however, carbon-14 disintegration continues *without the ^{14}C being replaced.* Consequently, the ^{14}C activity of the dead plant material decreases with the passage of time. The smaller the activity of carbon-14 in the plant, the longer the period of time between the death of the plant and the present. Assuming that ^{14}C activity in living plants was about the same hundreds or thousands of years ago as it is now, measurement of the ^{14}C beta activity of an artifact can be used to date an article containing carbon. The slight fluctuations of the ^{14}C activity in living plants for the past several thousand years have been measured by studying growth rings of long-lived trees, and the carbon-14 dates of objects can be corrected accordingly.

The time scale accessible to carbon-14 dating is determined by the half-life of ^{14}C. Therefore, this method for dating objects can be extended back approximately 50,000 years. This span of time is almost nine half-lives, during which the number of disintegrations per minute per gram of carbon would fall by a factor of about $(\frac{1}{2})^9 = 1.95 \times 10^{-3}$ from about 15.3 min^{-1} g^{-1} to about 0.030 min^{-1} g^{-1}, which is a disintegration rate so low that it is difficult to measure accurately.

PROBLEM-SOLVING EXAMPLE 20.7   Carbon-14 Dating

Charcoal fragments found in a prehistoric cave in Lascaux, France, had a measured disintegration rate of 2.4 min^{-1} g^{-1} carbon. Calculate the approximate age of the charcoal.

Answer   15,300 years old

Strategy and Explanation   We will use Equation 20.2 to solve the problem

$$\ln\left(\frac{A}{A_0}\right) = -kt$$

where A is proportional to the known activity of the charcoal (2.4 min^{-1} g^{-1}) and A_0 is proportional to the activity of the carbon-14 in living material (15.3 min^{-1} g^{-1}). We first need to calculate k, the rate constant, using the half-life of carbon-14, 5.73×10^3 yr.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.73 \times 10^3 \text{ yr}} = 1.21 \times 10^{-4} \text{ yr}^{-1}$$

Now we are ready to calculate the time, t.

$$\ln\left(\frac{2.4 \text{ min}^{-1} \text{ g}^{-1}}{15.3 \text{ min}^{-1} \text{ g}^{-1}}\right) = -kt$$

$$\ln(0.15686) = -(1.21 \times 10^{-4} \text{ yr}^{-1})t$$

$$t = \frac{1.8524}{1.21 \times 10^{-4} \text{ yr}^{-1}} = 1.53 \times 10^4 \text{ yr}$$

Thus, the charcoal is approximately 15,300 yrs old.

© images-of-france/Alamy

Prehistoric cave paintings from Lascaux, France.

✓ **Reasonable Answer Check** The disintegration rate has fallen a factor of six from the rate for living material, so more than two but less than three half-lives have elapsed. This agrees with our calculated result.

PROBLEM-SOLVING PRACTICE 20.7

Tritium, ^{3}H ($t_{1/2}$ = 12.3 yr), is produced in the atmosphere and incorporated in living plants in much the same way as ^{14}C. Estimate the age of a sealed sample of Scotch whiskey that has a tritium content 0.60 times that of the water in the area where the whiskey was produced.

EXERCISE **20.6** Radiochemical Dating

The radioactive decay of uranium-238 to lead-206 provides a method of radiochemically dating ancient rocks by using the ratio of ^{206}Pb atoms to ^{238}U atoms in a sample. Using this method, a moon rock was found to have a ^{206}Pb/^{238}U ratio of 100/109, that is, 100 ^{206}Pb atoms for every 109 ^{238}U atoms. No other lead isotopes were present in the rock, indicating that all of the ^{206}Pb was produced by ^{238}U decay. Estimate the age of the moon rock. The half-life of ^{238}U is 4.51×10^9 years.

CONCEPTUAL EXERCISE **20.7** Radiochemical Dating

Ethanol, C_2H_5OH, is produced by the fermentation of grains or by the reaction of water with ethylene, which is made from petroleum. The alcohol content of wines can be increased fraudulently beyond the usual 12% available from fermentation by adding ethanol produced from ethylene. How can carbon dating techniques be used to differentiate the ethanol sources in these wines?

Manufacture of Elements

Bombardment of stable nuclei with high speed particles has led to the production of a great variety of nuclei. The first particle, to be used by Rutherford and his group in 1919, was ^4_2He. The reaction;

$$^{14}_{7}N + ^4_2He \rightarrow ^{17}_{8}O + ^1_1H, \qquad (1.35)$$

produced the stable nucleus $^{17}_{8}O$. However, in many cases the product is radioactive, for example radioactive $^{32}_{15}P$ ($\frac{1}{2}$ life 14.3 days) is produced by the reaction;

$$^{31}_{15}P + ^2_1H \rightarrow ^{32}_{15}P + ^1_1H. \qquad (1.36)$$

Like many radioactive isotopes it is useful in tracer studies in biology agriculture, medicine and analytical investigations.

Neutrons are obtained from nuclear reactions such as:

$$^9_4Be + ^4_2He \rightarrow ^{12}_6C + ^1_0n, \qquad (1.37)$$

⠠� **reactions** in a cyclotron, or in nuclear reactors and are useful for producing isotopes.

It is now possible to produce elements heavier than Pu (as well as Tc and Pm), which do not occur on the earth. The following reactions are just a few that can be achieved(page 14).

Big bang
↓
^{1}H, ^{2}D, ^{3}He, ^{4}He, ^{7}Li
↓
Stars

^{1}H → ^{4}He — — — ▶ Hydrogen burning, (T~1 – 3 x 10^7 K)

^{4}He → ^{12}C, ^{16}O — — — ▶ Helium burning (T~ 1–3 x 10^8 K)

Small stars   Large stars
< 1.4 mass sun   >1.4 mass sun — — — ▶ Hydrogen burning
(white dwarf)   via C–N cycle

→ ^{24}Mg , ^{20}Ne, + — — — ▶ ^{12}C burning (T~6 x 10^8 K)

→ ^{32}S, ^{28}Si, + — — — ▶ ^{16}O burning (T~1–1.8 x 10^{9}K)

→ ^{32}S, ^{36}Ar, ^{56}Fe — — — ▶ ^{28}Si burning (T~3–5 x 10^9 K) ⎫
                                     + γ initiated ⎬ Equilbrium
                                        disintegrations ⎭

→ Ba, Pb, etc — — — ▶ Slow neutron capture

Supernova explosion
^{2}C, ^{16}O, ^{28}Si
explosive burning

U, Cf, Te, I etc — — ▶ Rapid neutron capture

^{19}F ^{21}Ne ^{115}Sn — — ▶ Rapid proton capture

^{9}Be, ^{6}Li , ^{7}Li, ^{10}B, ^{11}B — — — ▶ Cosmic ray bombardment (spallation)

Fig. 1.5. A brief summary of stellar nucleosynthesis. Source: Selbin, J., *J. Chem. Ed.*, 1973, 50, 306, 380.

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U + \gamma \rightarrow ^{239}_{93}Np + ^{0}_{-1}e \qquad (1.38)$$

$$\downarrow$$

$$^{239}_{94}Pu + ^{0}_{-1}e$$

$$(t_{\frac{1}{2}} = 24,360 \text{ yr})$$

$$^{239}_{94}Pu + ^{1}_{0}n \rightarrow ^{240}_{94}Pu + \gamma \overset{^{1}_{0}n}{\rightarrow} ^{241}_{94}Pu + \gamma \qquad (1.39)$$

$$\downarrow$$

$$^{241}_{95}Am + ^{0}_{-1}e$$

$$(t_{\frac{1}{2}} = 458 \text{ yr})$$

$$^{241}_{95}Am + ^{4}_{2}He \rightarrow ^{243}_{97}Bk + 2^{1}_{0}n \qquad (1.40)$$

$$(t_{\frac{1}{2}} = 4.5 \text{ hr})$$

$$^{252}_{98}Cf + ^{11}_{5}B \rightarrow ^{257}_{103}Lw + 6^{1}_{0}n \qquad (1.41)$$

$$(t_{\frac{1}{2}} = 8 \text{ sec})$$
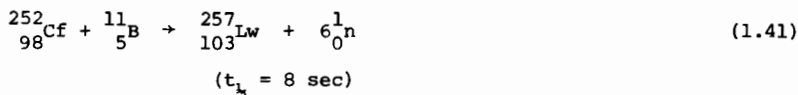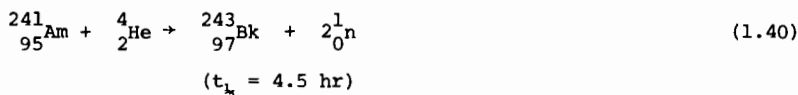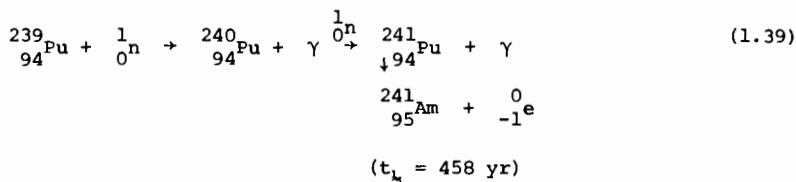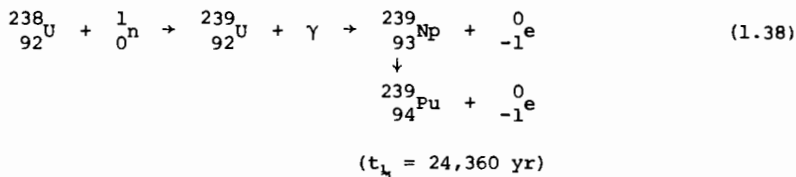
The amount of material produced is often small, 10^{-9}g, and special chemical techniques have been developed in order to study the chemistry of the trans-uranic elements.

Molecules in Interstellar Space

The material in stars is nuclear, i.e. atoms stripped of electrons, because of the high temperatures. However, at temperatures comparable with those on the earth, atoms exist, as for example in the space between stars and in certain "cloud-type" formations. This environment is a very good vacuum, much better than can be obtained in laboratories.

Since atoms exist in space it should not be too surprising to find molecules also. The first evidence of molecular species was found in 1937-1939 when the three diatomic species CN, CH and CH^{+} were discovered by detecting their ultraviolet emission spectra. Little else was discovered until the mid-sixties, because of the problems of interference in the detection of molecular radiation. For example, detection of infrared radiation is restricted by the heavy absorption of infrared by H_2O and CO_2 in our atmosphere. However, microwave radiation, the energy of which activates rotational energy levels of a molecule, is not so affected and the detection of it from interstellar molecules is now possible. A list of some of the molecules that have been detected is given in Table 1.4.

The molecules form from atoms and other molecular species on the surface of interstellar dust, such as particles of Fe and SiO_2. Two observations may be made concerning the type of compounds observed: (a) the large number of hydrogen containing species probably reflects the high abundance of hydrogen in the universe, and (b) many of the species have multiple bonds, hence strong

TABLE 1.4   Some Molecules Observed in Interstellar Space
(Abundance given by $(x) = 10^x$)

Diatomic		Tetraatomic		Hexaatomic	
H_2	(0)	NH_3	(-6)	CH_3OH	(-7)
OH	(-7)	H_2CO	(-8)	NH_2CHO	(-10)
CH	(-8)	H_2CS	(-10)	**Heptaatomic**	
CO	(-4)	HNCO	(-9)	CH_3CHO	(-10)
CN	(-8)	**Pentaatomic**		CH_3NH_2	(-10)
CS	(-7)	CH_2NH	(-10)	$H_2C \doteq CHCN$	(-10)
NS	(-8)	HCOOH	(-10)	$CH_3C \equiv CN$	(-9)
SO	(-7)	$HC \equiv CCN$	(-8)	$HC \equiv C-C \equiv CCN$	(-10)
SiO	(-7)			**Octaatomic**	
SiS	(-7)			$CH_3C \equiv CCN$	(-10)
Triatomic				$HCOOCH_3$	(-10)
HCO	(-8)	C_2H	(-7)	**Nonaatomic**	
HCO^+	(-7)	H_2S	(-8)	CH_3CH_2OH	(-10)
HCN	(-6)	SO_2	(-7)	CH_3COCH_3	(-10)
HNC	(-6)	OCS	(-8)		
N_2H^+	(-7)				

Source: Huntress, W.T., *Chem. Soc. Revs.*, 1977, 16, 295.

bonds between atoms may be an important factor. The "absence" of species such as O_2 and N_2, in which the bonding is strong, may be because they have not yet been detected, being molecules of high molecular symmetry and with no dipole moment. The reactivity of NO may prevent its accumulation.

The existence of species such as CH_2=NH and $HCONH_2$ in interstellar space, (precursors to amino acids?), has led to the suggestion, that before too long amino acids will be discovered.

THE FORMATION AND STRUCTURE OF THE EARTH

We will now consider the nature and formation, and the composition of the earth. The discussion will be directed at the distribution of the elements and chemical compounds in the earth.

Formation of the Solar System

One explanation of the formation of the solar system, is that cosmic dust clouds and interstellar atoms were attracted to each other by gravitational forces. This process, which probably began around 6×10^9 years ago, produced a massive ball containing over 99.8% of the total mass, the

remaining material being in a disc rotating around it. As the proto-sun undergoes gravitational collapse the heat generated raises the temperature to $1-3 \times 10^7$K sufficient to allow hydrogen burning to occur, while the disc must have split into zones within which local accretion occurred giving rise to the planets. Heating in the planets was much less owing to the small mass.

Structure of the Earth

The earth has three separate areas, the atmosphere, the hydrosphere and the solid material, a fourth category spanning all three, called the biosphere can also be considered. The atmosphere is principally gaseous, the main constituents being dinitrogen and dioxygen, the hydrosphere is liquid water containing dissolved and particulate material. The solid earth is the most complex of the three, and is heterogeneous in composition (Table 1.5).

TABLE 1.5   Structure of the Earth

Zone	Major Chemical Constituents	State of Matter
Atmosphere	N_2, O_2, H_2O, CO_2, noble gases, particles.	Gas, liquid, solid.
Hydrosphere	H_2O (liquid), ice, snow, dissolved minerals, Na^+, Cl^-, Mg^{2+}, Br^-, etc., particles.	Liquid (solution) suspended solids.
Biosphere	Organic material, mineral skeleton, H_2O, trace elements.	Solid, liquid, colloidal, gas.
Crust	Silicate rocks, oxide and sulphide minerals.	Solid (heterogenous) (intermixed with water and air).
Mantle	Silicate minerals, particularly olivine and pyroxene, (iron and magnesium silicates).	Solid
Core	Iron-nickel alloy.	Liquid (top) Solid (bottom)

Source: Mason, B., Principles of Geochemistry, 3rd Ed., J. Wiley and Sons, Inc., N.Y., 1966.

The solid earth is made up of a core, mantle and crust (Fig. 1.6). The inner core is probably solid and the outer core liquid, and composed mainly of iron and nickel. The mantle is principally composed of dense silicates of iron and magnesium. The crust, or the lithosphere, which is less than 0.4% of the mass of the earth, is the part we are most familiar with. Its composition is complex, being made up mainly of silicates (58.7% of the crust corresponds to the impirical formulation SiO_2). The other major component (15%) corresponds to the impirical formulation Al_2O_3.
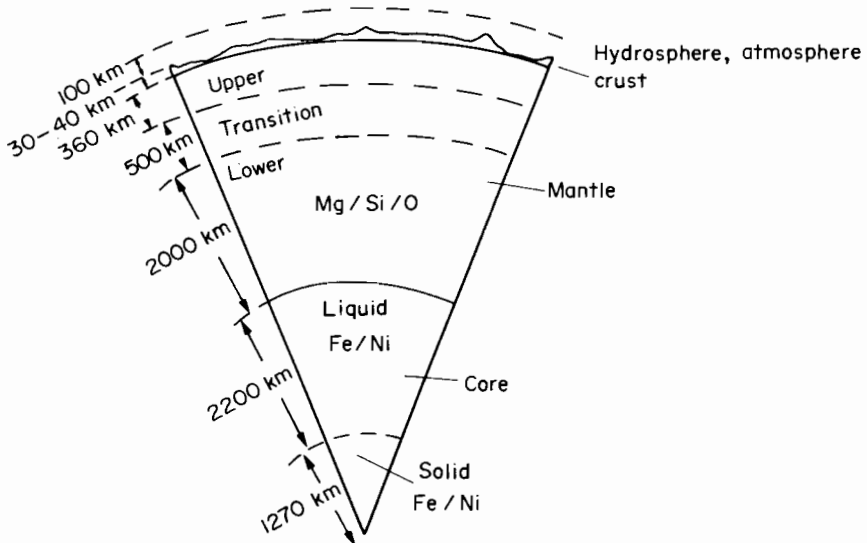
Fig. 1.6.   The structure of the earth.

Comparison of the elemental abundances of the three major divisions of the earth, the biosphere and the crust (Fig. 1.7) and the data given in Table 1.2 indicates that in the formation of the earth some fractionation of the elements has occurred.

Formation of the Earth

We will now consider some of the broad chemical processes that have led to the formation of the earth as we know it today.

The solid earth.   In one model it is proposed that during accretion of the earth, the silicates and iron condensed, and subsequent degassing and melting produced the internal structure and composition of the earth, the crust and also the atmosphere and the hydrosphere.   In a second model the early stages of the earth's formation are likened to the phases occurring in a blast furnace, in which molten iron sinks to the bottom while the less dense, and also less volatile, silicates float on top.

When the disc of material, which gave rise to the earth started to condense the temperature was probably around 2000K, so that all the material, would be present in an atomic and gaseous state.   On cooling the least volatile stable combinations of the elements in the disc would condense out.   It is believed that the first materials were calcium aluminium silicates, followed by the more volatile iron-nickel system, and then followed by magnesium silicates (Table 1.6).   Like a blast furnace, the materials would separate according to their densities producing the major components of the core, mantle and crust.   On further cooling the more volatile materials, such as
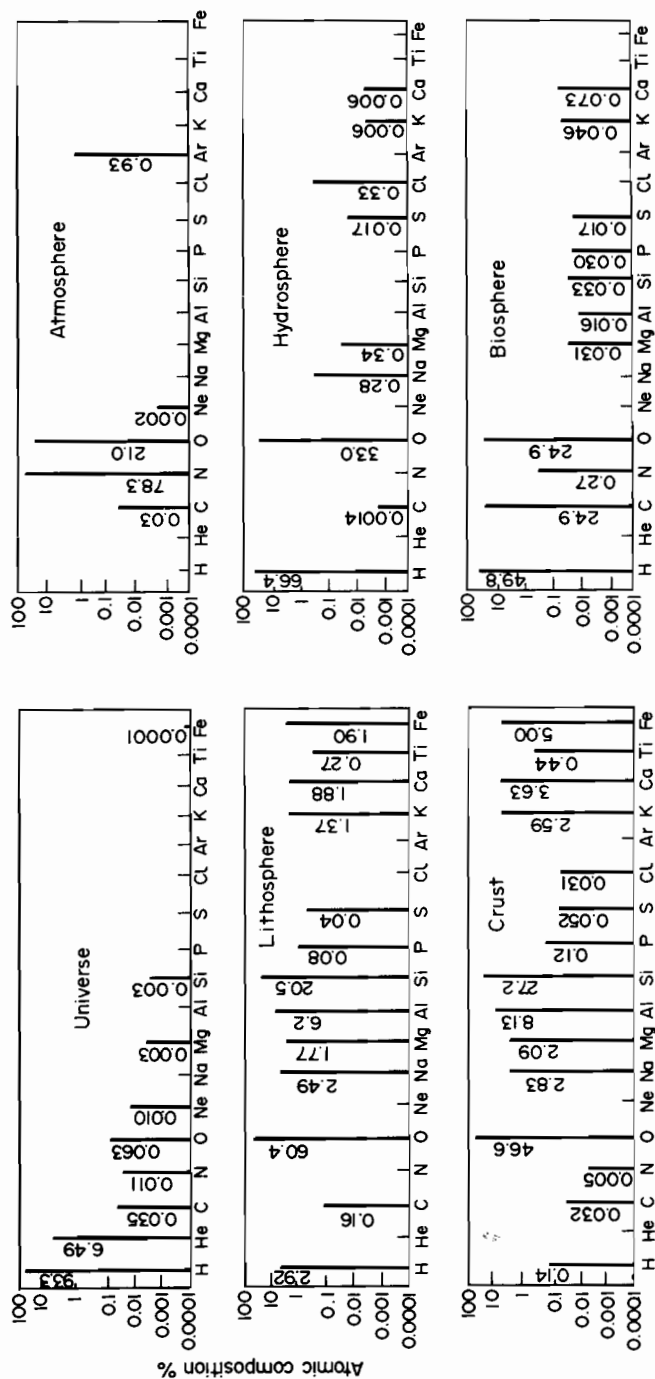
Fig. 1.7. Elemental abundances of the Universe, solid earth, atmosphere, hydrosphere and biosphere.

TABLE 1.6   Condensation Temperatures

Phase	Species	Condensation Temperature (K)	Phase	Species	Condensation Temperature (K)
Corundum	Al_2O_3	1758	Forsterite	Mg_2SiO_4	1444
Perovskite	$CaTiO_3$	1647	Anorthite	$CaAl_2Si_2O_8$	1362
Melilite	$Ca_2Al_2SiO_7$	1625	Enstatite	$MgSiO_3$	1349
Spinel	$MgAl_2O_4$	1515	Rutile	TiO_2	1125
Metallic iron	$Fe+12.5\ mol\%\ Ni$	1473	Magnetite	Fe_3O_4	405
Diopside	$CaMgSi_2O_6$	1450			

Source: Turekian,K.K.,Chemistry of the Earth,Holt,Rinehart,Winston, N.Y. 1972

lead, bismuth, thallium, hydrated silicates, iron compounds (sulphides and oxides) and water would condense, leaving gaseous materials in the atmosphere. These final stages of condensation would add only to the crust, but since the oldest rocks are around 3.5 billion years old, and since the earth was formed around 4.6 billion years ago it seems that during the first billion years a considerable reprocessing of the crust must have occurred. The reprocessing did not however, bring the core and crust materials together as the core materials remain in a reduced state, while crust materials are in an oxidised state.

The chemical and physical properties which influenced the chemical processes during the earth's formation were; reduction and oxidation, ionic size, bond strength, pressure, temperature, phase separation, elemental abundances and gravitational and magnetic fields. The earth's formation can be considered in three stages. The first, the primary differentiation of the elements, was influenced by the reduction potentials of the elements relative to iron. The secondary differentiation was influenced by the relative size of metal ions, the bonding tendencies of the elements, fractional crystallisation from the magma and the densities of compounds. The third process, still operating today, is the interaction of environmental factors with the earth's crust.

Primary differentiation of the elements. As insufficient oxygen and sulphur are available to oxidise all elements, and since iron is so abundant the primary distribution of the elements was influenced by the potential for the reduction $M^{n+} + ne \rightarrow M$ to proceed compared with the reaction $Fe^{2+} + 2e \rightarrow Fe$. Elements whose reduction potentials are more positive than iron are called *siderophiles* (Table 1.7).

As molten iron was pulled towards the centre of the earth it reduced sidero-phile metal ions to the metal which alloyed with the iron and were carried into the core. Nickel is a good example of this;

$$Fe - 2e \rightarrow Fe^{2+} \qquad -E^O = +0.429V, \qquad (1.42)$$

$$Ni^{2+} + 2e \rightarrow Ni \qquad E^O = -0.250V \qquad (1.43)$$

i.e. $\quad Fe + Ni^{2+} \rightarrow Fe^{2+} + Ni \qquad E = +0.179V, \qquad (1.44)$

TABLE 1.7 Reduction Potentials

Element	Reduction Potential		Element	Reduction Potential
Lithophiles			Chalcophiles	
Na^+/Na	−2.71		Zn^{2+}/Zn	−0.76
Ca^{2+}/Ca	−2.87		Pb^{2+}/Pb	−0.13
Al^{3+}/Al	−1.66		Cu^{2+}/Cu	+0.34
Cr^{3+}/Cr	−0.77		Ag^+/Ag	+0.80
		Siderophiles		
Fe^{2+}/Fe	−0.43		Pd^{2+}/Pd	+0.99
Ni^{2+}/Ni	−0.25		Au^+/Au	+1.69
Sn^{2+}/Sn	−0.14			

As a consequence siderophiles tend to be of low abundance in the earth's crust.

The majority of the remaining elements, most of which have more negative reduction potentials than iron, are classified according to their bonding potential with oxygen or sulphur (lithophiles or chalcophiles respectively) (Table 1.8).

TABLE 1.8 Geochemical Classification of the Elements[a]

```
                                                                        He

Li  Be                                       B   C │ N │ O │ F │ Ne
                               Lithophile

Na  Mg    Lithophile                         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      Ru  Rh  Pd │ Ag  Cd  In  Sn  Sb  Te│ I │ Xe

Cs  Ba  Ln  Hf  Ta │ W   Re  Os  Ir  Pt │ Au  Hg  Tl  Pb  Bi        │ Xe
                                                                    Atmophile
        Th          │      Siderophile    │      Chalcophile      │
        U
```

[a] Elements can display more than one type of behaviour

Lithophiles have more negative reduction potentials than chalcophiles (Table 1.7), their ions are relatively small in size and not readily polarised, whereas chalcophiles have larger ions more readily polarisable and therefore associate with the polarisable sulphide ion. This broad classification of the elements is recognizable in the dominant chemical form of the element that exists in nature (Table 1.1).

Secondary differentiation of the elements. As the magma cooled a variety of
minerals crystallised depending on their melting point and abundance of the
constituent elements. The number of phases produced may be predicted with
use of the phase rule $P + F = C + 2$, provided the system is at equilibrium.
For two degrees of freedom (pressure and temperature) $P = C$, and for six
components (e.g. O, Si, Al, Fe, Mg and Na) there is the possibility of forming
up to six phases, i.e. six different chemical species (minerals). More than
99% of igneous rocks are composed of seven principal minerals (the silica
minerals, feldspars, feldspathoids, olivine, pyroxenes, amphiboles and micas).

Fractional separation of minerals and therefore the elements occurs as the
magma cools producing in some cases ore bodies (see Chapter 3). The relative
temperatures at which minerals crystallise will depend in part on their
lattice energies which is related to the size of the ions and their charge,
because of the form of the lattice energy equation;

$$\Delta H_L = - \frac{NMZ^+Z^-e^2}{4\,\varepsilon_0(r_+ + r_-)} .\tag{1.45}$$

Minerals with small highly charged ions will have high lattice energies and
may crystallise first. For example, of the two feldspars $CaAl_2Si_2O_8$ (anorth-
ite) and $NaAlSi_3O_8$ (albite), anorthite has the higher melting point, and is
more dense. This is because of the greater lattice energy of anorthite and
because Ca^{2+} (At. wt. 40) is heavier than Na^+ (At. wt. 23). One finds that,
of the two minerals, anorthite lies deeper in the crust.

The less abundant elements often occur as a constituent of an abundant
minerals because of isomorphous replacement, that is, where one ion replaces
another in a crystal lattice. For this to happen the radii of the atoms or
ions must lie within 10 to 20% of each other (Table 1.9). Therefore, a

TABLE 1.9   Ionic Radii

Range (pm)	Ions (radii, pm)
10 - 29	$B^{3+}(20)$.
30 - 49	$Be^{2+}(31)$.
50 - 69	$Al^{3+}(53)$, $Ga^{3+}(62)$, $Fe^{3+}(60)$, $Ti^{4+}(61)$, $Mn^{3+}(62)$, $Cr^{3+}(64)$, $Mg^{2+}(65)$, $V^{3+}(66)$, $Li^+(68)$, $Sn^{4+}(69)$, $Nb^{4+}(69)$.
70 - 89	$Ni^{2+}(70)$, $Co^{2+}(72)$, $Cu^{2+}(73)$, $Fe^{2+}(75)$, $Zn^{2+}(75)$, $Ti^{3+}(79)$, $Mn^{2+}(80)$, $Hf^{4+}(83)$, $Zr^{4+}(84)$.
90 -109	$Na^+(98)$, $Eu^{2+}(98)$, $Ca^{2+}(99)$, $U^{4+}(100)$, $La^{3+}(105)$, $Th^{4+}(106)$.
110-139	$Sr^{2+}(112)$, $Pb^{2+}(118)$, $K^+(133)$, $Ba^{2+}(135)$.
140-170	$Ra^{2+}(143)$, $Rb^+(147)$, $Tl^+(147)$, $Cs^+(167)$.

range of feldspars with compositions lying between the extremes $NaAlSi_3O_8$
and $CaAl_2Si_2O_8$ exist, because the radius of the Na^+ and Ca^{2+} ions are similar
(note also the change in the Al:Si ratio but that the number of Al + Si atoms

remains constant). Those elements, whose ionic radius is similar to the ionic
radius of one of the abundant elements (Mg, Fe, Ca, Al, Si, Na, K) occur as
constituents in the common minerals. For example Ba^{2+} occurs in the potassium
feldspars because Ba^{2+} and K^+ have similar ionic radii (135 and 133 pm
respectively). Other common ion pairs that undergo isomorphous replacement
are: K^+ (133 pm), Rb^+(147 pm); Ga^{3+}(62 pm), Al^{3+}(53 pm); Si^{4+}(42 pm),
Ge^{4+} (47 pm). If the ionic radii of the less abundant elements are much
greater or less than the common elements they are not involved in isomorphous
replacement and tend to concentrate in the lowest melting fraction of the
magma.

The formation of an ore body may be explained in terms of a solid-liquid
freezing point or eutectic diagram (Fig. 1.8). If the magma containing
two components A and B has a composition designated by point Y, then when
the temperature reaches T, the solid A will crystallise out and will
continue to do so until the composition reaches point Z.
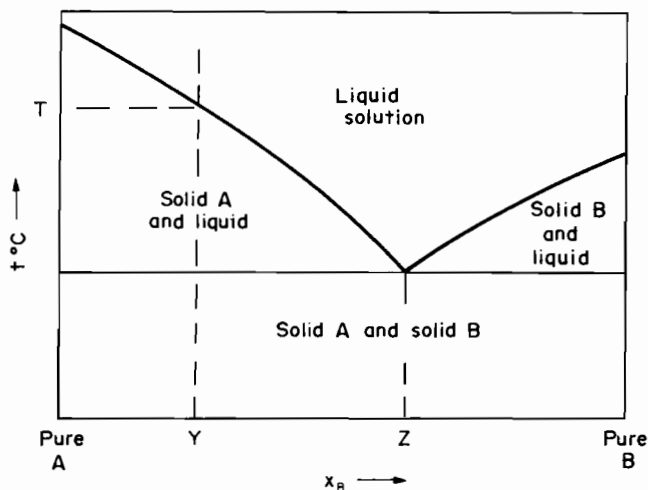
Fig. 1.8. Two component eutectic diagram.

The solid A that crystallised will settle out as a deposit at the bottom of
the solution (if it is more dense) and when the remaining solution finally
solidifies it will be rich in component B especially if the eutectic point
lies on the right of the diagram. A large platinum deposit in Southern
Africa was formed in this way.

Continuing changes. The earth's crust is undergoing continual change which,
over the centuries, has produced much of the world's mineral deposits (see
Chapter 3). The principal influence is weathering which is the interaction
of the crust with water and air at different temperatures and pressures.
Physical changes are produced by wide temperature variations, and by pressure
and force. Chemical weathering is achieved with water at different pH's
and temperatures and by the action of O_2 and CO_2.

Bauxite - Al_2O_3 rich deposits - have been produced by chemical weathering of aluminium rich rocks. The soluble ions, Na^+, K^+, Ca^{2+}, have been leached out by rainwater leaving kaolinite $(Al_4Si_4O_{10}(OH)_8)$, and then the less soluble silica is slowly dissolved at a pH 5 to 9 leaving enriched Al_2O_3, which may be contaminated with insoluble Fe_2O_3. The need for large quantities of water is obvious, and explains why many bauxite deposits occur in the wet tropics, or areas that have been wet and tropical. A more detailed discussion of weathering is given in Chapter 2.

Atmosphere and Hydrosphere. Comparison of the elemental abundances in the earth with those of the universe is measured by a *deficiency ratio* (= log[cosmic abundance]/[earth's abundance]) relative to silicon. For the elements occurring predominantly in the solid earth the relative abundances are similar (Table 1.10). The lighter elements (H, C, N), and the noble gases (He, Ne, Ar, Xe, Kr) are less abundant on the earth.

TABLE 1.10   Deficiency Ratios[a]

Element	Atomic Number	Deficiency Ratio	Element	Atomic Number	Deficiency Ratio
H	1	6.6	Al	13	0
He	2	14	Si	14	0
C	6	4.0	P	15	0.1
N	7	5.9	S	16	0.5
O	8	0.8	Cl	17	0.7
F	9	1.0	Ar	18	6.3
Ne	10	10.6	Fe	26	-0.6
Na	11	0	Kr	36	7.2
Mg	12	0	Xe	54	6.5

[a] $\log_{10}$ [Cosmic abundance/Earth abundance]

relative to $\log_{10} [Si_{Cosmic}/Si_{Earth}] = 0$

Source: Mason, B., Principles of Geochemistry, 3rd Ed., J. Wiley and Sons, Inc., N.Y., 1966.

Two processes were probably a factor in the formation of the atmosphere. A degassing of the solid material, which still occurs in the activity of volcanoes, geysers and fumaroles. The primitive atmosphere of the earth (H_2, He, N_2, H_2O, CO_2, CO, NH_3, CH_4) altered as the vertical velocities of the materials were sufficient to allow them to escape from the gravitational pull of the earth. At the temperatures of the earth's atmosphere today, H_2 and He can still escape; whereas in the days of the earth's formation, when temperatures were higher, the other gases would also have escaped. The moon has no atmosphere because of its smaller mass, so all gaseous substances escape.

The predominance of N_2 and O_2 in our atmosphere, and H_2O in the hydrosphere arises from their chemical properties. As the earth cooled dinitrogen (N_2) could not escape and it would concentrate in the atmosphere because of its low reactivity. In the case of O_2, which is reactive, its presence in the atmosphere, where it did not occur initially, is probably a result of photochemical decomposition of water;

GE - B

$$2H_2O \xrightarrow[\text{radiation}]{\text{UV}} 2H_2 + O_2 \qquad\qquad (1.46)$$

(note: H_2 will escape from the atmosphere), and a product of biochemical photosynthesis.

The high deficiency ratio of the heavy noble gases, Ar, Kr and Xe, is surprising. The elements are unreactive and gaseous, and would naturally be expected in the atmosphere. If the earth, initially, had no atmosphere then it would arise from degassing of the solid earth. Argon would also form from the decay of radioactive ^{40}K.

The hydrosphere formed as the earth cooled and the water condensed. In the early stages the water would quickly evaporate, and while hot would readily dissolve soluble ions producing the mineral content of the oceans.

Determining the Age of the Earth

It has been an interest of man to determine when events happened; fortunately when the earth was forming a natural clock, the decay of radioactive nuclei, produced as described earlier, was set into action.

The number of radioactive nuclei that decay within a time interval dt is proportional to the number of nuclei present as expressed by the decay law;

$$\frac{dN}{dt} = -\lambda N \qquad\qquad (1.47)$$

where N is the number of nuclei present during the time interval dt, dN is the number of nuclei that decayed in the time, and λ is the decay constant. The negative sign indicates that N is decreasing. Integration of the equation over the time interval t=o to t=t gives;

$$\ln\left(\frac{N}{N_o}\right) = -\lambda t, \qquad\qquad (1.48)$$

where N_o is the number of nuclei at t=o and N is the number at time t. The equation can be rewritten;

$$N = N_o e^{-\lambda t}. \qquad\qquad (1.49)$$

The half-life of radioactive nuclei, $t_{\frac{1}{2}}$, is the time taken for half of the nuclei to decay, i.e. when $N = \frac{1}{2}N_o$;

hence $\qquad \ln\left(\frac{\frac{1}{2}N_o}{N_o}\right) = -\lambda t_{\frac{1}{2}}, \qquad\qquad (1.50)$

which gives;

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda}. \qquad\qquad (1.51)$$

All radioisotopes have their own distinctive decay constant λ and $t_{\frac{1}{2}}$ values, and it is these properties which allow radioisotopes to be used for dating purposes.

Equation (1.49) may be rearranged as follows;

$$N_o = N e^{\lambda t}, \qquad\qquad (1.52)$$

FORMATION OF ORES

We will consider in more detail some of the ways ore bodies have formed in the earth's crust.

Occurrence of the Elements in Nature

A broad classification of the principal ore types that occur in nature, for each element, is given in Table 1.1. It must be noted that the boundaries are not sharp divisions, and the classification given is restricted to principal ore types. The difference between the ores for Group I and II elements relates to their ionic charges M^+ and M^{2+} respectively. The divalent alkaline earth metal ions form salts with high lattice energies and low solubility, while salts of the monovalent alkali metal ions have lower lattice energies and are more soluble. The metals that mainly occur as oxides tend to have compact ions, with few outer d-electrons and are not readily polarizable. They associate with the compact O^{2-} ion. On the other hand metals that mainly occur as sulphides are more polarizable, especially the heavier members, and unite with the polarizable S^{2-} ion. The oxide ion is described as a hard base and the sulphide ion as a soft base, each associating with hard and soft acids (metals) respectively. The platinum group metals that may occur free in nature, have oxidation states with favourable reduction potentials. A list of the principal ores for some abundant and rare elements are listed in Table 3.13.

Ore Formation

The geo-chemical processes involved in ore formation are diverse; different chemical and physical processes have lead to an enrichment of elements in certain areas. The processes fall into four principal catagories; cooling, heating, weathering and transport, and oxidation and reduction.

Cooling processes: *Magmatic concentration*. Materials crystallizing from the magma at different temperatures may settle out in bands, for example chromite deposits. At a later stage in the cooling process residual molten magma, may inject into rock crevices. The magnetite deposits at Kiruna, Sweden, were formed in this way.

Sublimation. Sublimation is the phase change from solid to gas, without passing through a liquid phase. The reverse process (gas to solid) is the way that some sulphur deposits were formed, for example in Sicily.

Hydrothermal processes. Hydrothermal fluid is heated, or superheated, aqueous solutions under pressure, which derive from the magma and which ascend through the crust. The many materials that the fluid contains may either re-deposit in rock cavities or substitute for materials already in rocks. The crystallization or precipitation of materials from solution occurs because of reduced solubility as the temperature and pressure drop during the ascent. Examples of cavity filling deposits are gold quartz at Bendigo, Australia, zinc and lead deposits in various areas and copper at Lake Superior. Reactions may also occur between the aqueous solutions and rocks, with substitution or replacement of a rock, such as limestone, with hydrothermal materials. Porphyrycopper deposits in a number of areas, sulphide ores in Spain, gold quartz in the South Island, New Zealand, are examples of such deposits. Such deposits can be quite massive.

TABLE 3.13   Principal Ores of the Technologically
Important Metals

The Abundant Metals

Principal Ores	Metal	Principal Ores
Magnetite, Fe_3O_4; hematite, Fe_2O_3; goethite, $HFeO_2$ siderite, $FeCO_3$	Titanium	Ilmenite, $FeTiO_3$; rutile, TiO_2
	Manganese	Pyrolusite, MnO_2; psilomelane, $BaMn_9O_{18}2H_2O$
Gibbsite, H_3AlO_3; diaspore, $HAlO_2$; boehmite, $HAlO_2$;		cryptomelane, KMn_8O_{16}; rhodocrosite, $MnCO_3$
kaolinite, $Al_4Si_4O_{10}(OH)_8$	Magnesium	Magnesite, $MgCO_3$; dolomite, $CaMg(CO_3)_2$

The Scarce Metals

forming sulfide minerals (Chalcopile)

Principal Ores	Metal	Principle Ores
Covellite, CuS, chalcocite, Cu_2S; digenite, Cu_9S_5	Cadmium	Substitution for Zn in sphalerite
chalcopyrite, $CuFeS_2$; bornite, Cu_5FeS_4; tetrahedrite, $Cu_{12}Sb_4S_{13}$	Cobalt	Linnaeite, Co_3S_4; substitution for Fe in pyrite, FeS_2;
Sphalerite, ZnS	Mercury	Cinnabar, HgS; metacinnabar, HgS
Galena, PbS	Silver	Acanthite, Ag_2S; substitution for Cu and
Pentlandite $(NiFe)_9S_8$; garnierite, $H_4Ni_3Si_2O_9$		Pb in their common ore minerals
Stibnite, Sb_2S_3	Bismuth	Bismuthinite, Bi_2S_3
Molybdenite, MoS_2		
Arsenopyrite, $FeAsS$; orpiment, As_2S_3; realgar, AsS		

found in the native form (Sideropile)

Principle Ores	Metal	Principle Ores
Calaverite, $AuTe_2$; krennerite, $(Au,Ag)Te_2$; sylvanite, $AuAgTe_4$; petzite, $AuAg_3Te_2$	Palladium	Arsenopalladinite, Pd_3As; michenerite, $PdBi_2$; froodite, $PdBi_2$
	Rhodium	—
Sperrylite, $PtAs_2$; braggite, PtS_2; cooperite, PtS	Iridium	—
	Ruthenium	Laurite, RuS_2
	Osmium	—

TABLE 3.13   Principal Ores of the Technologically
              Important Metals

The Scarce Metals

Commonly associated with oxygen (Lithophile)

Metal	Principal Ores	Metal	Principal Ores
Chromium	Chromite, Fe_2CrO_4	Niobium and Tantalum	Columbite, $FeNb_2O_6$; pyrochlore, $NaCaNb_2O_6F$; tantalite, $FeTa_2O_6$
Tin	Cassiterite, SnO_2		
Tungsten	Wolframite, $FeWO_4$; scheelite, $CaWO_4$	Thorium	Monazite, a rare-earth phosphate containing thorium by atomic substitution
Uranium	Uraninite(pitchblende), UO_2; carnotite, $K_2(UO_2)_2(VO_4)_2.3H_2O$; substituting for Fe in magnetite, Fe_3O_4	Beryllium	Beryl, $Be_3Al_2(SiO_3)_6$

Source: Skinner, B.J., *Earth Resources* (2nd Ed.) Prentice-Hall,New Jersey(19/‹

Heating processes: *Evaporation*. Ores formed by evaporation of seawater are called evaporites. They consist of the more soluble minerals such as sodium chloride, gypsum, $CaSO_4H_2O$, and Chili nitrates.

Metamorphism. Deposits of materials such as asbestos, talc and graphite were formed as metamorphic deposits through the action of heat and pressure on rock materials.

Weathering and transport. *Sedimentation*. Weathered material in solution or in suspension can be deposited in sufficient concentration to become an ore body. Iron deposits have occurred in this way, such as the detrital magnetite iron-sands of New Zealand.

Mechanical concentration. Minerals resistant to weathering can be moved around, principally by water, and concentrate in specific regions - to give placer deposits. Alluvial gold is an example of such an ore, as are deposits of ilmenite, $FeTiO_3$, and cassiterite, SnO_2.

Residual concentration. Material left behind after weathering, and resist-ant to further changes can become an ore. Examples are bauxite deposits, and iron deposits such as those at Lake Superior.

Oxidation and Reduction processes: The importance of oxidation and reduction in environmental chemistry has been mentioned in Chapter 2. We will now discuss two examples leading to ore formation.

Supergene enrichment. Surface weathering followed by the leaching of materials into the crust, and subsequent ore enrichment is a feature of the formation of certain copper ore bodies, for example in Chile and Arizona (U.S.A.).

Copper(II) ions released from copper minerals near the earth's surface by hydrolytic weathering (especially in acid conditions), can move into the crust through leaching. If the Cu^{2+} ions come into contact with sulphide minerals of other metals the sulphides Cu_2S and CuS will tend to form due t their low solubility ($K_{sp} = 1.6 \times 10^{-48}$ and 8.7×10^{-36} respectively).

$$Cu^{2+}_{(soln)} + ZnS_{(s)} \rightarrow CuS_{(s)} + Zn^{2+}_{(soln)}. \tag{3.1}$$
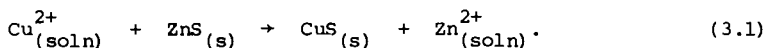
Reduction may also occur;

i.e. $$Cu^{2+} + e \rightarrow Cu^{+}. \tag{3.2}$$

$$S^{2-} + 4H_2O - 8e \rightarrow SO_4^{2-} + 8H^{+}, \tag{3.3}$$

$$2Cu^{+}_{(soln)} + S^{2-}_{(soln)} \rightleftharpoons Cu_2S_{(s)} \tag{3.4}$$

$$ZnS_{(s)} \rightleftharpoons Zn^{2+}_{(soln)} + S^{2-}_{(soln)}, \tag{3.5}$$

the overall reaction being;

$$8Cu^{2+}_{(soln)} + 5ZnS_{(s)} + 4H_2O \rightarrow 4Cu_2S_{(s)} + 5Zn^{2+}_{(soln)} + SO_4^{2-} + 8H^{+}. \tag{3.6}$$
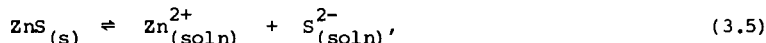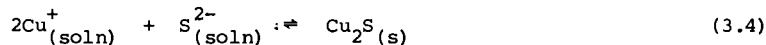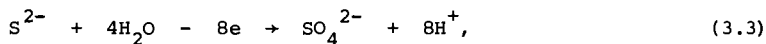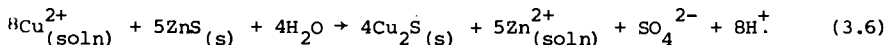
The zinc ions will be transported away.

Microbiological processes. Micro-organisms can contribute to ore body formation through their involvement in accumulating particular elements, modifying environmental conditions, causing oxidations or reductions by metabolic processes and producing organic material. Bacteria are either autotrophic, that is not dependent on organic material for their carbon, or heterotrophic, that is dependent on organic material. Autotrophic, bacteria are involved in mineralization reactions.

Sulphate reducing bacteria, such as *desulphovibrio desulphuricans*, are instrumental in producing sulphide minerals of metals such as Cu, Pb, Zn and Ag. The reduction of sulphate can be represented by the equation;

$$SO_4^{2-} + 2(CH_2O) + 2H^{+} \xrightarrow{bacteria} H_2S + 2CO_2 + 2H_2O, \tag{3.7}$$
$$\text{carbohydrate}$$
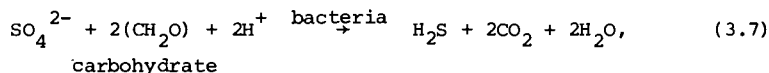
and this is followed by precipitation of an insoluble sulphide, e.g.,

$$Pb^{2+} + H_2S \rightarrow PbS + 2H^{+}. \tag{3.8}$$

Deposits of elemental sulphur (in Sicily), may have been formed by bacterial reduction of SO_4^{2-} to sulphide, similar to above, followed by oxidation to sulphur by bacteria such as *thiobacillus thiooxidans*;

$$2H_2S + O_2 \xrightarrow{bacteria} 2S + 2H_2O. \tag{3.9}$$
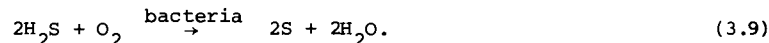
Bacteria that metabolise, Fe and Mn, are important in mineralization of these metals. Bacteria, such as *Ferrobacillus* and *Gallionella*, catalyse the oxidation of Fe(II) to Fe(III), the energy released is used by the bacteria in their metabolism. The reaction;

$$4FeCO_3 + O_2 + 6H_2O \xrightarrow{bacteria} 4Fe(OH)_3 + 4CO_2 \tag{3.10}$$
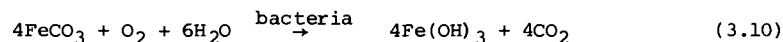
is an example. Production of 1 gram of cell carbon (from the CO_2 at 2% efficiency) requires 220 g of Fe(II). Therefore areas where iron oxidising bacteria abound, may be associated with large deposits of $Fe(OH)_3$. It is likely that bacteria are also involved in the formation of manganese nodules on the sea bed.

Trace metal concentration. The distribution of trace metals in the solid
magma depend on a number of factors, including the relative size of ions,
and stabilization in the solid compared with the melt. Trace metal
fractionation has been studied on the Skaergaard intrusion in Greenland,
and from the data a quantity;

$$\log R \;=\; \frac{[M^{n+}] \text{ after } X\% \text{ solidification}}{[M^{n+}] \text{ before solidification}} \qquad (3.11)$$

may be determined. A negative value of log R indicates concentration of the
metal ion in the solid, while a positive value represents concentration in
the residual melt. For the transition metals the distribution order in the
solid (-log R) is;

$$Ni^{2+} > Co^{2+} > Mn^{2+} > Fe^{2+} > Cu^{2+} \qquad (M^{2+} \text{ ions}) \qquad (3.12)$$

$$Cr^{3+} > V^{3+} > Sc^{3+} > Fe^{3+} \qquad (M^{3+} \text{ ions}) \qquad (3.13)$$
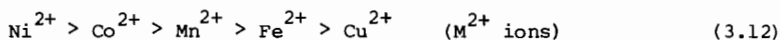
The trends correlate with the ligand field stabilization energies for the
metal ions in a weak octahedral field. The ligand field stabilization
energy (LFSE) is given by the equation;

$$LFSE \;=\; x(-\tfrac{2}{5}\Delta) \;+\; y(+\tfrac{3}{5}\Delta) \qquad (3.14)$$

where x and y are the number of electrons in the t_{2g} and e_g orbitals
respectively, and Δ is the ligand field splitting energy.

The correlation suggests that LFSE has some influence on the distribution.
It is, however, surprising that this energy, which is only 10% of the total
energy of an ion in a crystal lattice, has such a pronounced effect. It may
be because the LFSE is stereospecific rather than spherical in its influence
A similar correlation occurs between the distribution of the transition
metals and the ligand field stabilization achieved on crystallization.

$$M^{n+}_{(melt)} \;\rightarrow\; M^{n+}_{(crystal)} \qquad (3.15)$$

Stabilization is greater in the solid because the average coordination
number of a metal ion is higher in the solid than in the melt because of
reduced kinetic energy.

Ore Formation of Some Important Metals

We will now discuss briefly the formation of some ore deposits of the more
important metals.

Iron. The geochemistry of iron is dominated by oxidation and reduction and
the pH of the surrounding medium. Iron is immobilised in oxidising conditions
and in alkaline reducing conditions, but is mobilized in acidic reducing
conditions. Only in strong acid is Fe(III) mobilized.

The process which has produced most iron ore is the leaching of SiO_2 from
primary Precambrian banded-iron-formations, which were formed from marine
chemical precipitation. The Lake Superior deposits contain the four
minerals FeS_2, $FeCO_3$, $FeSiO_3$ and Fe_2O_3, which all exist within a narrow band

of E_h and pH values (Fig. 2.16). In wet tropical areas iron laterites (mainly goethite, $Fe_2O_3H_2O$) are found, their quality depends on the amount of aluminium in the original rocks and the amount of organic material which would preferentially stabilize Fe(II) and mobilise it. Hydrothermal iron ores, magnetite and hematite were formed by replacement of rocks such as limestone, e.g. Marmora, Canada. The Kiruna deposits in Sweden are probably magmatic in origin.

Aluminium. The principal, and widespread, source of aluminium is bauxite which is a general name for different mixtures of hydrated alumina: gibbsite, γ-Al_2O_3.$2H_2O$; boehmite, γ-Al_2O_3.H_2O and diaspore, α-Al_2O_3.H_2O. Bauxite is readily purified by the Bayer process except when the ore is mainly diaspore. As discussed before bauxite is the residual product of weathering in warm (>25^oC most of the time) humid climates.

Titanium. Titanium ores occur by two processes. Magmatic ores of ilmenite, $FeTiO_3$, appear as layers low down in the magma because of the mineral's high melting point and density (e.g. Allard Lake, Canada). The three principal minerals, rutile, TiO_2, ilmenite and sphene (or titanite), $CaTiSiO_5$, are all resistant to weathering and occur as placer deposits, again the high densities help in forming the deposits.

Copper. Copper is mainly associated with sulphur in its ore minerals, examples are chalcocite, Cu_2S, chalcopyrite, $CuFeS_2$ and bornite, Cu_5FeS_4. The majority of the world's copper ores are low grade hydrothermal deposits, mainly as $CuFeS_2$ and are called porphyry copper (cf. Chilian and Peruvian deposits). Sedimentary material is layered and may be associated with organic rich sediments called *Kupferschiefer*, that is red-bed copper deposits. Coordination of organic ligands to copper(II) may have been involved in formation of the ores. Central European deposits, and possibly the Zambian copper belt are examples of sedimentary ores. Supergene enrichment of copper ores has already been discussed. Finally native copper occurs in basic igneous rocks, as found in the Upper Michigan lava.

Nickel. Being a siderophile, nickel is associated with metallic iron, e.g. in meteorites. In ores nickel is associated mainly with sulphur, arsenic or in silicates. Early magmatic segregation produced ores containing the mineral pentlandite $(Fe,Ni)_9S_8$ (e.g. Sudbury, Canada). The other main ore source, found in the humid tropics, is due to the weathering of ultrabasic rocks (peridotites or serpentinites) which frees the Ni^{2+} ion. Because of its stability in aqueous solutions (in contrast to Fe^{2+} and Mn^{2+}) it can be transported long distances. Eventually as the pH rises sufficiently nickel is precipitated with hydrous silicates, e.g. garnierite $(Ni,Mg)_3Si_2O_5(OH)_4$ (in Cuba, New Caledonia and the Philippines).

Chromium. The principal chromium ore is chromite, $FeO.Cr_2O_3$, a member of the spinel group of structures $M^{2+}M^{3+}O_4$, i.e. $(Mg,Fe)O.(Al,Fe,Cr)_2O_3$, where the oxide ions are cubic close packed and half the octahedral cavities are filled with the trivalent cations. A range of compositions occur due to isomorphous replacement of cations, as the radii of the M^{3+} ions, Al^{3+} 53 pm, Cr^{3+} 64pm and Fe^{3+} 60 pm all lie within 20% of each other. Chromite ores occur as early magmatic crystallizations and as placer deposits, due to resistance to weathering of $FeO.Cr_2O_3$ and its high density.

Uranium. Pitchblende or uranite, UO_2, is the principal uranium ore. The oxide is insoluble and exists in granitic magmas. Weathering can lead to oxidation of the U(IV) to the stable U(VI) uranyl ion, UO_2^{2+}. This forms

soluble salts and allows uranium to be transported. Reduction of UO_2^{2+} in
the presence of organic material produces deposits of UO_2 in black carbon-
aceous rich shales as found in Sweden.

Zinc and Lead. The two metals have a similar geochemistry and very often
their ores occur together. The two principal minerals are sphalerite, ZnS,
and galena, PbS. Zinc has the same ionic radius size as Fe^{2+}(75 pm) and the
two ions often occur together. The larger Pb^{2+} ion (ionic radius 118 pm) can
replace K^+ ions (ionic radius 133pm) in materials such as potassium feldspar.
The richest zinc and lead ores are of hydrothermal origin, where limestone
has been replaced by the fluid which eventually produces crystalline minerals.
A good example of this is the ore body in the Mississippi Valley (U.S.A.).

                    EXTRACTION OF METALS

The first metals, or alloys, used by man were those which were, either
available as rich ores and could be readily obtained from the ore by heating
at a relatively low temperature, or metals which occurred free in nature.
Developments in extraction technology continues and new approaches are sought,
especially as richer finds are being worked out. In this section we will
consider some aspects of extraction of metals from their ores, including
some new techniques.

Extraction Processes for Metals

The primary reaction is reduction, as all metals in their ores are in an
oxidised state. Reduction can be considered as follows;

$$(3.16)$$
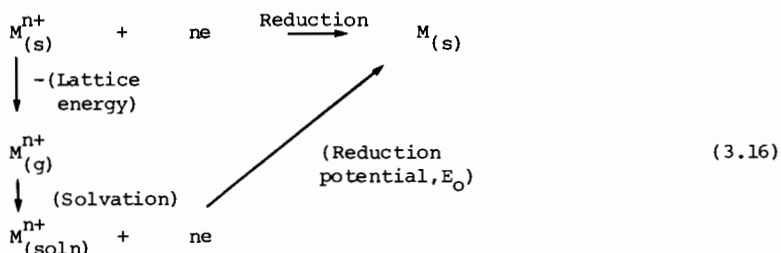
Since lattice and solvation energies are often of the same order of
magnitude, and opposite in sign, the value of E^O, the reduction potential,
may be used as a guide to the difficulty or ease of achieving the reduction.
The more negative the potential the harder it is to reduce the metal ion.
Reduction potentials for common metals are listed in Table 3.14, for metal
ions with $E^O < -1.66$ V, electrolytic reduction is necessary, while for less
negative potentials chemical reducing agents, such as Al, C and H_2, can be
used. Metal ions having positive reduction potentials may occur free in
nature (e.g. Cu) or they can be obtained by heating the ore without the need
to add a separate reducing agent:

$$2HgS_{(s)} + 3O_{2(g)} \rightarrow 2HgO_{(s)} + 2SO_{2(g)}, \qquad (3.17)$$

$$2HgO_{(s)} \xrightarrow{500^{\circ}C} 2Hg_{(l)} + O_{2(g)}, \qquad (3.18)$$
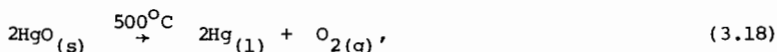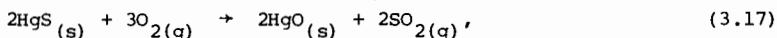
TABLE 3.14   Reduction Potential of Some Metal Ions

Element	E^O(n) *	Main Source	Extraction
K	-2.92 (+1)	*, KCl, KCl.MgCl$_2$	⎤
Na	-2.71 (+1)	NaCl	
Ca	-2.87 (+2)	CaSO$_4$, CaCO$_3$	Electrolysis of fused
		Ca$_3$(PO$_4$)$_2$	salts
		CaCl$_2$ (Solvay process) ⎦	
Mg	-2.36 (+2)	Mg salts	
Al	-1.66 (+3)	Al$_2$O$_3$	Electrolysis of Al$_2$O$_3$ in Na$_3$AlF$_6$
Mn	-1.18 (+2)	MnO$_2$ ⎤	Reduction with Al
Cr	-0.74 (+3)	FeO.Cr$_2$O$_3$ ⎦	(Thermite process)
Zn	-0.76 (+2)	ZnS ⎤	
Fe	-0.44 (+2)	Fe$_2$O$_3$, Fe$_3$O$_4$	Chemical reduction with
Co	-0.28 (+2)	CoAsS, Co$_3$S$_4$	carbon (or hydrogen).
Ni	-0.25 (+2)	Sulphides	First convert sulphides
Sn	-0.14 (+2)	SnO$_2$	to oxides by roasting.
Pb	-0.13 (+2)	PbS	
Cu	+0.34 (+2)	Metal, sulphide	
Hg	+0.85 (+2)	HgS ⎦	
Ag	+0.80 (+1)	Metal, Ag$_2$S, AgCl	Cyanide extraction
Au	+1.7 (+1)	Metal, tellurides	

* E^O for reaction, $M^{n+}_{(aq)}$ + ne → M (n given in parenthesis).

(i.e. $2Hg^{2+}_{(s)}$ + 4e → $2Hg_{(1)}$ reduction

$2O^{2-}$ - 4e → $O_{2(g)}$ oxidation.)

The information can also be represented diagramatically in terms of the
periodic table (Fig. 3.5). Comparison of Figs 3.5 and Table 1.1 indicates
correlations between the principal ore types for the elements and methods
of extraction.

Chemical Reducing Agents

Most metals are obtained from their oxides or oxy-anions directly, or after
conversion of the ore to an oxide. The reduction of an oxide, represented
by the equation;

$$yMO_{x(s)} + xA_{(s)} → yM_{(s)} + xAO_{y(g,1, or s)},$$ (3.19)
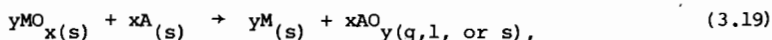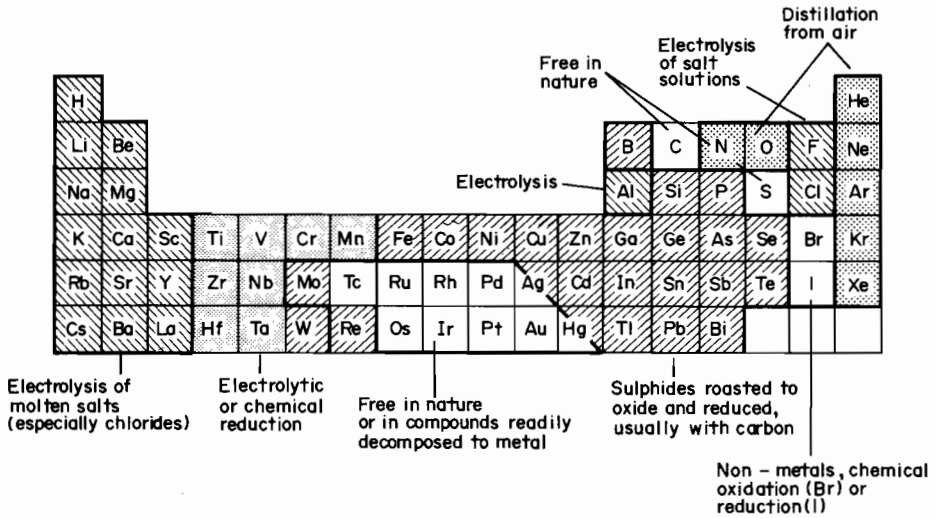
Fig. 3.5. A portrayal of the extraction of the elements
in terms of the periodic table.

proceeds if the overall free energy change is negative. The standard state
free energies of elements M and A are zero, hence the reaction depends on
the relative standard free energies of formation of the two oxides.

i.e. $\Delta G^O = x\Delta G^O_f(AO_y) - y\Delta G^O_f(MO_x)$ (3.20)

For the reaction;

$$2CaO_{(s)} + C_{(s)} \rightarrow 2Ca_{(s)} + CO_{2(g)},$$ (3.21)
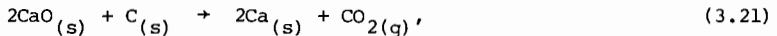
$$\Delta G^O = (-394.5) - 2(-604.2) \text{ kJ},$$ (3.22)

i.e. $\Delta G^O = 814.1$ kJ, an unfavourable reaction.

Similarly for the reaction;

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO,$$ (3.23)

$$\Delta G^O = 3(-137)-(-741) \text{ kJ},$$ (3.24)

i.e. $\Delta G^O = 330$ kJ, also an unfavourable reaction. However if the
reductions are carried out at high temperatures, the circumstances become
more favourable, because of the influence of the $T\Delta S^O$ term on ΔG^O.

The reaction;

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}, \tag{3.25}$$

has a standard entropy change of;

$$\Delta S^o = (213.6 - 5.7 - 205)J, \tag{3.26}$$

i.e. $\Delta S^o = 2.9J.$

If the quantities ΔH^o (-393.5 kJ) and $T\Delta S^o$ are plotted against T (K) then $\Delta G^o = \Delta H^o - T\Delta S^o$ shows that ΔG^o hardly varies with temperature (Fig. 3.6a). For the reaction;

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}, \tag{3.27}$$
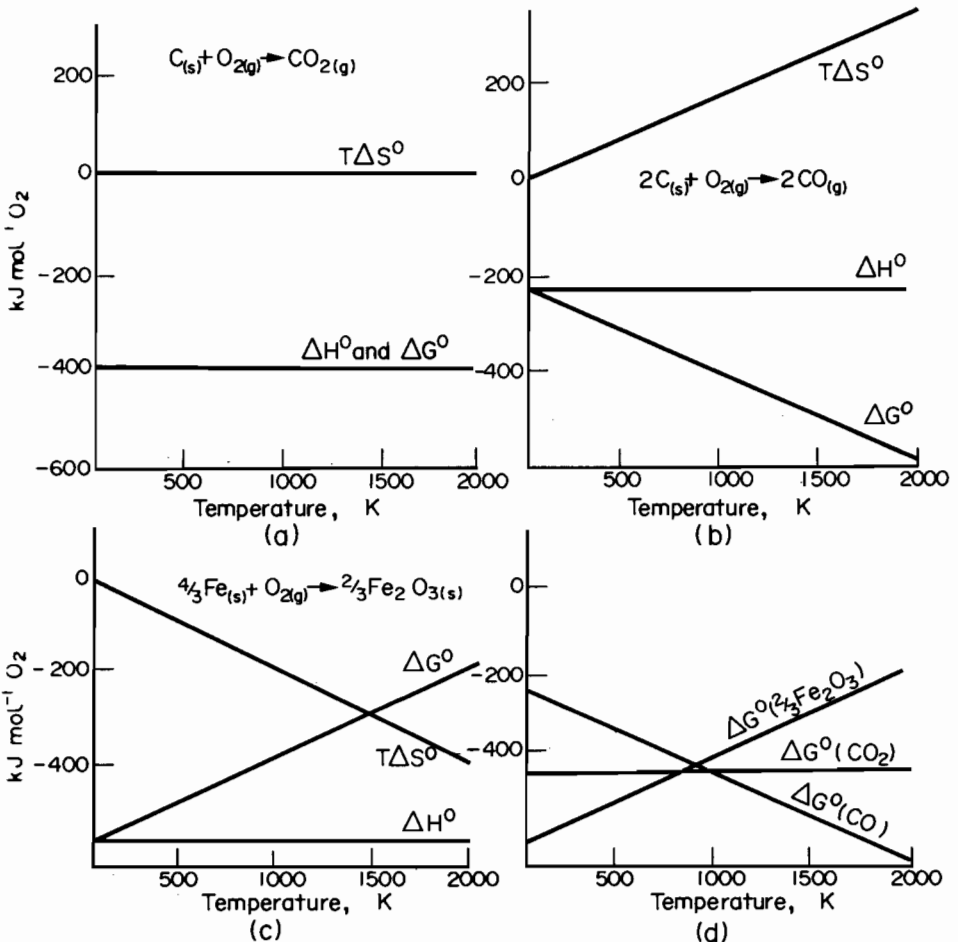
Fig. 3.6. $\Delta G^o/T$ plots for the formation of (a) CO_2, (b) 2CO, (c) $\frac{2}{3}Fe_2O_3$ and (d) combined.

the standard entropy change is;

$$\Delta S^O \quad = \quad (2 \times 198.5 - 2 \times 5.7 - 205)J \tag{3.28}$$

i.e. $\Delta S^O \quad = \quad 178.6J$

The ΔH^O, ΔG^O and $T\Delta S^O$ terms plotted against $T(K)$ are given in Fig. 3.6b, and in this case $\Delta G/T$ line has a steep negative slope.

For the formation of Fe_2O_3, (writing the equation so one mole of O_2 is consumed) we have;

$$\frac{4}{3}Fe \quad + \quad O_2 \quad \rightarrow \quad \frac{2}{3}Fe_2O_3. \tag{3.29}$$

The standard entropy change is;

$$\Delta S^O \quad = \quad (\frac{2}{3} \times 90 - \frac{4}{3} \times 27.2 - 205) \tag{3.30}$$

i.e. $\Delta S^O \quad = \quad -181.3 \ J.$

The plots of ΔH^O, ΔG^O and $T\Delta S^O$ versus T (per mole of O_2 consumed) are given in Figure 3.6c; in this case the $\Delta G^O/T$ line has a positive slope. Comparison of the three $\Delta G^O/T$ lines (Fig. 3.6d) shows that, because of the opposing slopes of the $\Delta G^O/T$ lines for $2CO$ and $\frac{2}{3}Fe_2O_3$, there is a temperature at which the free energy of formation of $2CO$ is more negative than that of $\frac{2}{3}Fe_2O_3$ (around 900 K). This means the reaction,

$$\frac{2}{3}Fe_2O_{3(s)} \quad + \quad 2C_{(s)} \quad \rightarrow \quad \frac{4}{3}Fe_{(s)} \quad + \quad 2CO_{(g)}, \tag{3.31}$$
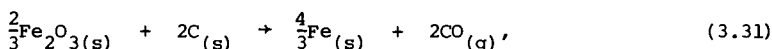
has a favourable ΔG^O above 900 K.

The free energy of formation of all metal oxides become less negative as the temperature increases, because of the unfavourable large entropy change ($-\Delta S^O$), as a result of the loss of a mole of oxygen. The $\Delta G^O/T$ lines for a number of metal oxides are given in Fig. 3.7 where the ΔG^O values are expressed per mole of O_2 consumed. Some of the lines for the metal oxides have more than one slope, since discontinuities occur at the melting points and boiling points of the metals and/or oxides.

Useful information can be obtained from the Ellingham diagram. Because the carbon lines (negative slope) cut the metal oxide lines (positive slopes), it becomes clear why carbon is a useful reducing agent; since at some temperature (above the point of cross-over) carbon is able to reduce many metal oxides. But in some cases the temperature required is so high, greater than 2000 K for Al_2O_3, that it is not economical to carry out the reduction, without some other energy input. The lines for metal oxides that are around $\Delta G^O = 0$, indicate that with sufficient heat these oxides become thermally unstable without the need to add a reducing agent (see above for mercury; equation (3.18)). Any metal oxide will be reduced by a metal whose oxide's $\Delta G^O/T$ line lies below that of the former, i.e. Al will reduce Cr_2O_3, but a high temperature is required to overcome the kinetic energy barrier. At 1000K ΔG for the reaction;

$$2Al \quad + \quad Cr_2O_3 \quad \rightarrow \quad 2Cr \quad + \quad Al_2O_3, \tag{3.32}$$
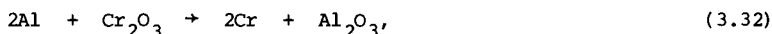
is -530 kJ. This method of extraction is called the thermite process.
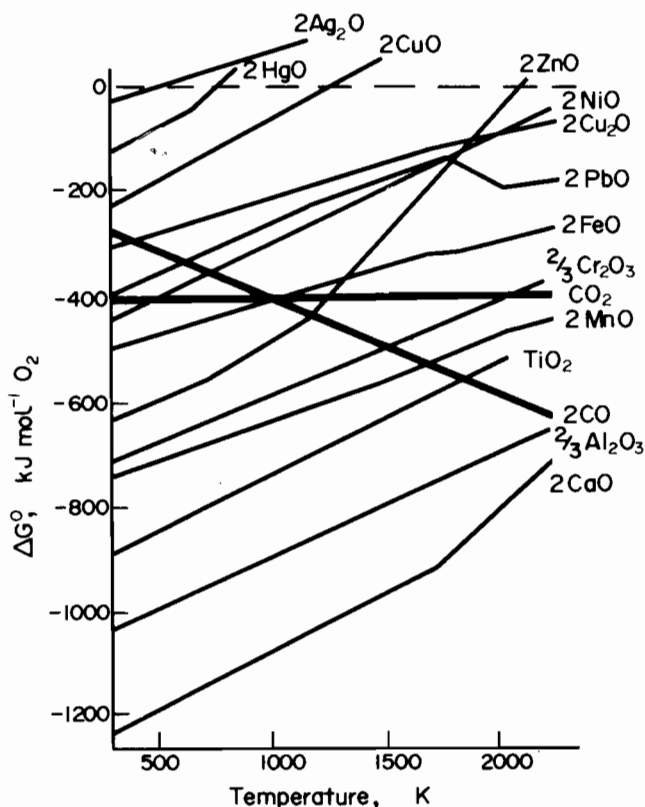
Fig. 3.7. Ellingham diagram, $\Delta G^O/T$, for oxide formation (discontinuities are due to phase changes of either metal or oxide). Source: D.J.G. Ives The Chemical Society, London, Monographs for Teachers, No. 3, 1969.

The two $\Delta G^O/T$ lines for the oxidation of carbon cross at approximately 925 K. Below this temperature CO is unstable relative to C and CO_2;

i.e.
$$2CO \rightarrow C + CO_2, \tag{3.33}$$

while above 925 K the reverse reaction occurs. Hence below 925 K the principal reducing agent is CO, while above 925 K it is carbon.

Many metals occur as sulphides, but because there is no CS analogue to CO there is no $\Delta G^O/T$ line with a steep negative slope. Therefore carbon is not a good reducing agent for sulphides. Roasting a sulphide ore to obtain the oxide is a necessary first step before reduction with carbon;

i.e.
$$2MS + 3O_2 \rightarrow 2MO + 2SO_2. \tag{3.34}$$
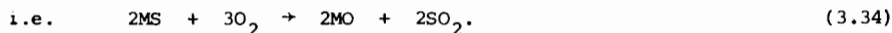
The same applies to H_2 as a reducing agent, as the $\Delta G^O/T$ line for

$$2H_2 + O_2 \rightarrow 2H_2O \tag{3.35}$$

has a positive slope and runs parallel to many metal oxide lines. Only
oxides whose formation lines lie above the H_2 line will be reduced by
dihydrogen. The other problem with H_2 as a reducing agent is that it can
remain dissolved in many metals affecting their properties.

Ore Processing

Prior to extraction of a metal from its ore it is often necessary to process
the ore by crushing and sorting to a correct size, also the ore may need to
be enriched. Many sorting processes make use of the physical properties of
the crushed ore. Magnetic material, such as magnetite, Fe_3O_4, can be
concentrated magnetically. In froth flotation certain minerals attach
themselves to air bubbles produced in a bath of water, and then float off in
the froth. Frothers are added to the bath, to maintain the bubbles (e.g.
pine oil or higher alcohols). Collectors, such as salts of organic acids or
bases, attach themselves to certain minerals in the pulverised ore making
them hydrophobic and carried away with the bubbles. Gravity separation
depends on the different densities of the materials in the ore. Chemical
processes may also be used to enrich an ore, such as leaching with acid or
alkali.

Extraction of Iron

The blast furnace is the main method by which iron is obtained from its ores.
The furnace (20 - 30m high and around 6 - 7m in diameter) lined with
refractory bricks is loaded from the top with ore (Fe_2O_3, Fe_3O_4), coke and
limestone. Hot air (> 800^oC) is blasted in at the bottom through "tuyères".
Molten iron is tapped off at the bottom and less dense molten slag is also
removed. The furnace gases are vented at the top, and if any CO remains it
is burnt to preheat the air blast. The chemical reactions that take place
at different temperatures and at different positions in the furnace are
given in Fig. 3.8.

Below 700—800^oC the principal reducing agent is CO, and the reactions are
called "indirect reductions". The reactions around 1000^oC are called direct
reductions because the overall stoichiometry is;

$$FeO_{(s)} \;+\; C_{(s)} \;\rightarrow\; Fe_{(s)} \;+\; CO_{(g)}. \qquad (3.36)$$
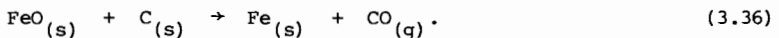
However, this does not represent the true situation because at 1000^oC the
two reactions;

$$FeO_{(s)} \;+\; CO_{(g)} \;\rightarrow\; Fe_{(s)} \;+\; CO_{2(g)}, \qquad (3.37)$$

and $$CO_{2(g)} \;+\; C_{(s)} \;\rightarrow\; 2CO_{(g)}, \qquad (3.38)$$
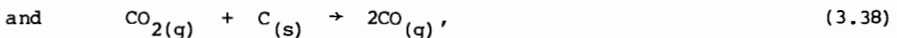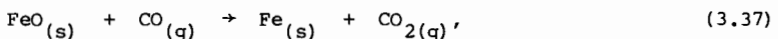
make up equation (3.36), i.e. the CO acts as an intermediate.

Since the reductions are of the type;

$$\text{Metal oxide(A)}_{(s)} + CO \;\rightarrow\; \text{metal oxide(B)}_{(s)} \text{ or metal} + CO_2 \quad (3.39)$$
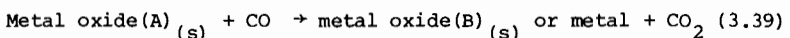
the position of equilibrium is given by the ratio P_{CO_2}/P_{CO}. At 600 - 700^oC
the ratio is around 1 (the temperature of cross-over of the CO_2 and CO $\Delta G^o/T$
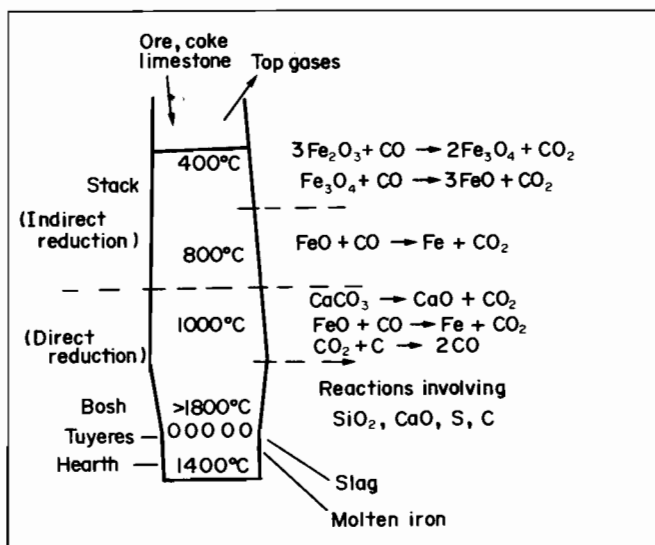
Fig. 3.8. A schematic diagram of a blast furnace,
          showing temperatures and chemical reactions.
          Source: T. Rosenqvist, Principals of
          Extractive Metallurgy. McGraw-Hill, N.Y., 1974.

lines in the Ellingham diagram, Fig. 3.7. The ratio is temperature dependent
and increases up the furnace as the gases become less reducing. For an
efficient furnace the exit gases will have a large ratio.

As the reaction $2CO \rightarrow C + CO_2$ occurs below 500-600°C, soot may be deposited
on the ore, which at a higher temperature is useful for reduction. However,
the soot tends to deteriorate the refractory bricks and is considered harm-
ful.

Limestone is added to remove acidic impurities, such as SiO_2, as slag;

$$CaO + SiO_2 \rightarrow CaSiO_3. \qquad (3.40)$$

Other material in the ore undergo various reactions in the blast furnace,
for example above 1000°C, Fe_3C forms which dissolves in the molten iron,
SiO_2 is reduced to Si above 1500°C which also dissolves in the iron.
Reduction of phosphate produces finally Fe_3P, and manganese oxides reduce to
the metal, which alloys with the iron. Any sulphur, mainly from the coke,
reacts with the iron to give FeS, but this is removed by the reaction;

$$FeS + CaO + C \rightarrow Fe + CO + CaS, \qquad (3.41)$$

the CaS appearing in the slag. The final product, brittle "pig iron",
may contain up to 4% C, 2.5% Mn, 2.5% Si, 2% P and 1% S.

Steel. Pig iron is converted into other forms of iron mainly by altering
the carbon content. Above 1000°C the carbide Fe_3C is formed which is
soluble in iron at low concentrations. The carbide has a carbon atom
surrounded by a near regular trigonal prism of iron atoms. Pure iron has a
melting point of 1539°C, reduced to 1015°C (the eutectic temperature) by
4.3% carbon (Fig. 3.9). Iron crystallises in three forms: α-iron, bcc,
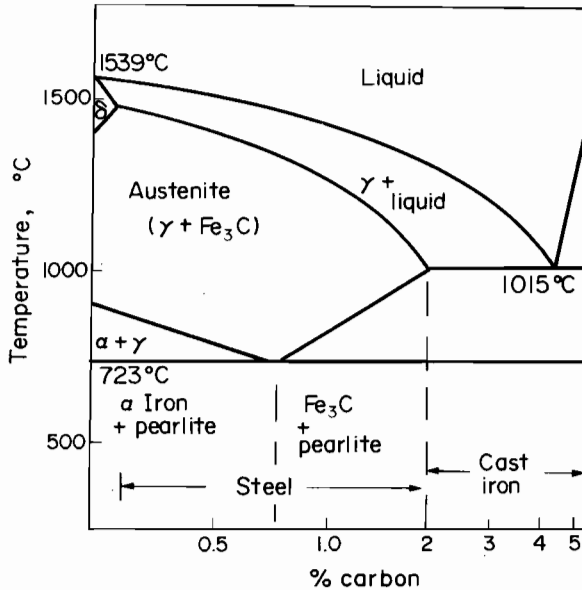
Fig. 3.9.   Phase diagram for Fe-C.

<910°C; γ-iron, fcc, 910-1400°C; and δ-iron, bcc, 1400-1539°C. The solid
solution of γ-Fe and Fe_3C (<2%C) called "austenite" is a tough form of iron
(steel) while α-Fe + Fe_3C (<2%C) is "pearlite", which is more malleable,
because its structure consists of alternating layers of α-iron and Fe_3C.
Austenite converts to pearlite by slow cooling but rapid cooling "freezes"
the steel in the austenite form called "martensite". Above 2%C the iron is
no longer steel and the carbide becomes unstable decomposing, in part, to
produce graphite;

$$Fe_3C \rightarrow 3Fe + C. \qquad (3.42)$$

Remaining Fe_3C occurs as coarse particles, and the result is pig or cast iron
which is hard and brittle.

Steel is produced by blowing oxygen through or over molten pig iron. At
1600°C the reaction;

$$2C + O_2 \rightarrow 2CO, \qquad (3.43)$$

has a favourable free energy (ΔG^O = -552 kJ). Methods used to bring about
the oxidation include the open hearth furnace, rotor process, the basic

oxygen furnace and electric arc furnace.

In order to improve the qualities of steel it can be annealed. To prevent its oxidation an atmosphere of CO_2 and CO is used in order to give the ratio $p_{CO}/p_{CO_2} > 1$ to ensure the reaction;

$$CO_{2(g)} + Fe_{(s)} \rightarrow FeO_{(s)} + CO_{(g)} \tag{3.44}$$
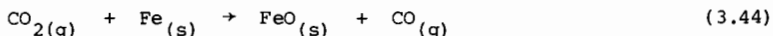
lies on the left.

Other materials in pig iron are also removed by oxidation. Silicon and manganese are oxidised and the molten oxides float on the iron as slag. The oxides of S and P are unstable with respect to the formation of FeO, at the temperatures of steel making, and therefore have to be converted to slag with the use of a basic oxide such as CaO.

There are a number of special steels whose properties depend on the amount of other materials in the iron. For example 2.5% Si makes the steel elastic and can be used in springs, 0.4 - 1.6% Mn gives steel a high tensile strength, 12-15% chromium gives stainless steel, and the cutting edge of steel is maintained by the addition of tungsten.

Extraction of Aluminium

In order to produce aluminium using carbon a temperature of $2000^{O}C$ is required (see Fig. 3.7), which is too expensive. It is therefore necessary to use another energy source and to work at a lower temperature. An electrolytic method called the Hall-Héroult process, discovered independently by Hall (U.S.A.) and Héroult (France) in 1866, uses cryolite, Na_3AlF_6, as a non-aqueous solvent for Al_2O_3. A 2-8% solution of Al_2O_3 in Na_3AlF_6 has a melting point of $960-980^{O}C$.

The principal aluminium ore, bauxite, contains aluminium oxide (30-70%) with ferric oxide and silica as the other main components. The oxide is purified by making use of the differing acidic and basic properties of the oxides (Bayer process).

$$
\left.
\begin{array}{l}
Al_2O_3 \\
\text{(amphoteric)} \\[6pt]
Fe_2O_3 \\
\text{(basic)} \\[6pt]
SiO_2 \\
\text{(acidic)}
\end{array}
\right\}
+ 30\% \text{ NaOH} \xrightarrow[460K]{800kPa} AlO_{2(aq)}^{-} + SiO_{3(aq)}^{2-} + Fe_2O_{3(s)} \tag{3.45}
$$
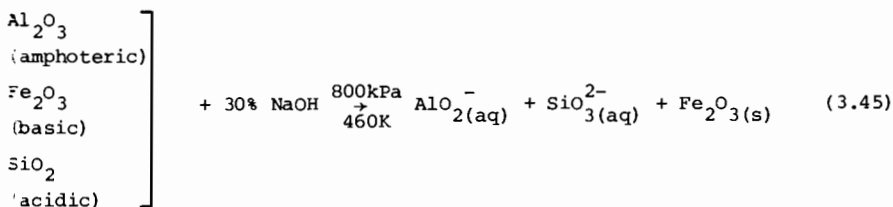
The insoluble materials are removed by sedimentation, and purfied alumina precipitates as $Al_2O_3 3H_2O$ (or $Al(OH)_3$) by treating the solution with CO_2 and $Al_2O_3 3H_2O$ seed crystals. The silica remains in solution. Non-aqueous conditions are required for the electrolysis so the oxide is first heated to 1500 K to give αAl_2O_3.

The aluminium oxide is then fed into the cell (Fig. 3.10) containing cryolite.
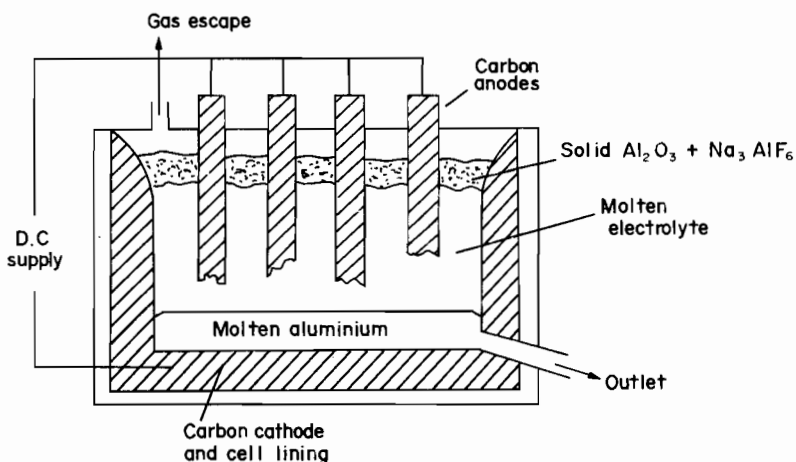
Fig. 3.10.   A schematic diagram of the Hall-Héroult cell
for the production of aluminium.

The inputs to the cell to produce 1000 kg of Al from 4000 kg of ore (assuming a 50% Al_2O_3 content) are given in Fig. 3.11.   The electrochemical reactions are;

$$Al^{3+} + 3e \rightarrow Al_{(1)} \qquad \text{(cathode)} \qquad (3.46)$$

$$O^{2-} - 2e \rightarrow \frac{1}{2}O_2 \qquad \text{(anode)} \qquad (3.47)$$
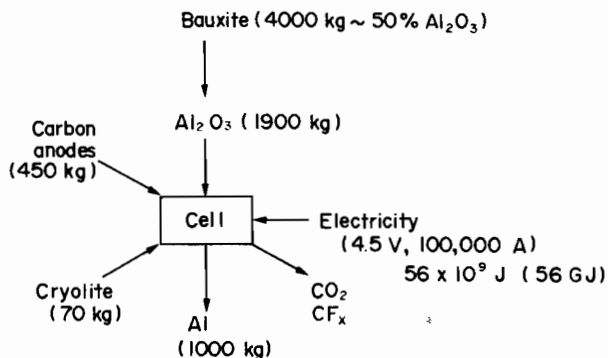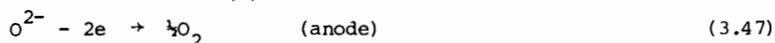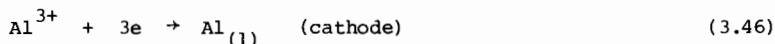
Fig. 3.11.   Inputs to produce 1000 kg of aluminium

which add up to;

$$Al_2O_3 \xrightarrow{\text{electrolysis}} 2Al + \frac{3}{2}O_2, \quad \Delta G_{1260 \text{ K}} = 1255 \text{ kJ}. \tag{3.48}$$
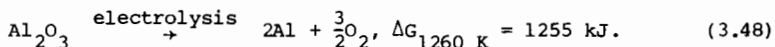
The oxygen reacts with the carbon anodes;

$$\frac{3}{2}O_2 + \frac{3}{2}C \rightarrow \frac{3}{2}CO_2, \quad \Delta G_{1260 \text{ K}} = -603 \text{ kJ}. \tag{3.49}$$
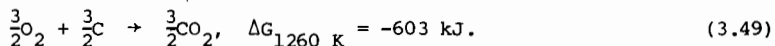
This reaction, which consumes the carbon anodes, thermally assists in the production of aluminium;

$$Al_2O_3 + \frac{3}{2}C \rightarrow 2Al + \frac{3}{2}CO_2, \quad \Delta G_{1260 \text{ K}} = 652 \text{ kJ}. \tag{3.50}$$
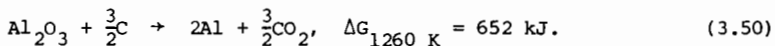
Hence, indirectly, carbon reduces the oxide, and just a little more than half of the expected energy is required. However, energy is necessary to produce the anodes, but is less than the above saving in power.

The major energy inputs in the production of 1000.kg of aluminium are: (a) the Bayer process, 44 GJ, (b) dehydration of $Al_2O_3 3H_2O$, 9 GJ, (c) electrolysis, 168 GJ assuming 33% efficiency in the handling of electrical power, and (d) carbon anode production, 14 GJ. This gives a total of 235 GJ making aluminium production expensive in the use of power (see Table 3.11).

Refinement of Metals

Metals are sometimes needed in a high state of purity, and have to be refined. The treatment of pig iron to make steel is an example. We will discuss electrolytic refinement of copper and zone refinement of silicon.

Refinement of copper. Impure copper is refined by making it the anode of a cell with pure copper as the cathode. The cell, which runs at 50-60°C, contains dilute $H_2SO_4/CuSO_4$ as the electrolyte, and over 2-3 weeks a 4.5-5.0 kg cathode will increase to 100-125 kg. Metal impurities in the copper anode either go into solution, if their reduction potentials are less than for copper; or drop on the cell floor as a sludge as the anode disappears, if their reduction potentials are greater than for copper. For example consider copper with Ag and Ni as impurities. The reduction potentials are; Cu(+0.34 V), Ag(+0.80 V) and Ni(-0.25 V). If the cell is run so that the anode reaction is;

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e \tag{3.51}$$

then the Ni will also go into solution, but not the Ag. If the cathode reaction is;

$$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}, \tag{3.52}$$

the Ni^{2+} will not be discharged. The electrolyte has to be changed as the impurities build up in solution, and because some impurities may tend to be discharged with the copper. The latter is more likely to happen at high concentrations of the impurity metals. The anode sludge is a good source of rare and precious metals, such as Ag, Au and the platinum metals.

Refinement of Silicon. It is necessary to obtain very pure silicon (1 part in 10^{10}) for use in the transistor industry. This is achieved by zone refinement. A bar of silicon is allowed to move slowly through a small circular induction heater (Fig. 3.12a), melting the silicon, which then solidifies as the bar moves out of the heater. Since the impurities are generally more soluble in the liquid phase they accumulate in the melt as it moves along the bar leaving behind purified silicon. The process can be repeated a number of times, always in the same direction. If we assume that an impurity X and silicon form a solid solution the phase changes are repre- sented by the section of a phase diagram given in Fig. 3.12b. If the concentration of the impurity is C_x, as the liquid cools to temperature T_A at point A solid separates with composition C_x' (point B), i.e. the solid is now more pure and the liquid as a consequence becomes richer in X. On the next treatment the solid with concentration C_x' melts and on cooling at temperature T_B gives an even purer solid with C_x'' as the concentration of X. The purified silicon is then doped by adding controlled amounts of material such as boron and arsenic to give p and n type semiconductors respectively.
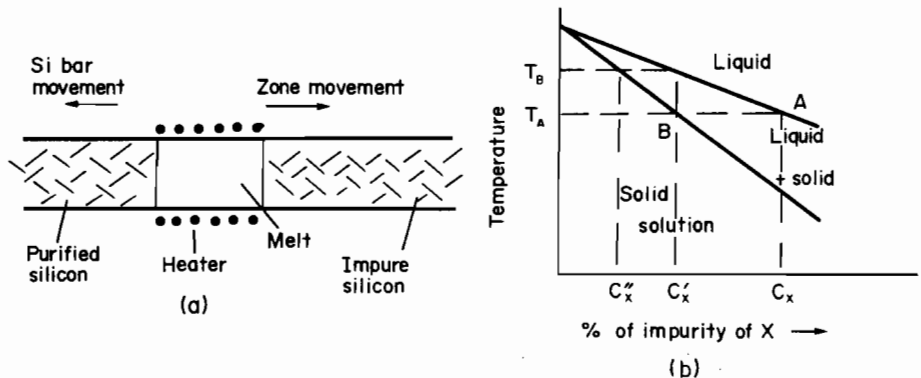
Fig. 3.12. Refinement of silicon, (a) diagram of technique, (b) part of a silicon-impurity phase diagram.

EXTENDING MINERAL RESOURCES

A way of maintaining, or extending, mineral resources is to investigate new methods of extraction where low grade ores can be used without too great an expenditure in energy. Another approach is to search for new materials for specific tasks. The recycling of materials is also of increasing importance, as are methods of protecting materials from corrosion.

Discovery of New Ore Bodies

The search for new mineral resources continues, particularly for ore bodies whose presence is not obvious from a study of the earth's surface. Geochem- ical and geophysical techniques (with a sound understanding of geology) are the principal methods employed. Geochemical analytical results of trace elements in rocks, sediments and plants can indicate ore bodies. Studies of the dispersion of elements around an ore body can provide information of use in later exploration. For example, around the Robinson mining area in

Nevada, U.S.A., 2000 samples were analysed for 30 elements. The results, when analysed, produced a pattern of contours of element concentration extending out from the copper ore body. It was discovered that thallium and indium had moved furtherest from the ore, and therefore their presence else-where may suggest concealed ore deposits.

An area for exploration that is still in its infancy is the sea bed. Manganese nodules are one example of a mineral discovered on the ocean floor. This extension of mineral exploration (including oil), raises political problems of ownership and environmental problems which need to be resolved before developments get too far advanced. The Arctic and Antarctic are also two areas that need careful consideration.

New Methods of Ore Processing and Extraction

Improved methods of ore processing and metal extraction are being investigated for a variety of reasons. These include the use of new ores or low grade ores, pollution control, replacement of an expensive reagent and small scale processes for handling small ore deposits.

Titanium dioxide for use as a pigment is obtained either from rutile by chlorination to give $TiCl_4$ from which TiO_2 is obtained;

$$TiO_{2(s)} + C_{(s)} + 2Cl_{2(g)} \rightarrow TiCl_{4(\ell)} + CO_{2(g)}, \tag{3.53}$$

$$TiCl_4 + O_2 \xrightarrow{650-750^\circ C} TiO_2 + 2Cl_2, \tag{3.54}$$
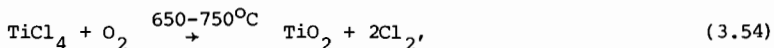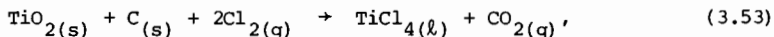
or by treating ilmenite with sulphuric acid. The problem with the latter process is the disposal of the $FeSO_4 7H_2O$. Chlorination of ilmenite has been proposed but this uses up expensive chlorine in producing $FeCl_3$

$$2FeTiO_3 + 3C + 7Cl_2 \rightarrow 2FeCl_3 + 2TiCl_4 + 3CO_2. \tag{3.55}$$
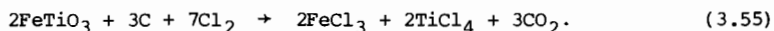
However, this problem has been overcome by separating the $FeCl_3$ from the $TiCl_4$, by fractional condensation, and recovery of the Cl_2 by the reaction;

$$4FeCl_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6Cl_2. \tag{3.56}$$

Both low grade copper and uranium ores have been enriched *in situ* by leaching. Copper oxide ores (Emerald Isle mine Arizona, U.S.A.), after fracturing and while still in the mine, have been leached with acid solutions and the metal recovered from solution by cementation;

$$Cu^{2+}_{(aq)} + Fe \rightarrow Fe^{2+}_{(aq)} + Cu. \tag{3.57}$$

Uranite ores have been leached *in situ* by circulating carbonate/bicarbonate solutions, under oxidising conditions, into the ore strata. Oxidation to U(VI) is achieved and the uranium which dissolves is then recovered using ion exchange techniques.

Mercury has been long used to concentrate gold by amalgamation. This has two disadvantages, pollution and the limited mercury resources. Activated charcoal successfully absorbs gold, which is then separated by flotation. The gold is recovered from the charcoal either by smelting or using cyanide leaching solutions.

In order to obtain the most from small deposits of zinc and lead ores, small
scale extraction methods need to be developed. This rules out conventional
pyrometallurgical methods. The U.S. Bureau of Mines has developed chlorin-
ation of the sulphide ores to give $PbCl_2$, $ZnCl_2$ and S.

$$PbS/ZnS + 2Cl_2 \rightarrow PbCl_2 + ZnCl_2 + 2S. \hspace{2cm} (3.58)$$
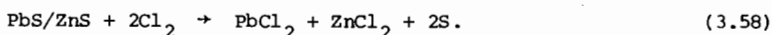
The lead chloride is crystallised from brine solutions and the fused salt
electrolysed to obtain lead and recover the chlorine.

$$Pb^{2+} + 2e \rightarrow Pb \hspace{1cm} \text{(cathode)} \hspace{2cm} (3.59)$$

$$2Cl^- - 2e \rightarrow Cl_2 \hspace{1cm} \text{(anode)} \hspace{2cm} (3.60)$$

Zinc chloride is obtained at a later stage from the original solution, as it
is more soluble than $PbCl_2$.

Recycling of Metals

Interest in, and the practice of, recycling metals fluctuates with social,
political and economic conditions. Prior to, and during, World War II metal
recycling was a significant industrial process, and the amounts of Cu, Pb
and Al recycled as a percentage of the total consumption were 44%, 39% and
28% respectively. However, the proportion of recycled metals has decreased,
probably as a result of the cost and effort of processing, and optimism
over resources. The energy inputs for purifying scrap metal (Table 3.15)

TABLE 3.15   Recycling of Metals - Energy Requirements

Metal	Energy Requirement as % of energy to extract metal from ores*	Metal	Energy Requirement as % of energy to extract metal from ores*
Steel	45 – 50	Aluminium	4.5
Titanium	20	Magnesium	2
Copper	10		

*   Does not allow for energy consumption in collection and separation.

indicate the advantage of using scrap over ore. The percentage figures are
based on data which excludes the energy component in getting the scrap
ready for processing, though this is considered not to a significant energy
factor.

The various methods of producing steel make use of scrap iron. The basic
oxygen furnace can use 30% scrap, the open hearth furnace 40% and the electric
arc furnace 98%. The growing popularity of the basic oxygen method (U.S.A.
production in 1977; basic oxygen furnace 63%, electric furnace 22%, open
hearth 16%), a process that generates its own scrap, may be a factor in
reduced recycling of iron (from 60 to 40% between 1972-74).

Two problems in recycling metals are physical separation of materials, and
dealing with alloys. Iron, because of its ferro-magnetism, is one of the
easier metals to separate, and the colour of copper is an advantage in

Extraction of Metals

Aluminum : from Bauxite Al_2O_3
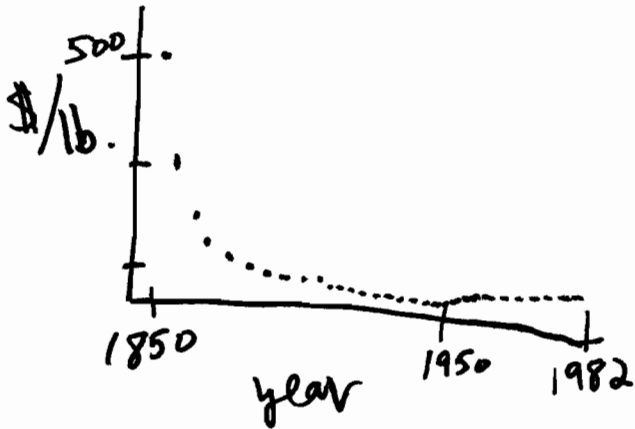
1850 ~$500/lb.

there was no way to reduce it.

1854 Process to make $Na(s)$ by electrolysis invented

then $Al_2O_3 + 6 Na \rightarrow 2 Al + 3 Na_2O$

price $500 \rightarrow 25$
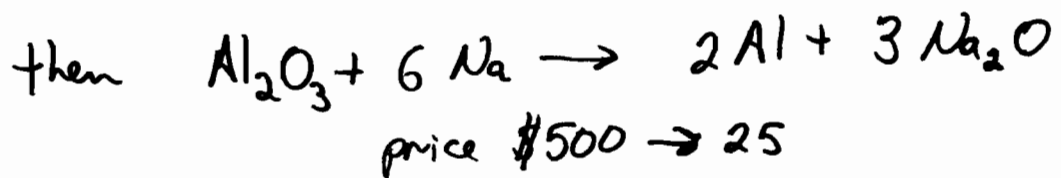
1886 direct electrolysis of Al_2O_3

price $25 \rightarrow $1

all hard to reduce metals are made by electrolysis

problem w/ electrolysis: reactants need to be in liquid phase

Al_2O_3 melting pt. is too high.

make a salt mixture of

mixture melts low 980°C

$\begin{cases} 80\% & Na_3AlF_6 \text{ (cryolite)} \\ 7\% & CaF_2 \\ 7\% & AlF_3 \\ 6\% & Al_2O_3 \end{cases}$

the Al_2O_3 can thus be in l. phase

Al_2O_3 gets used up & is continually recharged.

The rest just stays there.

Voltage used = 4 - 5.5U   very low for the power company
                           very high for chemical reactants

Gold : exists as small particles of $Au(s)$

used to just get it out of sand by density diff.

Sand : $2.3 g/cm^3$ Au $19.3 g/cm^3$

these are gone.

2 modern methods: 1st crush up rock into powder; ~25 ppm Au

1. amalgamation

$$Hg(l) + Au(s) \longrightarrow Hg(l) \text{ with } \underline{dissolved} \text{ gold}.$$
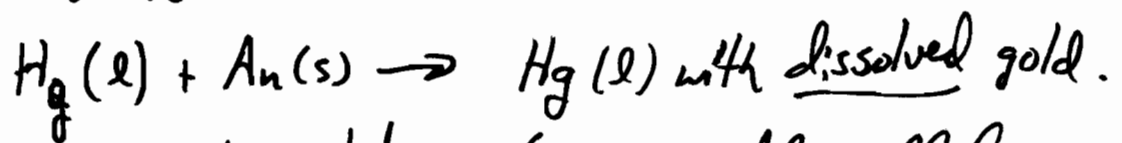
Hg solutions of other metals called
                                    amalgams (dentistry)

2. cyanide process : leach out gold

a. $4Au(s) + 8 Na CN(aq) + O_2(g) + 2H_2O \longrightarrow$

$$4 Na Au(CN)_2(aq) + 4 NaOH(aq)$$

b. $2Au(CN)_2^- + Zn(s) \longrightarrow Zn^{2+}(aq) + 4 CN^-(aq) + Au(s)$
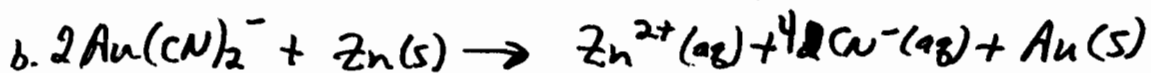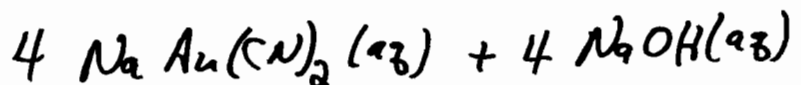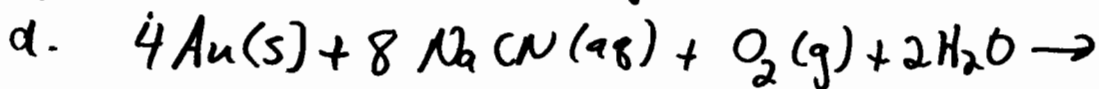
Extraction of Metals from Metal Oxides

Selected Thermodynamic Values

	$\Delta H°$(kJ/mol)	$S°$(J/K•mol)
Al(s)	0	28.3
Al$_2$O$_3$(s)	-1675.7	50.92
Ca(s)	0	41.59
CaO(s)	-635.1	38.2
Fe(s)	0	27.78
Fe$_2$O$_3$(s)	-824.2	87.4
Ag(s)	0	42.55
Ag$_2$O(s)	-31.1	121.3
C(s)	0	5.6
CO(g)	-110.525	197.67
CO$_2$(g)	-393.51	213.74
O$_2$(g)	0	205.07
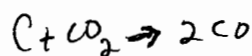
$$C + CO_2 \rightarrow 2CO$$
$$\Delta H = +172.5$$
$$\Delta S = +176$$
$$T_{\Delta G=0} = \underline{980\ K}$$

$$2Fe_2O_3 + 3C \rightarrow 3CO_2 + 4Fe$$
$$\Delta H = 3(-393.5) - 2[-824.2] = +467.9\ kJ$$
$$\Delta S = 3(213.7) + 4(27.8) - [3(5.6) + 2(87.4)] = +560.7\ J$$
$$T_{\Delta G=0} = \frac{467.9}{.5607} = \underline{834K}$$
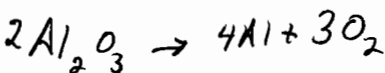
$$2Al_2O_3 \rightarrow 4Al + 3O_2$$
$$\Delta H = +3351.4\ kJ$$
$$\Delta S = 626.4\ J/k$$
$$T_{\Delta G=0} = 5350\ K$$

$$2Al_2O_3 + 3C \rightarrow 3CO_2 + 4Al$$
$$\Delta H = +2169.5\ kJ$$
$$\Delta S = +635.7$$
$$T_{\Delta G=0} = \frac{2169.5}{.6357} = \underline{3413\ k}$$
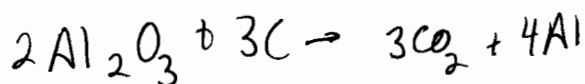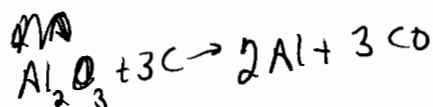
$$Al_2O_3 + 3C \rightarrow 2Al + 3CO$$
$$\Delta H = +1344.2$$
$$\Delta S = +581.9$$
$$T_{\Delta G=0} = \frac{1344.2}{.5819} = 2310\ K$$

Decomposition
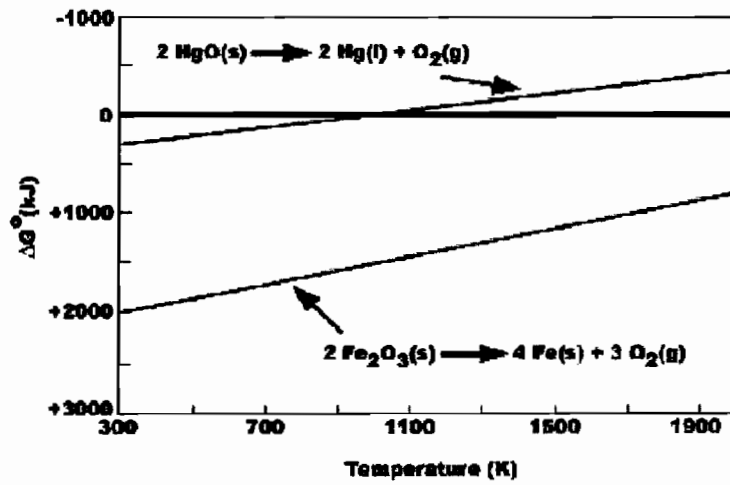
Chemical Reduction with Carbon
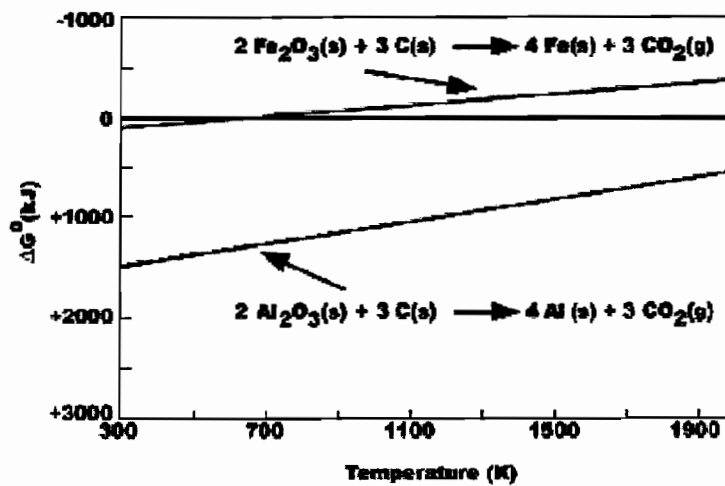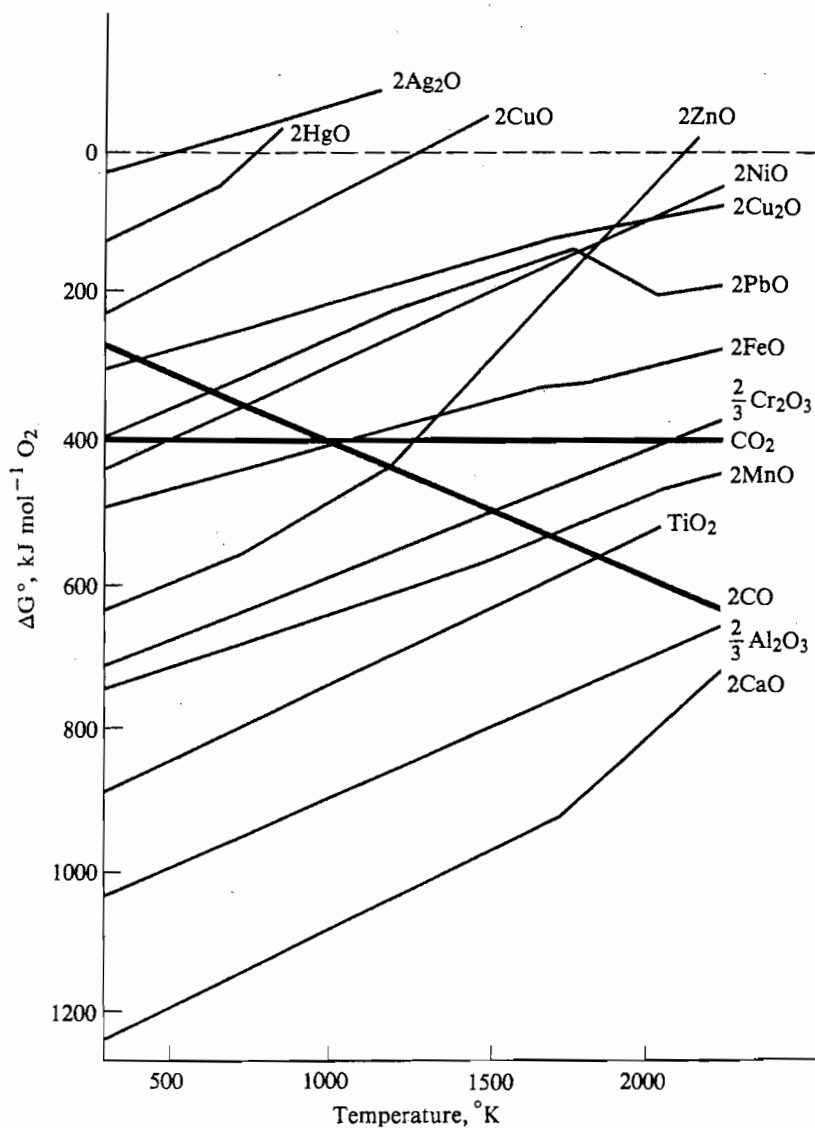
Figure 5.7 An Ellingham diagram showing the free energies of decomposition of metal oxides as a function of temperature. (Discontinuities result from phase changes of either the metal or the oxide.) From D. J. G. Ives, *Monographs for Teachers, Number 3*, The Chemical Society, London, 1969. Reprinted with permission.

Charge of ore, coke, and limestone

Flue gas

400 °C

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

800 °C

$FeO + CO \rightarrow Fe + CO_2$

Hot gases used
to preheat air

1000 °C

$CaCO_3 \rightarrow CaO + CO_2$
$FeO + CO \rightarrow Fe + CO_2$
$CO_2 + C \rightarrow 2\,CO$

Reducing zone

1800 °C

$CaO + SiO_2 \rightarrow CaSiO_3$

Heated
air

Molten iron, 1400 °C

Slag
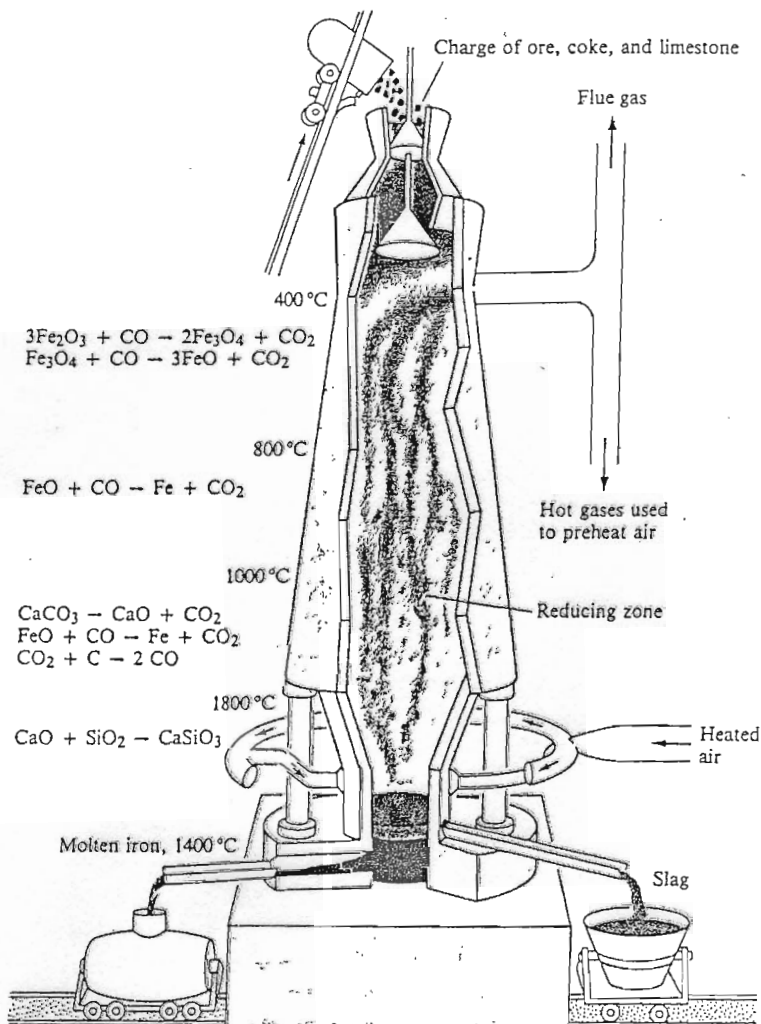
Figure 5.12 Schematic diagram
of a blast furnace, showing tem-
peratures and chemical reac-
tions occurring in different parts
of the furnace. Adapted from
Modern Descriptive Chemistry by
E. G. Rochow. Copyright © 1977
by W. B. Saunders Company.
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College Publishing.

from their ores, that of pollution control. As you can appreciate on rereading the descriptions of the processes of beneficiation, conversion, reduction, and puri- fication, many kinds of impurities form that can be solid, water, and air pollutants. The design of emission controls and waste disposal processes [6, 7] plays an increasingly important part in the economics of the production of the elements.

5.8

Study Objectives

1. Balance oxidation-reduction equations and half-reaction equations (review from general chemistry).

Black-and-White Film

Before

AgBr crystals

film

$$Br^-(s) + h\nu \longrightarrow Br(s) + e^-$$
$$Ag^+(s) + e^- \longrightarrow Ag(s)$$

speck

⬇ Shine light

AgBr w/ speck of Ag(s)

exposed film

⬇ "developer" = reducing agent

Ag crystals

$$2\,AgBr(s) + \underset{H}{\overset{H}{O}}\!\!-\!\!\langle \rangle\!\!-\!\!OH \longrightarrow 2\,Ag(s) + 2\,Br^-(aq) +$$

$$O=\langle \rangle=O$$
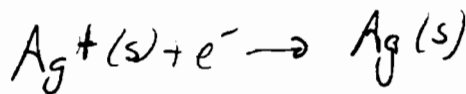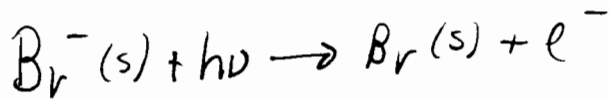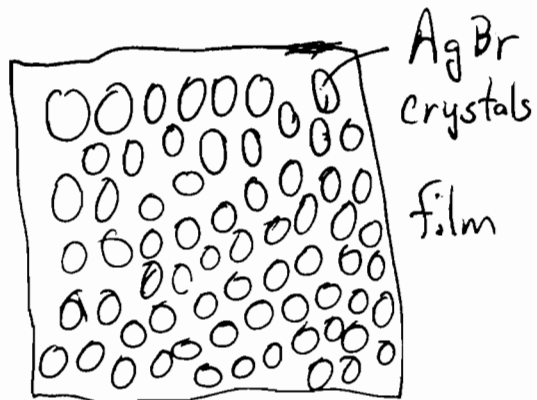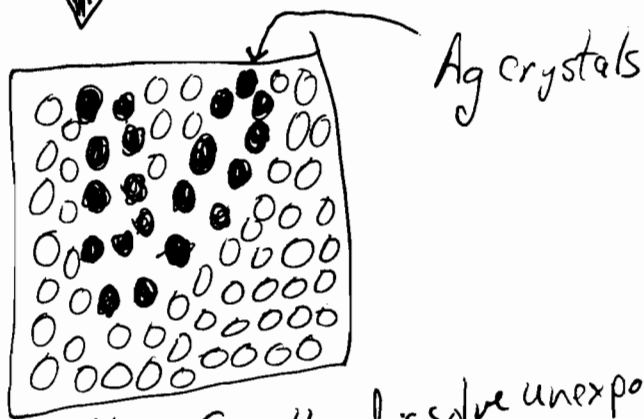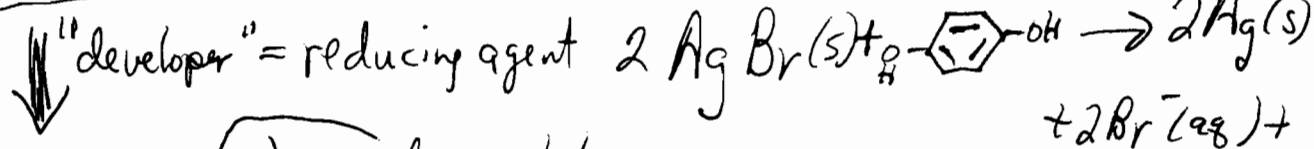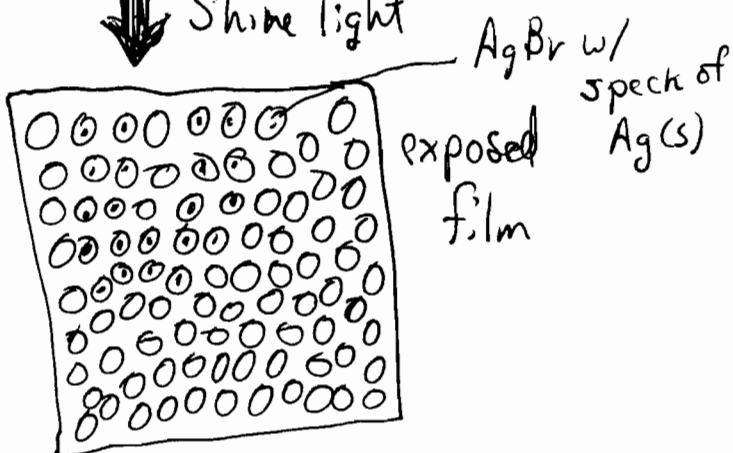
⬇ "fixer" = dissolve unexposed AgBr.

$$AgBr(s) + 2\,S_2O_3^{2-}(aq) \longrightarrow Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$$
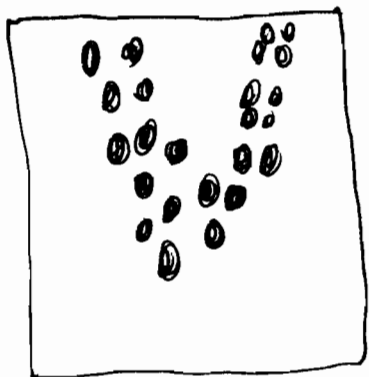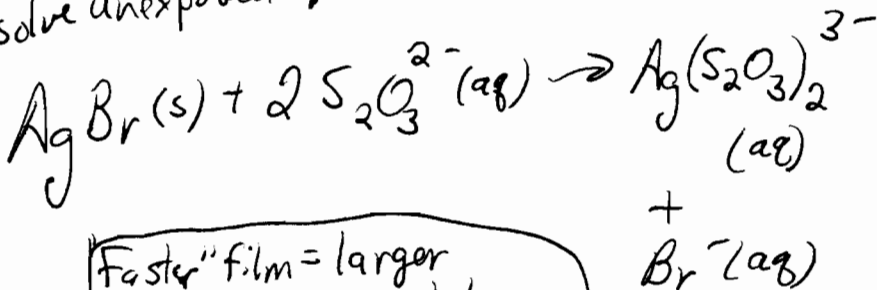
"Faster" film = larger crystals

"Higher resolution" = smaller crystals

The gold is recovered from the $Au(CN)_2^-$ either by the replacement reaction:

$$2Au(CN)_2^-(aq) + Zn(\text{dust}) \rightarrow Zn(CN)_4^{2-}(aq) + 2Au(s)$$
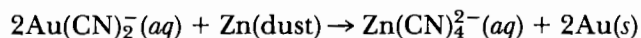
or by electrolysis. Some important gold compounds are listed in Table 11-14.

Silver is a lustrous, white metal whose ductility and malleability are exceeded only by gold and palladium. Pure silver has the highest electrical conductivity of all metals. Most of the silver produced nowadays is a by-product of the production of other metals such as copper, lead, and zinc. Silver is used in jewelry, silverware, high-capacity batteries, coinage, and photography. About a third of the silver produced is used in photography.

The sensitivity of silver halide crystals to light is the basis of the photographic process. Photographic film consists of very small silver halide crystals dispersed uniformly throughout some gelatinous substance, which itself spread over a transparent film. Such a dispersion is known as an *emulsion*. Silver bromide is commonly used, but silver iodide is used for fast film. When a photon of light falls upon a silver halide crystal, a halide ion loses an electron, which eventually migrates to the surface of the crystal and reduces a silver ion:

$$X^-(s) + h\nu \rightarrow X(s) + e^-$$
$$Ag^+(s) + e^- \rightarrow Ag(s)$$
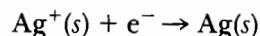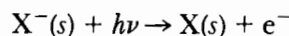
The silver, being very finely divided, appears black, and the pattern of silver atoms throughout the emulsion at this stage is called a *latent image*. The latent image is now intensified by a *developer*, which is a mild reducing agent that reduces more silver

ions. A common developer is hydroquinone, HO—⟨ ⟩—OH, and the half-reactions are

$$AgX(s) + e^- \rightarrow Ag(s) + X^-$$

HO—⟨ ⟩—OH $\longrightarrow$ O=⟨ ⟩=O $+ 2H^+ + 2e^-$
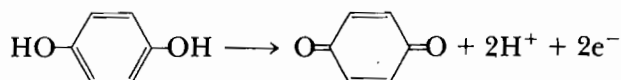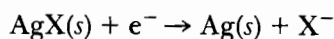
Table 11-14 Some important gold compounds

Compound	Uses
aurothioglycanide, $C_8H_8AuNOS(s)$	antiarthritic agent
gold(I) stannate, $Au_2SnO_2(s)$	manufacture of ruby glass, colored enamels, and porcelain
tetrachloroauric(III) acid, $HAuCl_4(s)$	photography; gold plating; gilding glass and porcelain

Table 11-15 Some important silver compounds

Compound	Uses
silver iodide, $AgI(s)$	dispersed in clouds to induce rain; photography (fast film)
silver nitrate, $AgNO_3(s)$	photography; manufacture of mirrors; silver-plating; hair-darkening agent; eye drops for newborn infants
silver oxide, $Ag_2O(s)$	purification of drinking water; polishing and coloring glass (yellow)
silver bromide, $AgBr(s)$	photography; photosensitive lenses

The overall reaction is catalyzed by the silver atoms of the latent image, and so the reduction occurs preferentially in those areas of the emulsion that received the most light.

The film is *fixed* by removing all the remaining silver halide to prevent further reduction. This is commonly done with a solution of sodium thiosulfate (*hypo*), which reacts with the silver halide according to

$$AgX(s) + 2Na_2S_2O_3(aq) \rightarrow Na_3[Ag(S_2O_3)_2](aq) + NaX(aq)$$
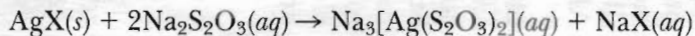
The resulting image is called a *negative* because the area that corresponds to the most light appears the darkest. A positive print is obtained by allowing light to pass through the negative onto printing paper, which is developed and fixed by the above process. Some important silver compounds are given in Table 11-15.

Like gold and silver, mercury has been known for thousands of years. Mercury is the only metal that is a liquid at 0°C and used to be called quicksilver. The principal ore of mercury is *cinnabar*, HgS, which was widely used in the ancient world as a vermilion pigment. The most extensive and richest deposits of cinnabar occur in the Almadén region of Spain, the world's largest producer of mercury. The metal is easily recovered from its ore by roasting:

$$HgS(s) + O_2(g) \rightarrow Hg(l) + SO_2(g)$$
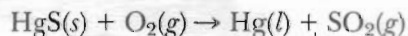
and the mercury is purified by distillation.

Mercury is not very reactive. On being h....
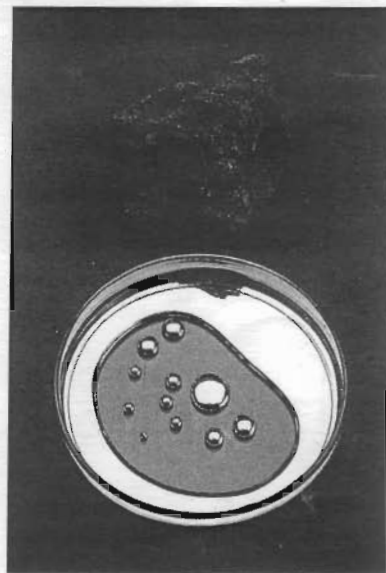
Cinnabar, $HgS(s)$, and mercury, $Hg(l)$.

■ The symbol Hg is derived from the Latin *hydragyrum*, meaning liquid silver.

CHEM 241

NUCLEAR FUEL PRODUCTION and USE

http://www.world-nuclear.org/education/ne/ne.htm
http://www.eia.doe.gov

Uranium-235

U.S. Forward-Cost Uranium Reserves by State, December 31, 2003						
	$30 per pound			$50 per pound		
State(s)	Ore (million tons)	Grade[a] (percent U_3O_8)	U_3O_8 (million pounds)	Ore (million tons)	Grade[a] (percent U_3O_8)	U_3O_8 (million pounds)
Wyoming	41	0.129	106	238	0.076	363
New Mexico	15	0.280	84	102	0.167	341
Arizona, Colorado, Utah	8	0.281	45	45	0.138	123
Texas	4	0.077	6	18	0.063	23
Other[b]	6	0.199	24	21	0.094	40
Total	74	0.178	265	424	0.105	890

Extracting U from Ore and converting to UF6.

The vast majority of all nuclear power reactors in operation and under construction require 'enriched' uranium fuel in which the content of the U-235 isotope has been raised from the natural level of 0.7% to about 4%. The enrichment process removes 85% of the U-238 by separating gaseous uranium hexafluoride into two streams: One stream is enriched to the required level and then passes to the next stage of the fuel cycle. The other stream is depleted in U-235 and is called 'tails'. It is mostly U-238.

So little U-235 remains in the tails (usually less than 0.3%) that it is of no further use for energy, though such 'depleted uranium' is used in metal form in yacht keels, as counterweights, and as radiation shielding, since it is 1.7 times denser than lead.

A. Extracting U from Ore

The ore is crushed and ground to liberate the mineral particles. It is then leached with sulfuric acid:

The UO_2 is oxidized to UO_3. Then, UO3 is reacted with sulfuric acid to dissolve it:

UO_3 (s) + 2 H$^+$(aq) ====> UO_2^{2+}(solid salt) + H_2O

UO_2^{2+}(solid salt) + 3 SO_4^{2-}(aq) ====> $UO_2(SO_4)_3^{4-}$(aq)
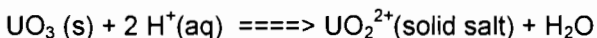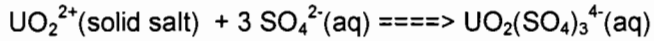
KEY: The $UO_2(SO_4)_3^{4-}$ is soluble in water and leaches out of the crushed ore.

Concentration and Precipitation of Leached U Compounds

$2R_3N + H_2SO_4$ ====> $(R_3NH)_2SO_4$
$2 (R_3NH)_2SO_4 + UO_2(SO_4)_3^{4-}$ ====> $(R_3NH)_4UO_2(SO_4)_3$ (aq) + $2SO_4^{2-}$ (aq)

$(R_3NH)_4UO_2(SO_4)_3 + 2(NH_4)_2SO_4$ ====> $4R_3N + (NH_4)_4UO_2(SO_4)_3 + 2H_2SO_4$
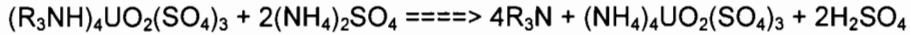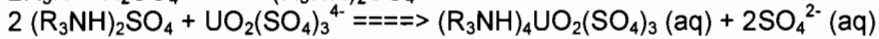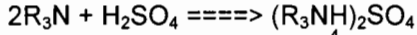
Precipitation of ammonium diuranate is achieved by adding gaseous ammonia to neutralise the solution (though in earlier operations caustic soda and magnesia were used).

$2NH_3 + 2UO_2(SO_4)_3^{4-}$ (aq) ====> $(NH_4)_2U_2O_7$ (s) + $4SO_4^{2-}$ (aq)
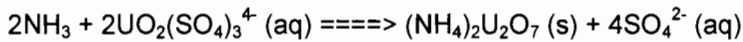
The diuranate is then dewatered and roasted to yield U_3O_8 product, which is the form in which uranium is marketed and exported.

U_3O_8 is then reacted to make pure UO_3.

KEY: UO_3 formed is pure.

B. Conversion to UF₆ prior to Enrichment

Most nuclear reactors require uranium to be enriched from its natural isotopic composition of 0.7% U-235 (most of the rest being U-238) to 3.5-4% U-235. The uranium therefore needs to be in a gaseous form and the most convenient way of achieving this is to convert the uranium oxides to uranium hexafluoride.

After purification, the uranium oxide UO_3 is reduced in a kiln by hydrogen to UO_2.

$UO_3(s) + H_2(g)$ ====> $UO_2(s) + H_2O$ .... delta H = -109 kJ/mole
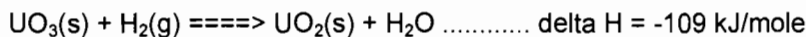
This reduced oxide is then reacted with gaseous hydrogen fluoride in another kiln to form uranium tetrafluoride, UF_4, though in some places this is made with aqueous HF by a wet process.

$UO_2(s) + 4HF(g)$ ====> $UF_4(s) + 2H_2O(l)$ .... delta H = -176 kJ/mole
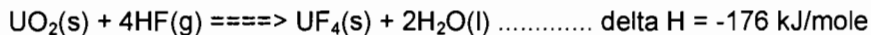
The uranium tetrafluoride is then fed into a fluidised bed reactor with gaseous fluorine to produce uranium hexafluoride, UF_6. Hexafluoride is condensed and stored.

$UF_4(s) + F_2(g)$ ====> UF_6(l or g)
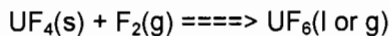
KEY: UF_6 is a liquid with a boiling point near 50 $^\circ$C and can easily be handled as a gas.

C. Enrichment of ^{235}U

KEY: Need to get greater fraction of ^{235}U; lower fraction of ^{238}U

Use difference in molecular speeds of the two gases:

^{235}UF$_6$: Molecular mass = 349 amu ^{238}UF$_6$: Molecular mass = 352 amu

Two methods: diffusion through porous barriers (10^9 pores/cm^2) and gas centrifuges.

Fuel-Level Enrichment: 4%

4% Enriched U-235

Natural U: 0.7% U-235

Disposable U-238
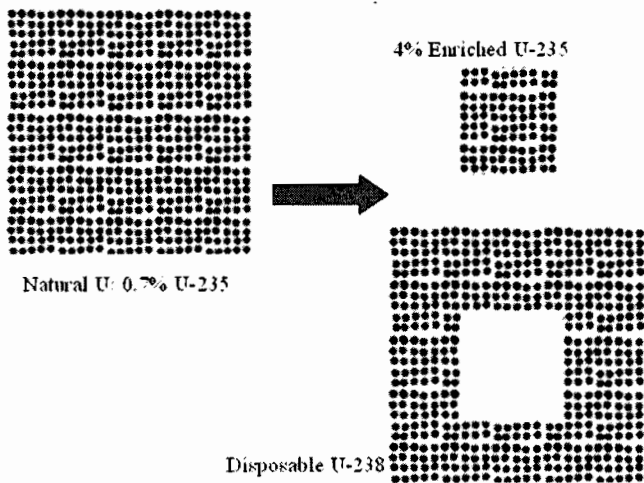
Bomb-Level Enrichment: 90%

90% Enriched U-235

4% Enriched U-235

Disposable U-238
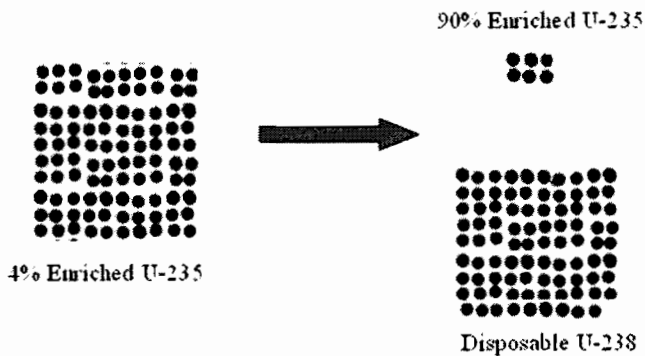
Efficiencies:

diffusion = 1.002/stage

Final Fraction = 0.7 x $(1.002)^{\#cycles}$

gas centrifuge: 1.2/stage

Final Fraction = 0.7 x $(1.2)^{\#cycles}$

Enrichment Plant
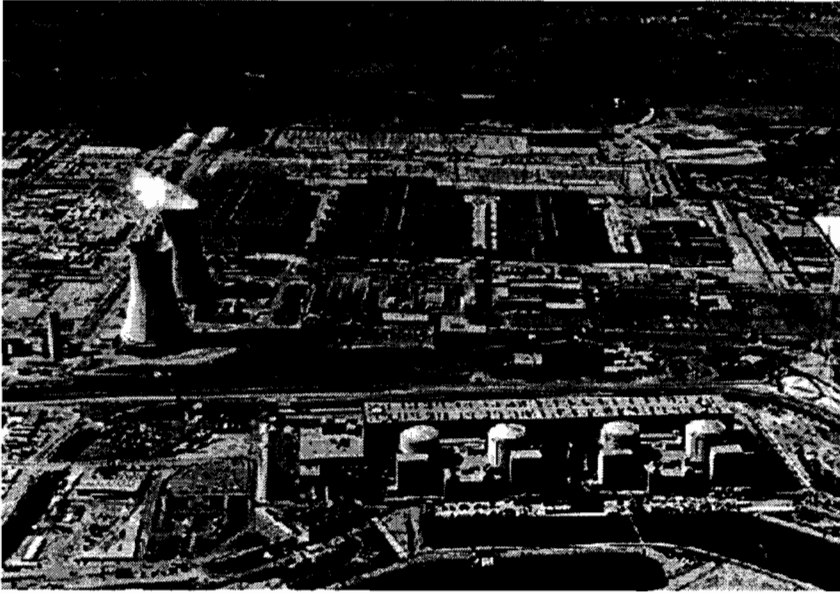
On the Horizon: *Laser* Enrichment Process

Another notable event was USEC's decision in May 1999 to abandon the Advanced Vapor Laser Isotope Separation (AVLIS) enrichment process as its future technology. The AVLIS process used lasers passing through high-temperature uranium metal vapor to selectively excite the ^{235}U isotope and separate it in order to produce reactor-grade enriched uranium. There were reports that although the physics of atomic laser separation were quite effective, the engineering obstacles associated with handling vaporous uranium metal may have been too difficult or costly to overcome.

Reacting the Fuel: Fission Reactions

After enrichment, the hexafluoride is turned into UO_2, which is made into pellets and these are assembled into fuel rods for the reactor.

In the reactor the nuclear fission chain reaction produces neutrons which cause further fission in U-235 atoms. The fission of a U-235 atom typically releases about 200 MeV*, or 3.2×10^{-11} Joule, (contrasting with 4 eV or 6.5×10^{-19} J per molecule of carbon dioxide released in the combustion of carbon). The fission reaction produces fission products such as Ba, Kr, Sr, Cs, I, and Xe with atomic masses distributed around 95 and 135.

For example,

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{236}_{92}U \begin{cases} \nearrow ^{160}_{62}Sm + ^{72}_{30}Zn + 4\,^{1}_{0}n + \text{energy} \\ \nearrow ^{146}_{57}La + ^{87}_{35}Br + 3\,^{1}_{0}n + \text{energy} \\ \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n + \text{energy} \\ \searrow ^{144}_{55}Cs + ^{90}_{37}Rb + 2\,^{1}_{0}n + \text{energy} \\ \searrow ^{144}_{54}Xe + ^{90}_{38}Sr + 2\,^{1}_{0}n + \text{energy} \end{cases}$$
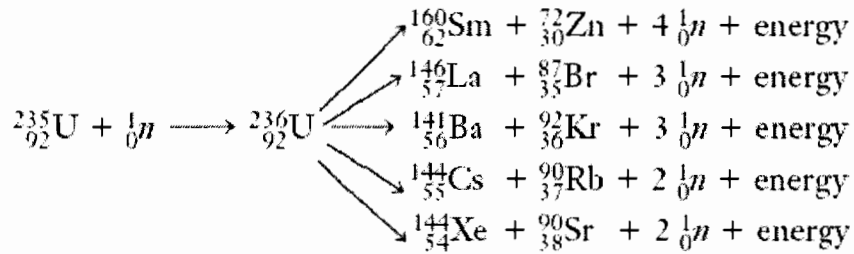
Neutrons released can induce reactions in other ^{235}U nuclei, which in turn release neutrons, propagating a chain reaction.
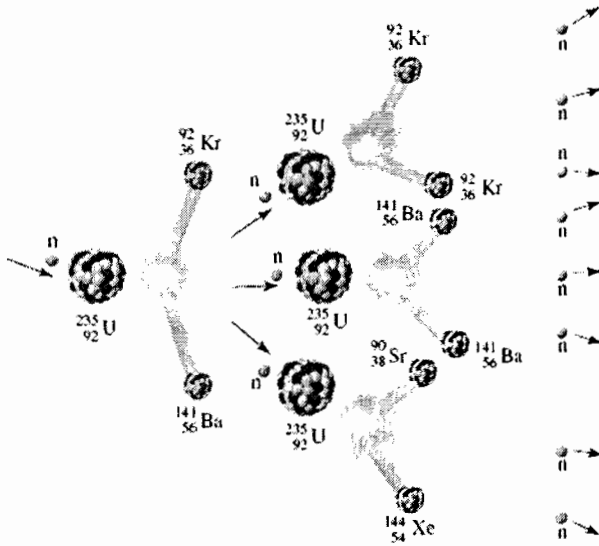
In a typical coal or nuclear power station making steam to turn turbines, the thermal efficiency is usually around 33%. That is to say, the energy released by combustion or fission results in about one third as much energy being produced as electricity.

The chain reaction is controlled by limiting the proximity of ^{235}U nuclei to other ^{235}U nuclei. In a reactor, this is done using "Control Rods," which contain B. B absorbs neutrons readily, limiting their reaction with other ^{235}U nuclei.

$$^{10}_{5}B + ^{1}_{0}n \longrightarrow ^{7}_{3}Li + ^{4}_{2}\alpha$$
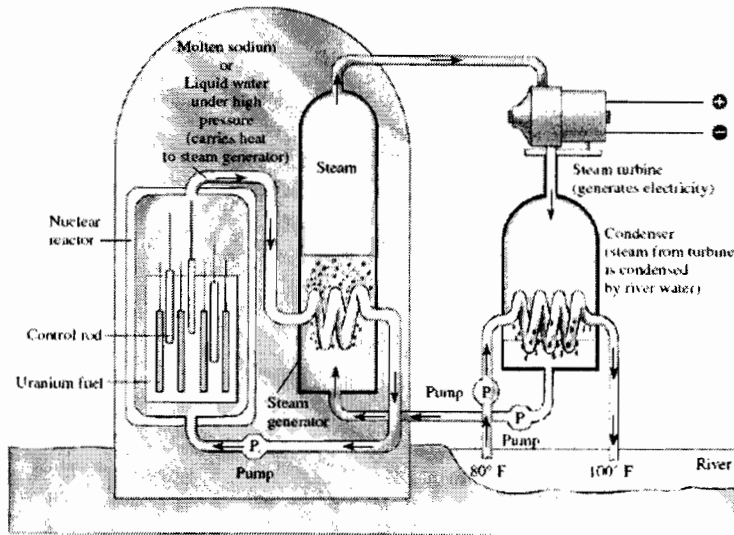
Fast neutron reactors (Also called fast breeder reactors)

Fast neutron reactors are a different technology from those considered so far. They generate power from plutonium by much more fully utilizing the uranium-238 in the reactor fuel assembly, instead of needing just the fissile U-235 isotope used in most reactors. If they are designed to produce more plutonium than they consume, they are called Fast Breeder Reactors (FBR). For many years the focus has been on the potential of this kind of reactor to produce more fuel than they consume, but today, with low uranium prices and the need to dispose of plutonium from military weapons stockpiles, the main interest is in their role as incinerators.

In the closed fuel cycle it can be seen that conventional reactors produce two "surplus" materials; plutonium (from neutron capture, separated in reprocessing) and depleted uranium (from enrichment). The fast neutron reactor uses plutonium as its basic fuel while at the same time converting depleted (or natural) uranium, basically U-238, comprising a "fertile blanket" around the core, into fissile plutonium. In other words it "burns" and can "breed" plutonium*, as shown in Figure 13. Depending on the design, it is possible to recover from reprocessing the spent fuel enough fissile plutonium for its own needs, with some left over for future breeder reactors or for use in conventional reactors.

Some of the U-238 in the reactor core becomes plutonium-239 and Pu-240. The Pu-239 is fissile in the same way as U-235, and typically releases about 210 MeV* per fission. Atomic masses of fission products are distributed around 100 and 135.

$$^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \xrightarrow[t_{1/2} = 23.4 \text{ min}]{\beta \text{ decay}} {}^{239}_{93}Np \xrightarrow[t_{1/2} = 2.35 \text{ days}]{\beta \text{ decay}} {}^{239}_{94}Pu$$
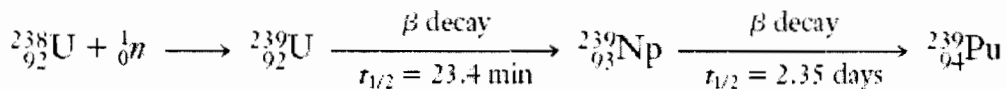
* Both U-238 and Pu-240 are "fertile" (materials), i.e. by capturing a neutron they become (directly or indirectly) fissile Pu-239 and Pu-241 respectively.

HYDROGEN
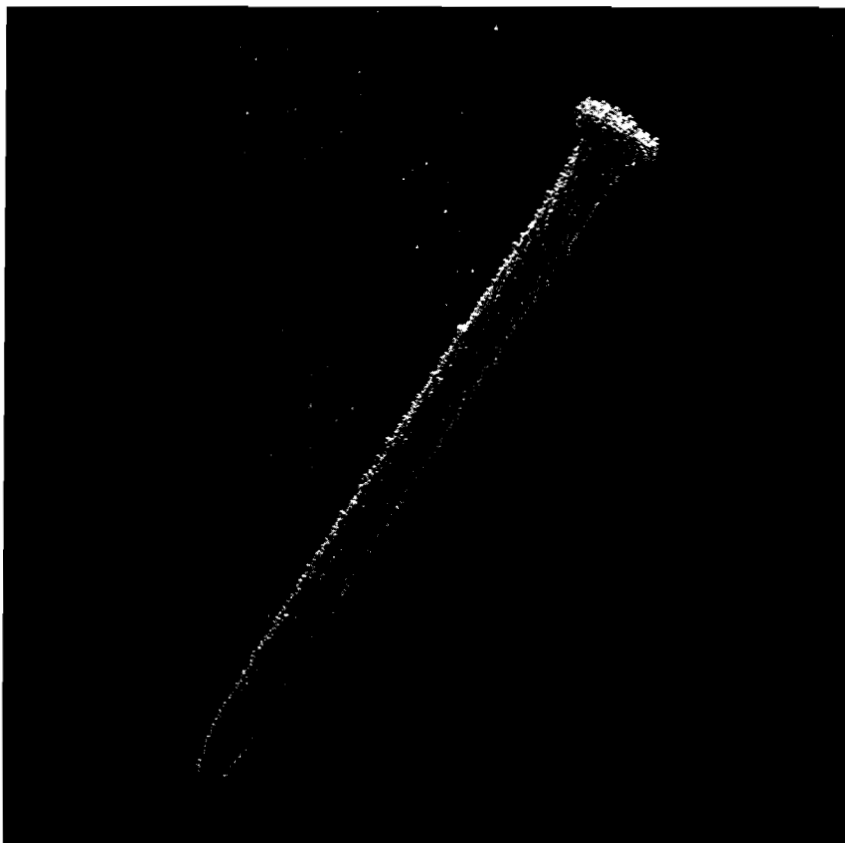
Iron metal reacts with dilute aqueous sulfuric acid to liberate hydrogen gas. Other reactive metals undergo similar reactions.

The ground-state electron configuration of atomic hydrogen is $1s^1$, so it is usually placed at the top of Group 1 in the periodic table because, like the Group 1 metals, it has a single electron in an outer s orbital. However, hydrogen is not a metal; rather, it exists as a diatomic gas under ordinary conditions. The oxidation states of hydrogen are $+1$, 0, and -1. The $+1$ oxidation state is exclusively covalent; the only ionic species is the -1 oxidation state of the *hydride ion*, H^-, which occurs in metallic hydrides formed from reactive metals and hydrogen. Because of its nonmetallic character and the existence of H^-, hydrogen is placed at the top of Group 7 in some versions of the periodic table.

Table 2-1 Isotopes of hydrogen

Isotope	Atomic mass/amu	Natural abundance/atom
^1_1H	1.0078	99.985
^2_1H (D)	2.0141	0.0148
^3_1H (T)	3.0160	minute trace (about 1 in 10^{18} hydrogen atoms)

■ On a mass basis hydrogen is the most exothermic fuel known.

Hydrogen gas has a lower molecular mass than that of any other gas and can be poured upward through the air from one container to another container. The low molecular mass of H_2 makes it the most effective gas for lighter-than-air balloons and aircraft. However, because hydrogen forms explosive mixtures with air, it is no longer used. Helium, being nonflammable, is now used for such applications. However, because of its low mass and its very exothermic reaction with oxygen, liquid hydrogen is used as a fuel in large booster rockets.

2-1 THERE ARE THREE HYDROGEN ISOTOPES

The element hydrogen, which has an atomic number of 1 and the lowest atomic mass (1.0079) of all the known elements, occurs as three different isotopes with mass numbers of 1, 2, and 3, respectively (Table 2-1). The mass 1 isotope is by far the most abundant of the three isotopes. The mass 2 isotope, which is called *deuterium,* is often denoted by the symbol D, and comprises only 1 out of about 6700 naturally occurring hydrogen atoms. Some of the physical properties of H_2 and D_2 are given in Table 2-2. The mass 3 isotope, which is called *tritium,* is often denoted by the symbol T, and comprises only about 1 out of 10^{18} hydrogen atoms. Tritium is radioactive and emits β particles (see Chapter 24 of the text).

$$^3_1\text{H} \rightarrow {}^3_2\text{He} + {}^{\ 0}_{-1}\text{e} \qquad t_{1/2} = 12.4 \text{ yr}$$

Naturally occurring tritium is produced in the upper atmosphere primarily by the reaction of cosmic ray neutrons with $^{14}_7\text{N}$:

$$^{14}_7\text{N} + \underset{\substack{\text{cosmic ray} \\ \text{neutron}}}{{}^1_0\text{n}} \rightarrow {}^3_1\text{H} + {}^{12}_6\text{C}$$
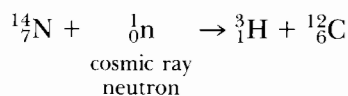
Tritium is produced for commercial use and in hydrogen bomb explosions by the reaction

$$^6_3\text{Li} + {}^1_0\text{n} \rightarrow {}^3_1\text{H} + {}^4_2\text{He}$$
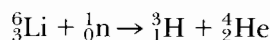
Atmospheric tritium levels increased over a hundredfold as the result of atmospheric nuclear tests during the 1950s.

Table 2-2 Physical properties of H_2 and D_2

Property	H_2	D_2
enthalpy of dissociation at 25°C/kJ · mol^{-1}	435.93	443.35
bond length/pm	74	74
melting point/K	14.0	18.7
boiling point/K	20.4	23.7
$\Delta \overline{H}^{\circ}_{vap}$/kJ · mol^{-1}	0.90	1.23
$\Delta \overline{H}^{\circ}_{fus}$/kJ · mol^{-1}	0.12	0.20
gas density at 0°C and 1 atm/g · L^{-1}	0.0899	0.180

2-2 HYDROGEN IS THE MOST ABUNDANT ELEMENT IN THE UNIVERSE

Under ordinary terrestrial conditions elemental hydrogen occurs as the colorless, odorless and tasteless diatomic gaseous molecule, H_2. Very little H_2 exists in the earth's crust or in the atmosphere, although some H_2 is found in volcanic gases and natural gas deposits. Hydrogen is rare in the atmosphere because it escapes the gravitational attraction of the earth. Most of the earth's hydrogen is combined with oxygen in water. Hydrogen also occurs frequently in combination with carbon, sulfur, and nitrogen and is a constituent of all plant and animal matter.

On a mass basis, hydrogen is the ninth ranked element in the earth's crust, comprising about 0.9 percent by mass of the crust, which includes the oceans. However, on an atomic basis, hydrogen comprises about 15 percent of the atoms in the earth's crust and ranks third in atomic abundance behind oxygen and silicon. Over 30 percent of the mass of the sun is atomic hydrogen, and most of the atoms in interstellar space are hydrogen atoms. On both an atomic basis and a mass basis, hydrogen is by far the most abundant element in the universe.

■ Ten percent by mass of the human body is hydrogen.

■ The name hydrogen, which was coined by Lavoisier, means water former.

2-3 HYDROGEN IS USUALLY PREPARED BY SINGLE-REPLACEMENT REACTIONS

Small quantities of hydrogen gas can be prepared in the laboratory by the reaction of zinc metal with aqueous hydrochloric acid:

$$Zn(s) + 2HCl(aq) \rightarrow H_2(g) + ZnCl_2(aq)$$
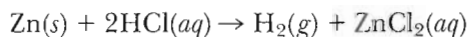
Any metal whose standard reduction voltage E^0 for the half-reaction

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$
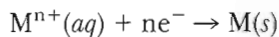
is less than zero volts (see Table 21-1 of the text) is capable of liberating $H_2(g)$ from aqueous acids. Hydrogen can also be prepared by the reaction of calcium metal with cold water (Figure 2-1):

$$Ca(s) + 2H_2O(l) \rightarrow H_2(g) + Ca(OH)_2(aq)$$
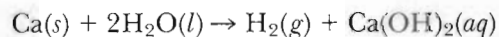
The Group 1 metals also react with water to produce hydrogen, but these reactions are too violent to use for the routine preparation of hydrogen. For example, the reaction of potassium metal with water in the presence of air usually results in an explosion (Figure 2-2).

$$2K(s) + 2H_2O(l) \rightarrow H_2(g) + 2KOH(aq)$$

Figure 2-1 Calcium metal reacts with cold water to produce hydrogen gas and calcium hydroxide.
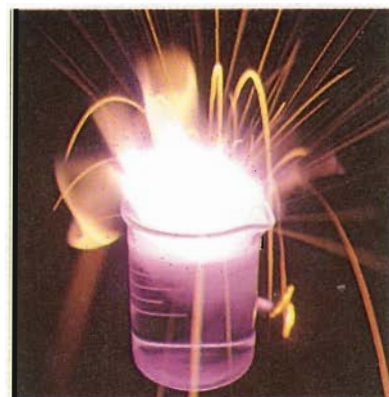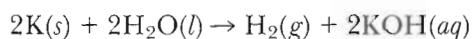
Figure 2-2 Potassium metal reacts explosively on contact with water.

The explosion occurs because the reaction of potassium with water is very fast and highly exothermic, and the resulting hot $H_2(g)$ reacts explosively with $O_2(g)$ in the air:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$
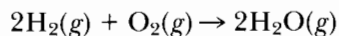
Hydrogen is prepared both commercially and for laboratory use by the electrolysis of aqueous solutions of sulfuric acid using either platinum or nickel electrodes (Figure 2-3).

$$2H_2O(l) \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)$$
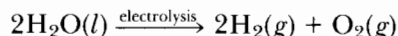
The role of the sulfuric acid is that of an electrolyte, carrying the ionic current through the solution and thereby decreasing the resistance of the solution. Numerous other electrolytes with nonoxidizable anions could be used. The half-reactions occurring at the cathode and the anode in the electrolysis of an $H_2SO_4(aq)$ solution are

$$4H^+(aq) + 4e^- \rightarrow 2H_2(g) \qquad \text{(cathode, reduction)}$$
$$2H_2O(l) \rightarrow 4H^+(aq) + 4e^- + O_2(g) \qquad \text{(anode, oxidation)}$$
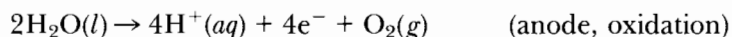
The sum of the two half-reactions gives the overall net reaction.

The major industrial methods for the preparation of hydrogen involve endothermic reactions of high-temperature steam with hydrocarbons from natural gas or oil-refinery sources using nickel catalysts. For example,

■ Over 200 million pounds of hydrogen are produced annually in the United States.
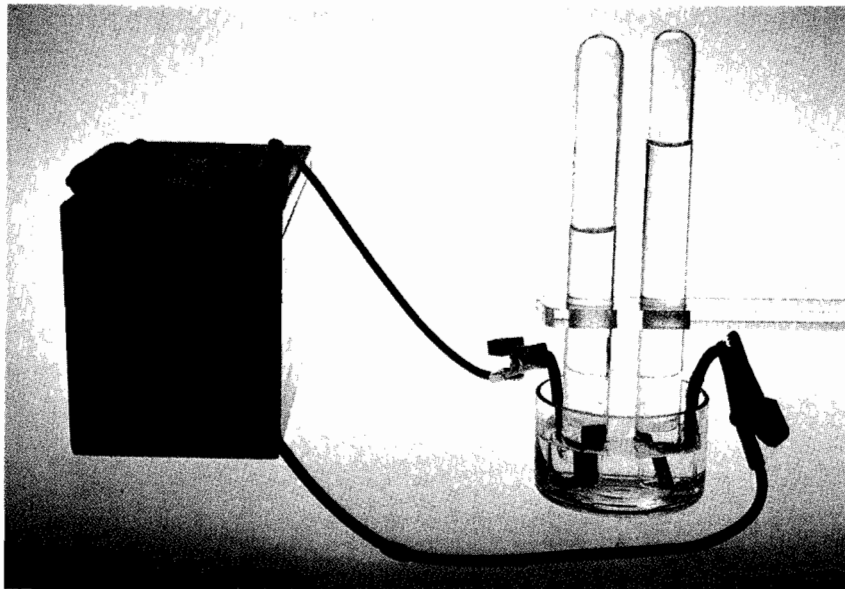
Figure 2-3 Preparation of hydrogen by electrolysis of an aqueous sulfuric acid solution. Hydrogen gas is liberated at the cathode, and oxygen gas is liberated at the anode. Note, as is required by the reaction stoichiometry, that the volume of $H_2(g)$ liberated is twice as great as that of $O_2(g)$.

$$CH_4(g) + H_2O(g) \xrightarrow[1000°C]{Ni} CO(g) + 3H_2(g) \qquad \Delta H^°_{rxn} = +206 \text{ kJ at } 25°C$$
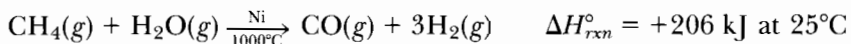
Another important industrial process for hydrogen production is the *water-gas reaction:*

$$C(coke) + H_2O(g) \xrightarrow[1000°C]{Fe \text{ or } Ru} CO(g) + H_2(g) \qquad \Delta H^°_{rxn} = +130 \text{ kJ at } 25°C$$
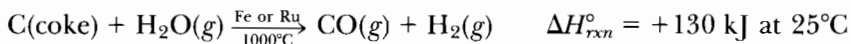
The coke is obtained by heating coal in the absence of oxygen to vaporize volatile constituents of the coal. In both of these processes, additional hydrogen is generated by reacting the carbon monoxide with additional steam at about 400°C over an iron oxide catalyst.

$$CO(g) + H_2O(g) \xrightarrow[400°C]{Fe_2O_3} CO_2(g) + H_2(g) \qquad \Delta H^°_{rxn} = -41.2 \text{ kJ at } 25°C$$
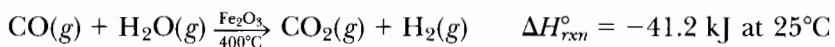
2-4 THE H$_2$ MOLECULE IS FAIRLY UNREACTIVE BECAUSE OF THE STRONG BOND

The molar enthalpy of dissociation of H_2 is $436 \text{ kJ} \cdot \text{mol}^{-1}$ at 25°C:

$$H_2(g) \rightarrow 2H(g) \qquad \Delta H^°_{rxn} = 436 \text{ kJ} \cdot \text{mol}^{-1}$$

and thus the single sigma bond ($1\sigma^2$) in H_2 is a relatively strong bond. The strong H—H bond makes H_2 a fairly unreactive molecule, because this bond must be broken in order for H_2 to react. The lack of reactivity of H_2 can be illustrated by the following data (25°C):

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \begin{aligned} \Delta H^°_{rxn} &= -242 \text{ kJ} \\ \Delta G^°_{rxn} &= -229 \text{ kJ} \end{aligned}$$

$$3H_2(g) + 2N_2(g) \rightarrow 2NH_3(g) \qquad \begin{aligned} \Delta H^°_{rxn} &= -92 \text{ kJ} \\ \Delta G^°_{rxn} &= -33 \text{ kJ} \end{aligned}$$
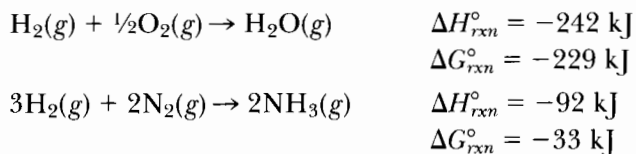
In both cases the reaction products are thermodynamically favored under standard conditions ($\Delta G^°_{rxn} < 0$), but if we prepare the reaction mixtures at 25°C, the reactions do not occur at a measurable rate. Although the $H_2 + O_2$ reaction can be initiated by a spark, most reactions involving H_2 require the presence of catalysts. For example, many reactions involving H_2 are catalyzed by platinum and palladium. These catalysts work by facilitating the dissociation of H_2 into H atoms on the surface of the metal:

$$H_2(g) \xrightarrow{Pt} 2H(\text{surface})$$
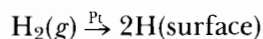
where the surface H atoms are attached to Pt atoms on the metal surface.
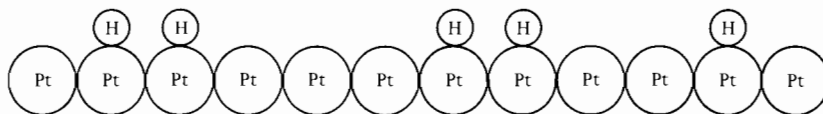
A dramatic illustration of the catalytic activity of platinum metal on hydrogen can be seen by passing hydrogen plus air over finely divided platinum. At room temperature, the platinum will glow sufficiently to ignite the hydrogen. When this process was first discovered in the early 1800s, it was used to produce lighters.

2-5 THE MAJOR INDUSTRIAL USE OF HYDROGEN IS IN THE SYNTHESIS OF AMMONIA

Ammonia is produced commercially by the *Haber process,* which involves the reaction

$$3H_2(g) + N_2(g) \xrightarrow[\text{300 atm, 500°C}]{\text{Fe + Mo}} 2NH_3(g)$$
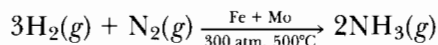
The activation energy for this reaction is $336 \text{ kJ} \cdot \text{mol}^{-1}$ in the absence of the catalyst and about $150 \text{ kJ} \cdot \text{mol}^{-1}$ in the presence of the catalyst. About 32 billion pounds of ammonia are produced annually in the United States via the above reaction (see Section 15-11 of the text for a more detailed discussion of the Haber process).

Large quantities of hydrogen are used in the platinum-and-nickel-catalyzed hydrogenation of unsaturated liquid vegetable oils to produce saturated solid fats, such as margarine. These addition reactions are of the type
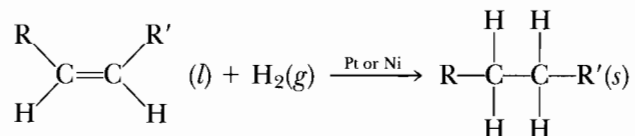
where R and **R'** are hydrocarbon segments. Hydrogen is also used on a large scale in the manufacture of various organic chemicals, especially methanol by the reaction

$$2H_2(g) + CO(g) \xrightarrow{\text{cobalt}} CH_3OH(l) \qquad \Delta G^\circ_{rxn} = -29 \text{ kJ at 25°C}$$
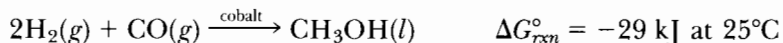
Hydrogen is also used in metallurgy to reduce metal oxides such as those of molybdenum and tungsten to the metal. For example,

$$MoO_3(s) + 3H_2(g) \xrightarrow[\text{600°C}]{} Mo(s) + 3H_2O(g)$$

When the catalytic effect of platinum metal on the combustion of hydrogen was discovered in the early 1800s, the process was used to produce cigar lighters, which became very fashionable.

The reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$
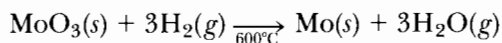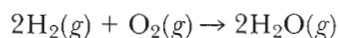
is used in the oxy-hydrogen torch. The oxy-hydrogen torch has a flame temperature of about 2500°C and is used in cutting and welding metals. The explosive reaction of the gases is prevented by mixing them just before they reach the burner orifice.

Temperatures of up to 4000°C are produced in the atomic hydrogen torch, where hydrogen atoms are generated in an electric arc and are allowed to recombine on a metal surface to produce H_2. The energy liberated by bond formation produces very high temperatures, which can be used to weld high-melting metals such as tungsten and tantalum.

2-6 METAL HYDRIDES ARE FORMED BY THE DIRECT REACTION OF ACTIVE METALS WITH H_2

The very reactive Group 1 and Group 2 metals react directly with H_2 to produce metal hydrides, which are white ionic crystals that contain the hydride ion, H^-.

$$2Na(s) + H_2(g) \rightarrow \quad 2NaH(s)$$
$$\text{sodium hydride}$$

$$Ca(s) + H_2(g) \rightarrow \quad CaH_2(s)$$
$$\text{calcium hydride}$$
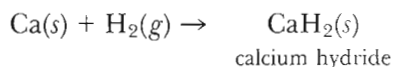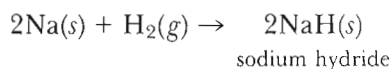
The reactions of the Group 2 metals with hydrogen are more vigorous than those of the Group 1 metals; for example, beryllium and magnesium burst into flame on reaction with hydrogen. The Group 1 and Group 2 metal hydrides are powerful reducing agents that liberate hydrogen from water; for calcium hydride,

$$CaH_2(s) + 2H_2O(l) \rightarrow H_2(g) + Ca(OH)_2(aq)$$
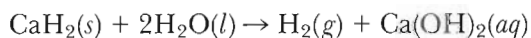
Some transition-metal hydrides have well-defined stoichiometry—for example, $TlH_2(s)$, $CuH(s)$, $CeH_2(s)$, and $CeH_3(s)$—but many others are *nonstoichiometric compounds*, in which the hydrogen atoms occupy cavities in the crystal lattice. Nonstoichiometric compounds are compounds in which the elements are not combined in definite small whole-number ratios. For example, hydrogen reacts with palladium to form a substance of the composition PdH_x, where the observed value of x ranges from zero to somewhat less than 1. The fact that x can have a continuous range of values is in sharp contrast to that of NaH, where the Na/H ratio is one.

Hydrogen forms more compounds than any other element. Compounds of hydrogen with the nonmetals are covalently bonded low-boiling, molecular compounds. These compounds are discussed under the individual groups of the elements.

An oxy-hydrogen torch. The flame temperature is about 2500°C.

Calcium hydride (CaH_2), a white crystalline ionic solid, reacts readily with water to produce hydrogen gas.

■ Nonstoichiometric compounds are called berthollide compounds.

TERMS YOU SHOULD KNOW

hydride ion
deuterium
tritium
water-gas reaction

Haber process
nonstoichiometric compound
berthollide compound

QUESTIONS

2-1. Using the data in Table 2-1, calculate the atomic mass of naturally occurring hydrogen.

2-2. Suggest how tritium can be used to study the movement of ground water.

2-3. Calculate the number of disintegrations per second in a sample consisting of one micromole of tritium.

2-4. A sample of water containing a trace amount of T_2O is found to have 1.12×10^4 disintegrations per second. What will be its activity after 50 years?

2-5. Complete and balance the following equations.

(a) $Fe_2O_3(s) + H_2(g) \xrightarrow{\text{high T}}$

(b) $LiH(s) + H_2O(l) \rightarrow$

(c) $Mg(s) + H_2(g) \rightarrow$

(d) $K(s) + H_2(g) \rightarrow$

(e) $H_2(g) + H_2C{=}CH_2(g) \xrightarrow{\text{Pt}}$

2-6. Complete and balance the following equations.

(a) $Zn(s) + HBr(aq) \rightarrow$

(b) $C(s) + H_2O(g) \xrightarrow[1000°C]{\text{Fe}}$

(c) $D_2(g) + N_2(g) \xrightarrow{\text{Fe/Mo}}$

(d) $Li(s) + D_2O(l) \rightarrow$

(e) $W(s) + H_2O(g) \xrightarrow{\text{high T}}$
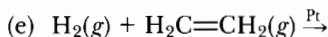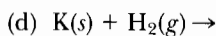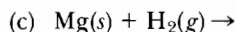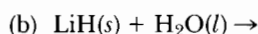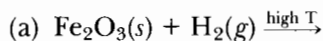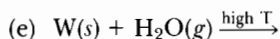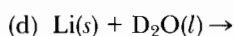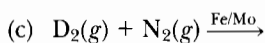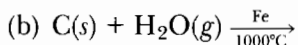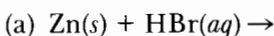
2-7. In the Three Mile Island nuclear power plant accident, a large quantity of hydrogen gas was produced in the high temperature reaction between steam and the zirconium metal in the fuel rod assemblies. Given that ZrO_2 is the formula for the zirconium oxide formed, write a balanced equation for the reaction.

2-8. Complete and balance the following equation:

$$C_3H_8(g) + H_2O(g) \xrightarrow[1000°C]{\text{Ni}}$$
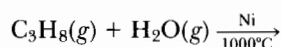
2-9. Lithium metal is often cleaned by treatment with ethanol, C_2H_5OH. By analogy with the reaction of $Li(s)$ with water, complete and balance the following equation:

$$Li(s) + CH_3CH_2OH(l) \rightarrow$$

2-10. Hydrogen is the most exothermic fuel on a mass basis. Suggest some reasons why hydrogen is not a widely used fuel.

2-11. How many grams of zinc are required to generate 500 mL of hydrogen at 20°C and 740 torr by the reaction between zinc and hydrochloric acid?

2-12. Calculate the relative masses of hydrogen produced by the reaction of hydrochloric acid with 100 g of iron and 100 g of zinc.

2-13. What volume of hydrogen at 250°C and 10.0 atm is required to reduce 2.50 metric tons of tungsten (VI) oxide to the metal?

2-14. Calculate the enthalphy of combustion of one gram of hydrogen.

2-15. Given that $\Delta G_{rxn}° = -191$ kJ at 25°C for the reaction

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$
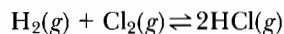
calculate the maximum voltage that can be obtained from a fuel cell utilizing this reaction with each gas at 1.00 atm pressure.

2-16. Given that $\Delta G_{rxn}° = -237$ kJ at 25°C for the reaction

$$H_2(g) + ½O_2(g) \rightleftharpoons H_2O(l)$$
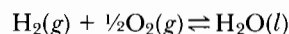
calculate the minimum voltage required to decompose water electrolytically.

THE ALKALI METALS

The reaction of sodium with water. The piece of molten sodium is propelled along the water surface by the evolved hydrogen. The production of NaOH(aq) is shown by the pink color of the acid-base indicator phenolphthalein, which is colorless in acidic or neutral solution and pink in basic solution. The heat of the reaction is sufficient to melt the sodium.

The Group 1 elements, lithium, sodium, potassium, rubidium, cesium, and francium, are reactive metals with electron configurations of the type [noble gas]ns^1. These elements attain a noble-gas electron configuration by the loss of one electron.

$$M\{[\text{noble gas}]ns^1\} \rightarrow M^+[\text{noble gas}] + e^-$$
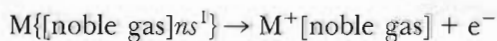
Because of their relatively low first-ionization energies and high second ionization energies, the chemistry of these elements involves primarily the metals and the +1 ions. As a family, the Group 1 metals show clearly the effect of increasing atomic

number on physical and chemical properties. Their atomic and ionic radii increase uniformly and their ionization energies decrease uniformly with increasing atomic number. With few exceptions, the reactivity of the Group 1 elements increases from lithium to cesium. As in all the s-block and p-block groups, the first member of a family differs in a number of respects from the other members. For example, although most salts of the Group 1 metals are soluble in water, a number of lithium salts (LiOH, LiF, Li_2CO_3) are only sparingly soluble. The anomalous properties of lithium can be attributed to its rather small ionic radius (76 pm). In fact, the radius of Li^+ is similar to that of Mg^{2+} (72 pm), and lithium has some chemical properties similar to those of magnesium. Many magnesium salts are less water soluble than the heavier members of Group 2. The similarity between lithium and magnesium is an example of a diagonal relationship between elements in the periodic table.

3-1 THE GROUP 1 ELEMENTS DO NOT OCCUR AS THE FREE METAL IN NATURE

Because the Group 1 metals have relatively low ionization energies, they are all very reactive and do not occur as the free metal in nature. Lithium is a fairly rare element, occurring in the earth's crust to the extent of about 20 ppm (parts per million) by mass. Because of its chemical similarity to magnesium, lithium is found associated with several magnesium minerals. The most important ore of lithium is *spodumene*, $LiAlSi_2O_6$, large deposits of which occur in South Dakota, Manitoba, the U.S.S.R., and Brazil. Lithium salts also occur in certain brine lakes in California and Nevada (Figure 3-1).

Sodium and potassium are the sixth and seventh most abundant elements, respectively, in the earth's crust. Vast deposits of the salts of both metals have resulted from the evaporation of ancient seas. Although a number of salts serve as commercial sources of these two metals, NaCl (*halite*) and KCl (*sylvite*) are the most important. Both rubidium and cesium occur in small quantities with the other alkali metals. There are no stable isotopes of francium; the longest-lived isotope is ^{223}Fr, with a half life of only 22 minutes. Table 3-1 summarizes the principal commercial sources and uses of the alkali metals.

Figure 3-1 Owens Lake, a brine lake in California near Death Valley.

3-2 THE PROPERTIES OF THE GROUP 1 METALS DEPEND UPON THE SIZE OF THE ATOMS

The Group 1 metals are all fairly soft and can be cut with a sharp knife (Figure 3-2). When freshly cut they are bright and shiny, but they soon take on a dull finish because of the reactions with

Table 3-1 The sources and uses of the alkali metals

Metal	Sources	Uses
lithium	spodumene, $LiAlSi_2O_6(s)$; certain mineral springs and salt lakes	alloys, organic reactions, degasification of copper
sodium	salt waters, $NaCl(s)$, $NaNO_3(s)$	synthesis of tetraethyllead, production of titanium metal, small nuclear reactor coolant
potassium	ancient ocean and salt lake beds; occurs in numerous mineral deposits at low levels, $KNO_3(s)$, $KCl(s)$	heat exchange alloys
rubidium	mineral springs (Searles Lake, Calif.; Manitoba; Michigan brines), certain rare minerals found in Elba	photocells; getter (O_2 remover) in vacuum tubes
cesium	water from certain mineral springs (Bernic Lake, Manitoba),	ion propulsion systems; atomic clocks

air (Figure 3-2). They must be stored under an inert substance such as kerosene, because they react spontaneously with oxygen and water vapor in air. The Group 1 metals are also called the *alkali metals,* because their hydroxides, MOH, are all soluble, strong bases in water (alkaline means basic). The atomic and

Figure 3-2 The Group 1 metals are soft. Here we see sodium being cut with a knife. Note the shiny surface of the freshly cut metal and the tarnished surface that results on exposure to air.

Table 3-2 The atomic properties of the Group 1 elements

Property	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium
chemical symbol	Li	Na	K	Rb	Cs	Fr
atomic number	3	11	19	37	55	87
atomic mass	6.941	22.98977	39.0983	85.4678	132.9054	(223)
number of naturally occurring isotopes	2	1	3	2	1	0
ground-state electron configuration	$[He]2s^1$	$[Ne]3s^1$	$[Ar]4s^1$	$[Kr]5s^1$	$[Xe]6s^1$	$[Rn]7s^1$
atomic radius/pm	145	180	220	235	266	~290
ionic radius/pm	60	95	133	148	169	~185
first ionization energy of $M(g)$/ $kJ \cdot mol^{-1}$	520	496	419	403	376	~370
Pauling electronegativity	1.0	0.9	0.8	0.8	0.7	0.7

physical properties of the alkali metals are given in Tables 3-2 and 3-3, respectively.

The periodic trends of the alkali metals are easily seen in the data given in Tables 3-2 and 3-3. The first ionization energy and the electronegativity decrease as we go down the group, whereas the atomic radius and ionic radius increase (Table 3-2). These trends are a direct consequence of the increase in size of the atoms resulting from the increase in the number of electrons with increasing atomic number.

In Table 3-3 we note that as we descend the group, there is a decrease in the melting and boiling points and in the enthalpies of fusion and vaporization. All these decreases are a result of the increasing size of the alkali metals as we move down the group. The increase in density as we descend the group is a consequence of the increase in atomic mass.

• Lithium is the least dense of all the elements that are solid or liquid at 20°C.

Table 3-3 The physical properties of the Group 1 elements

Property	Lithium	Sodium	Potassium	Rubidium	Cesium
melting point/°C	181	98	64	39	29
boiling point/°C	1347	892	774	696	670
density at 20°C/g $\cdot$ cm^{-3}	0.53	0.97	0.86	1.53	1.88
$\Delta \overline{H}_{fus}$/kJ $\cdot$ mol^{-1}	2.93	2.64	2.39	2.20	2.09
$\Delta \overline{H}_{vap}$/kJ $\cdot$ mol^{-1}	148	99	79	76	67
E^0/V at 25°C for $M^+(aq) + e^- \rightarrow M(s)$	−3.05	−2.71	−2.93	−2.93	−2.92
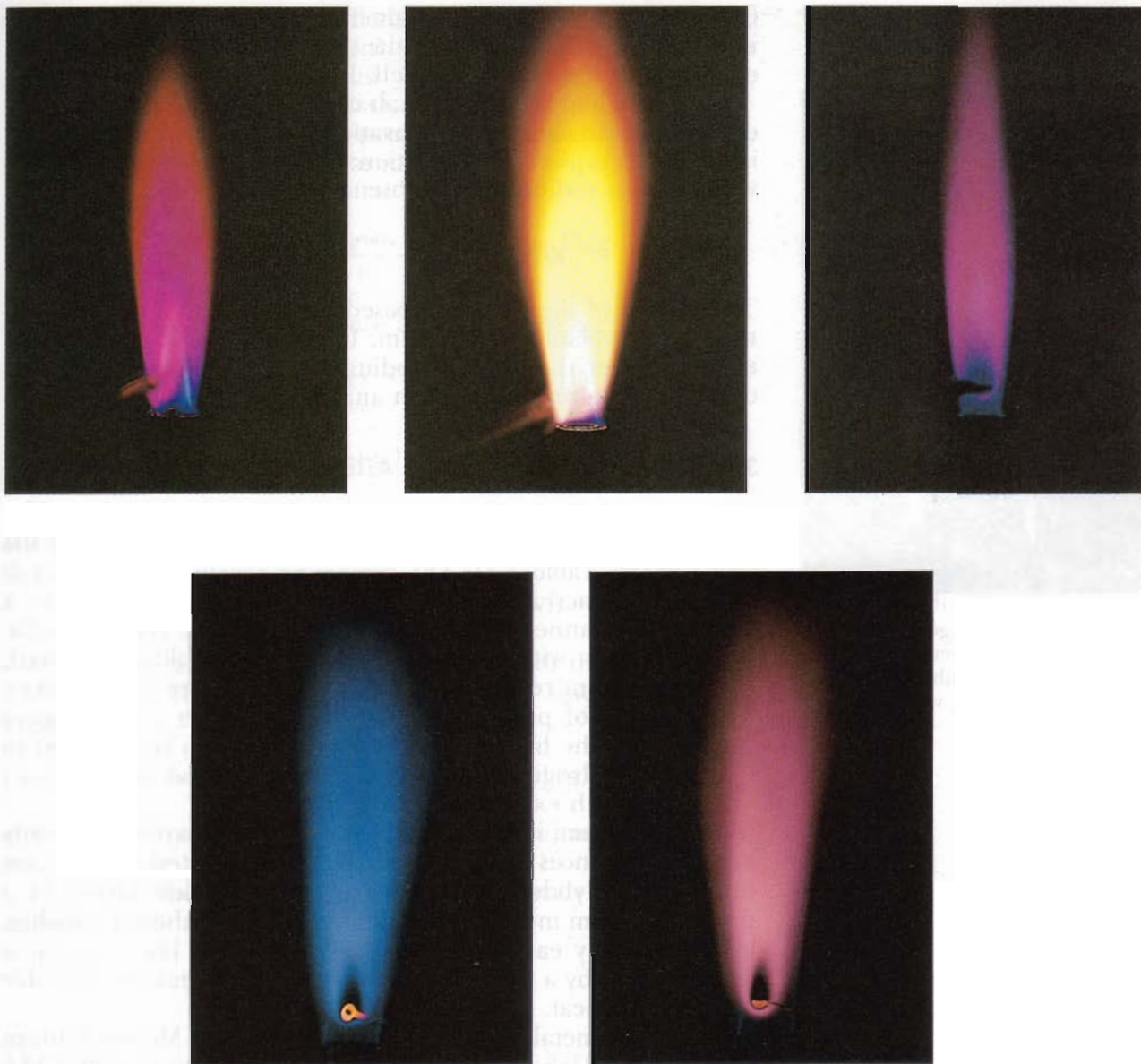
Flames of the Group 1 metals. In the top row from the left: lithium (crimson), sodium (yellow), and potassium (violet); in the second row, rubidium (blue) and cesium (pale violet). The colors, which arise from electronic transitions in the electronically excited metal atoms, are used in qualitative analysis to detect the presence of alkali metal ions in a sample. Ions are reduced to the gaseous metal atoms in the lower central region of the flame.

3-3 THE ALKALI METALS CAN BE OBTAINED BY ELECTROLYSIS OF THE MOLTEN CHLORIDES

Sodium metal is obtained by electrolysis of molten mixtures of sodium chloride and calcium chloride:

$$2NaCl \text{ [in } CaCl_2(l)] \xrightarrow[600°C]{\text{electrolysis}} 2Na(l) + Cl_2(g)$$
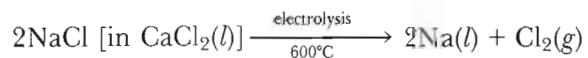
Cesium (which is a gold color) and rubidium (silver). They are stored in vacuum tubes to prevent them from reacting with the air.

Chlorine gas is a useful by-product of the electrolysis. The $CaCl_2$ is added to the NaCl to lower the temperature necessary for the operation of the electrolysis cell. Pure NaCl melts at 800°C.

Potassium and the other alkali metals also can be obtained by electrolysis. An alternate preparation of, for example, potassium involves the replacement reaction of molten potassium chloride with gaseous sodium in the absence of air.

$$KCl(l) + Na(g) \xrightarrow{780°C} NaCl(s) + K(g)$$
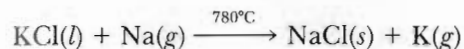
The success of the process is based on the fact that potassium is much more volatile than sodium. The boiling point of potassium is 118°C lower than that of sodium (Table 3-3). Rubidium and cesium can be produced in an analogous manner.

3-4 GROUP 1 COMPOUNDS ARE GENERALLY IONIC, WATER-SOLUBLE SALTS

The alkali metals react directly with all the nonmetals except the noble gases (Table 3-4). The increasing reactivity of the alkali metals with increasing atomic number is demonstrated in a spectacular manner by their reaction with water. When metallic lithium reacts with water, hydrogen gas is slowly evolved, whereas sodium reacts vigorously with water (see frontispiece). The reaction of potassium with water produces a fire (Figure 2-2) because the heat generated by the reaction is sufficient to ignite the hydrogen gas evolved. Rubidium and cesium react with water with explosive violence.

Molten lithium is an exceedingly reactive substance. The only known substances that do not react with molten lithium are tungsten, molybdenum, and low-carbon stainless steels. If a piece of lithium metal is melted in a glass tube, then the molten lithium rapidly eats a hole through the glass. The reaction is accompanied by a brilliant green-yellow flame and considerable evolution of heat.

The alkali metals react directly with oxygen. Molten lithium ignites in oxygen to form $Li_2O(s)$; the reaction is accompanied by

Table 3-4 Some of the more common reactions of the alkali metals

reaction with oxygen	reaction with water
$4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$	$2M(s) + 2H_2O(l) \rightarrow 2MOH(s) + H_2(g)$
$2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$	
$K(s) + O_2(g) \rightarrow KO_2(s)$	reaction with sulfur
$Cs(s) + O_2(g) \rightarrow CsO_2(s)$	$2M(s) + S(s) \rightarrow M_2S(s)$
$Rb(s) + O_2(g) \rightarrow RbO_2(s)$	
	reaction with hydrogen
reaction[a] with halogens	$2M(s) + H_2(g) \xrightarrow{500-800°C} 2MH(s)$
(denoted by X_2)	
	reaction with nitrogen[b]
$2M(s) + X_2 \rightarrow 2MX(s)$	$6M(s) + N_2(g) \xrightarrow{600°C} 2M_3N(s)$

[a] M(s) denotes any one of the alkali metals.
[b] Li(s) reacts with N_2 at room temperature.

a bright red flame. The reactions of the other alkali metals do not yield the oxides M_2O. With sodium the *peroxide* Na_2O_2 is formed, and with potassium, rubidium, and cesium the *superoxides* KO_2, RbO_2, and CsO_2 are formed.

Both sodium peroxide and potassium superoxide are used in self-contained breathing apparatus. In the case of Na_2O_2, the relevant reaction is

$$2Na_2O_2(s) + \underset{\text{exhaled air}}{2CO_2(g)} \rightarrow 2Na_2CO_3(s) + O_2(g)$$
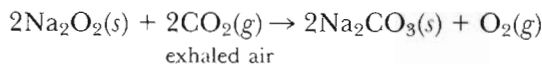
and in the case of $KO_2(s)$, there are two key reactions:

$$4KO_2(s) + \underset{\text{exhaled air}}{2H_2O(g)} \rightarrow 3O_2(g) + 4KOH(s)$$

$$KOH(s) + CO_2(g) \rightarrow KHCO_3(s)$$
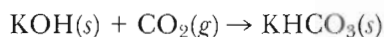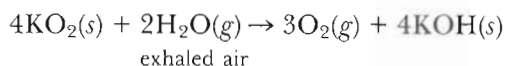
The alkali metals react directly with hydrogen at high temperatures to form hydrides. For example,

$$2Na(l) + H_2(g) \xrightarrow{500°C} 2NaH(s)$$
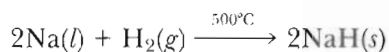
The alkali metal hydrides are ionic compounds that contain the hydride ion, H^-. The hydrides react with water to liberate hydrogen,

$$NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$$
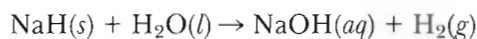
and are used to remove traces of water from organic solvents. In such cases, the metal hydroxide precipitates from the solution.

Lithium is the only element that reacts directly with nitrogen at room temperature:

$$6Li(s) + N_2(g) \rightarrow \underset{\text{lithium nitride}}{2Li_3N(s)}$$
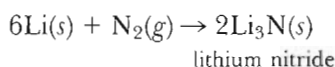
The other alkali metals react with $N_2(g)$ at higher temperatures.

Compounds of the alkali metals are for the most part white, high-melting ionic solids. With very few exceptions, alkali metal salts are soluble in water and the resulting solutions are electrolytic as a result of the dissociation of the salt into its constituent ions. As noted earlier, some lithium salts are insoluble in water.

The alkali metals have the unusual property of dissolving in liquid ammonia to yield a blue electrolytic solution. The properties of such a solution are interpreted in terms of *solvated electrons* and alkali metal ions:

$$M(s) \xrightarrow[NH_3(l)]{} M^+(amm) + e^-(amm)$$
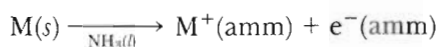
When the blue solutions are concentrated by evaporation, they become bronze in color and behave like liquid metals.

Lithium nitride, Li_3N.

■ Anions of the alkali metals (alkalide ions) can be prepared by dissolving the metal in ethylenediamine, $H_2NCH_2CH_2NH_2$, in the presence of certain organic chelating agents; on cooling, a salt of the type $Na^+(chelate)Na^-$ forms, which involves the alkalide ion Na^-.

3-5 MANY ALKALI METAL COMPOUNDS ARE IMPORTANT COMMERCIALLY

Sodium hydroxide is the seventh ranked industrial chemical. Over 20 billion pounds of it is produced annually in the United States. Sodium hydroxide sometimes is called *caustic soda* and is prepared by the electrolysis of concentrated aqueous sodium chloride solutions:

$$2NaCl(aq) + 2H_2O(l) \xrightarrow{\text{electrolysis}} 2NaOH(aq) + H_2(g) + Cl_2(g)$$
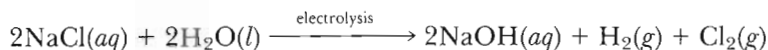
or by the reaction between calcium hydroxide (called slaked lime) and sodium carbonate:

$$Na_2CO_3(aq) + Ca(OH)_2(aq) \rightarrow 2NaOH(aq) + CaCO_3(s)$$
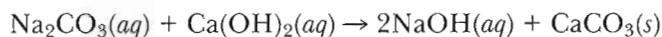
The formation of the insoluble $CaCO_3$ is a driving force for this second reaction. The alkali metal hydroxides are white, translucent, corrosive solids that are extremely soluble in water; at 20°C the solubility of NaOH is 15 M and that of KOH is 13 M.

Sodium carbonate, which is called *soda ash*, is the tenth ranked industrial chemical. The annual United States production of sodium carbonate exceeds 16 billion pounds. It is prepared from sodium chloride by the *Solvay process,* which was devised by the Belgian brothers Ernest and Edward Solvay in 1861. In this process, carbon dioxide is bubbled through a cooled solution of sodium chloride and ammonia. The reactions are

$$NH_3(aq) + CO_2(aq) + H_2O(l) \rightarrow NH_4^+(aq) + HCO_3^-(aq)$$

$$NaCl(aq) + NH_4^+(aq) + HCO_3^-(aq) \xrightarrow{15°C}$$

$$NaHCO_3(s) + NH_4Cl(aq)$$
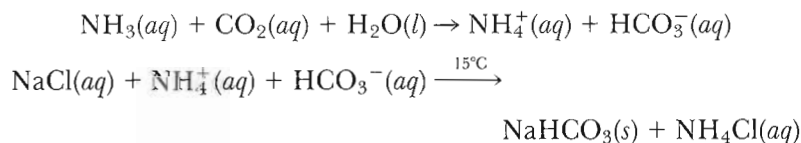
At 15°C the sodium hydrogen carbonate precipitates from the solution. Part of the sodium hydrogen carbonate is converted to sodium carbonate by heating:

$$2NaHCO_3(s) \xrightarrow{80°C} Na_2CO_3(s) + H_2O(l) + CO_2(g)$$
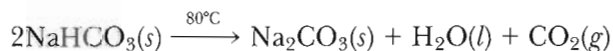
The carbon dioxide produced in this reaction is used again in the first reaction.

The commercial success of the Solvay process requires the recovery of the ammonia, which is relatively expensive. The ammonia is recovered from the NH_4Cl by the reaction

$$2NH_4Cl(aq) + Ca(OH)_2(s) \rightarrow 2NH_3(g) + CaCl_2(aq) + 2H_2O(l)$$
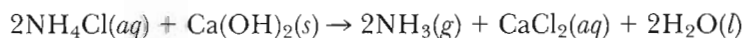
The calcium hydroxide and the carbon dioxide used in the process are obtained by heating limestone (primarily $CaCO_3$).

The raw materials of the Solvay process are ammonia, sodium chloride, limestone, and water. The ammonia is recovered, and

■ About 90 percent of the soda ash produced in the U.S. is obtained from natural deposits of the mineral *trona*, which is $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O(s)$.

the other three substances are inexpensive. The principal use of sodium carbonate is in the manufacture of glass.

Some other important alkali metal compounds and their uses are given in Table 3-5.

Table 3-5 Some commercially important alkali metal compounds and their uses

Compound	Uses
lithium aluminum hydride, $LiAlH_4(s)$	production of many pharmaceuticals, perfumes, and organic chemicals
lithium borohydride, $LiBH_4(s)$	strong reducing agent, used in organic synthesis
lithium carbonate, $Li_2CO_3(s)$	to treat schizophrenia
lithium fluoride, $LiF(s)$	flux for aluminum soldering and welding; large crystals used as prisms in infrared spectrometers
sodium hydrogen carbonate (sodium bicarbonate), $NaHCO_3(s)$	manufacture of effervescent salts and beverages, baking powder, gold plating
sodium carbonate, $Na_2CO_3(s)$	manufacture of glass, pulp and paper, soaps and detergents, textiles
sodium hydroxide, $NaOH(s)$	production of rayon, cellulose, paper, soaps, detergents, textiles, oven cleaner
sodium sulfate decahydrate (Glauber's salt), $Na_2SO_4 \cdot 10H_2O(s)$	solar heating storage, air conditioning
sodium bisulfite, $NaHSO_3(s)$	disinfectant and bleaching agent
sodium and potassium chlorite, $NaClO_3(s)$ and $KClO_3(s)$	explosives, fireworks, and matches; weed killer
sodium cyanide, $NaCN(s)$	extraction of gold and silver from ores; electroplating solutions; fumigant for fruit trees
sodium peroxide, $Na_2O_2(aq)$	bleaching agent, air purifier
potassium carbonate (potash), $K_2CO_3(s)$	manufacture of special glass for optical instruments and electronic devices, soft soaps
potassium nitrate, $KNO_3(s)$	pyrotechnics, explosives, matches; tobacco treatment
potassium permanganate(s), $KMnO_4$	decolorizer, bleaching agent, manufacture of saccharine
dipotassium hydrogen phosphate(s), K_2HPO_4	buffer agent
cesium bromide, $CsBr(s)$, and cesium iodide, $CsI(s)$	spectrometer prisms, fluorescent screens
cesium chloride, $CsCl(s)$	brewing, mineral waters

TERMS YOU SHOULD KNOW

spodumene
halite
sylvite
alkali metals
peroxide

superoxide
caustic soda
soda ash
Solvay process

QUESTIONS

3-1. Why must the alkali metals be stored under kerosene?

3-2. Explain why the reactivities of the alkali metals increase with atomic number.

3-3. How is sodium metal produced commercially?

3-4. What are the raw materials in the Solvay process? Write chemical equations for the reactions in this process.

3-5. Complete and balance the following equations.
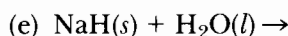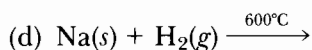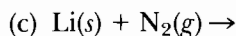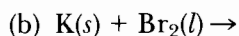
(a) $Na(s) + H_2O(l) \rightarrow$

(b) $K(s) + Br_2(l) \rightarrow$

(c) $Li(s) + N_2(g) \rightarrow$

(d) $Na(s) + H_2(g) \xrightarrow{600°C}$

(e) $NaH(s) + H_2O(l) \rightarrow$

3-6. Complete and balance the following equations.

(a) $Li(s) + O_2(g) \rightarrow$

(b) $Na(s) + O_2(g) \rightarrow$

(c) $K(s) + O_2(g) \rightarrow$

(d) $Cs(s) + O_2(g) \rightarrow$

3-7. Complete and balance the following equations

(a) $KO_2(s) + H_2O(g) \rightarrow$

(b) $Na_2O_2(s) + CO_2(g)$

(c) $NaOH(s) + CO_2(g) \rightarrow$

(d) $NaNH_2(s) + H_2O(l) \rightarrow$
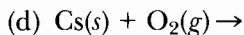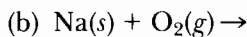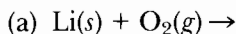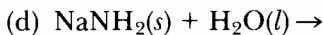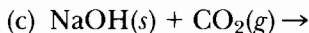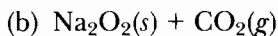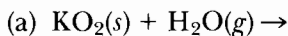
3-8. The sodium-sulfur battery has been extensively studied as a potential power source for electric powered vehicles. This high-temperature battery uses the elements sodium and sulfur in molten form. Write the anode and cathode half-reactions and the net cell reaction on discharge.

3-9. Explain why sodium metal cannot be prepared by the electrolysis of an $NaCl(aq)$ solution.

3-10. Solutions of sodium metal in liquid ammonia decompose in the presence of a rusty nail, liberating hydrogen gas and forming a white precipitate. Postulate a balanced chemical equation to explain these observations. Formulate your answer by analogy with the reaction between sodium metal and water.

3-11. Sodium peroxide is prepared by first oxidizing sodium to Na_2O in a limited supply of $O_2(g)$ and then reacting this further to give Na_2O_2. Why can't the peroxides of potassium, rubidium, and cesium be prepared in this manner?

3-12. Use molecular orbital theory (Section 12-13 in the text) to argue that the superoxide ion is paramagnetic, and that the peroxide ion is diamagnetic (not paramagnetic).

3-13. Sodium hydride is used to extract titanium from $TiCl_4$ according to

$$TiCl_4(g) + 4NaH(s) \xrightarrow{400°C} Ti(s) + 4NaCl(s) + 2H_2(g)$$
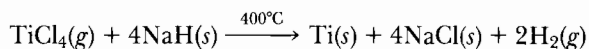
How many grams of NaH are required to react with one kilogram of $TiCl_4$?

3-14. Sodium hydride reacts with SO_2 to produce sodium dithionite, $Na_2S_2O_4$, according to

$$2SO_2(l) + 2NaH(s) \rightarrow Na_2S_2O_4(s) + H_2(g)$$
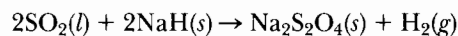
How many grams of sodium dithionite can be obtained from 100 grams of NaH?

3-15. Potassium superoxide is used in self-contained breathing apparatus. What volume of oxy-

gen (37°C and 1.0 atm) can be obtained from 454 g KO_2?

3-16. Lithium peroxide is used as an oxygen source for self-contained breathing apparatus on space capsules. The relevant reaction is

$$2Li_2O_2(s) + 2CO_2(g) \rightarrow 2Li_2CO_3(s) + O_2(g)$$
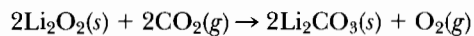
What volume of oxygen (at 37°C and 1.0 atm) can be obtained from 454 g Li_2O_2?

3-17. Use the data in Table 3-3 to compute the values of $\Delta\overline{S}_{vap}$ for the alkali metals. Explain briefly why the $\Delta\overline{S}_{vap}$ values are similar. (Hint: Recall Trouton's rule.)

THE ALKALINE EARTH METALS

The Group 2 elements. Top row; beryllium, magnesium, and calcium. Bottom row; strontium and barium.

The Group 2 elements, beryllium, magnesium, calcium, strontium, barium, and radium, are reactive metals with electron configurations of the type [noble gas]ns^2. These elements attain a noble-gas electron configuration by the loss of the two electrons in the outermost s orbital.

$$M\{[\text{noble gas}]ns^2\} \rightarrow M^{2+}[\text{noble gas}] + 2e^-$$
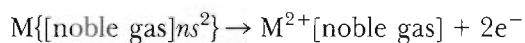
They are not as reactive as the Group 1 metals, but they are much too reactive to be found in the free state in nature.

The Group 2 metals also are called the *alkaline earth metals*. Beryllium is a relatively rare element, but occurs as localized

Table 4-1 Major sources and uses of the alkaline earth metals

Metal	Sources	Uses
beryllium	beryllium aluminum silicates, including *beryl*, $Be_3Al_2Si_6O_{18}$	lightweight alloys (improves corrosion resistance and resistance to fatigue and temperature changes); gyroscopes; nuclear reactors (absorbs neutrons); windows in X-ray tubes
magnesium	*dolomite*, $CaMg(CO_3)_2$; carbonates and silicates; seawater and well brines	alloys for airplanes; flashbulbs; pyrotechnics (white flame); batteries; corrosion protection for metals
calcium	*limestone*, $CaCO_3$; *gypsum*, $CaSO_4 \cdot 2H_2O$; *fluorite*, CaF_2; *apatite*, $Ca_{10}(OH)_2(PO_4)_6$ (major constituent of tooth enamel)	alloys; "getter" (removes gases from electronic tubes); production of chromium and other metals
strontium	*celestite*, $SrSO_4$; *strontianite*, $SrCO_3$	alloys and "getter"
barium	*witherite*, $BaCO_3$; *barite*, $BaSO_4$	lubricant on rotors of anodes in vacuum X-ray tubes; spark-plug alloys
radium	*pitchblende* and *carnotite* ores	skin cancer treatments

surface deposits of the mineral *beryl* (Figure 4-1). Essentially unlimited quantities of magnesium are readily available in seawater, where $Mg^{2+}(aq)$ occurs at a concentration of 0.054 M. Calcium, strontium, and barium rank 5th, 18th, and 19th in abundance in the earth's crust, occurring primarily as carbonates and sulfates (Table 4-1). All isotopes of radium are radioactive, with the longest-lived one (Ra-226) having a half-life of 1600 years.

The chemistry of the Group 2 elements involves primarily the metals and the +2 ions. With few exceptions the reactivity of the Group 2 elements increases from beryllium to barium. As in all the *s*-block and *p*-block groups, the first member of the family differs in several respects from the other members of the family. The anomalous properties of beryllium are attributed to the very small ionic radius of Be^{2+}. The radius of Be^{2+} is similar to that of Al^{3+}, and beryllium(II) has some chemical properties like those of aluminum(III), in keeping with the diagonal relationships found between the first member of a group and the second member of the following group.

The atomic and physical properties of the Group 2 elements are given in Tables 4-2 and 4-3. The periodic trends in the atomic properties of the Group 2 elements are shown clearly in the data in Table 4-2, except for radium, which in some cases appears anomalous. As we go down the group, the ionization

Figure 4-1 The mineral beryl $Be_3Al_2Si_6O_{18}$, occurs in light-green hexagonal prisms. Beryl is the chief source of beryllium and is used as a gem.

Smithsonian

Table 4-2 The atomic properties of the Group 2 elements

Property	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
chemical symbol	Be	Mg	Ca	Sr	Ba	Ra
atomic number	4	12	20	38	56	88
atomic mass	9.0218	24.305	40.08	87.62	137.33	(223)
number of naturally occurring isotopes	1	3	6	4	7	4
Ground-state electron configuration	$[He]2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$	$[Rn]7s^2$
atomic radius/pm	110	160	190	210	220	225
ionic radius of M^{2+} ion/pm	31	65	94	110	129	150
sum of first and second ionization energies of $M(g)$/ $kJ \cdot mol^{-1}$	2656	2187	1734	1608	1462	~1480
Pauling electronegativity	1.5	1.2	1.0	1.0	0.9	0.9

energy and the electronegativity decrease, whereas the atomic radii and ionic radii increase. These trends are a direct consequence of the increase in size of the atoms and ions with increase in atomic number.

The molar enthalpies of fusion and vaporization decrease (except for Ra) as we descend the group because of the increase in size of the atoms. The standard reduction voltages, E^0, become more negative as we descend the group, which is opposite to the trend exhibited by the Group 1 metals. The melting points, boiling points, and densities show irregularities in their trends, which are not explained easily.

Table 4-3 The physical properties of the Group 2 elements

Property	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
melting point/°C	1278	651	845	769	725	~700
boiling point/°C	2970	1107	1487	1384	1740	~1740
density at 20°C/g $\cdot$ cm^{-3}	1.85	1.74	1.55	2.54	3.51	6.0
$\Delta \overline{H}_{fus}$/kJ $\cdot$ mol^{-1}	9.8	9.2	9.1	8.2	7.5	8.0
$\Delta \overline{H}_{vap}$/kJ $\cdot$ mol^{-1}	140	95	80	76	65	110
E^0/V at 25°C for $M^{2+}(aq) + 2e^- \rightarrow M(s)$	-1.85	-2.36	-2.87	-2.89	-2.91	-2.92

4-1 THE SMALL SIZE OF Be²⁺ MAKES THE CHEMISTRY OF BERYLLIUM DIFFERENT FROM THAT OF THE OTHER GROUP 2 METALS

The chemistry of beryllium is significantly different from that of the other Group 2 elements, because of the small size of the Be^{2+} ion. All Be(II) compounds involve appreciable covalent bonding and there are no crystalline compounds or solutions involving Be^{2+} as such. The other Group 2 metals have larger sizes and lower ionization energies, making them more electropositive than beryllium. As a consequence, the ionic nature of the compounds of the alkaline earth metals increases down through the group.

Beryllium metal is steel gray, light, very hard, and high-melting. The free element is prepared on a commercial scale by electrolysis of the halides and by reduction of BeF_2 with magnesium.

Beryllium metal is fairly unreactive at room temperature. Hot (400°C) beryllium metal reacts with oxygen to form the oxide, $BeO(s)$, with nitrogen to form the nitride, $Be_3N_2(s)$, and with halogens to form the halides, BeX_2. Some of the more common reactions of beryllium are diagrammed in Figure 4-2. Beryllium is amphoteric. Aqueous solutions of Be(II) salts are acidic, owing to the acid dissociation of $Be(H_2O)_4^{2+}(aq)$:

$$Be(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons BeOH(H_2O)_3^+ + H_3O^+(aq)$$
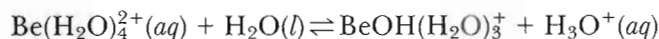
In strong base the $Be(H_2O)_4^{2+}(aq)$ ion is converted to the beryllate ion, $Be(OH)_4^{2-}$:

$$Be(H_2O)_4^{2+}(aq) + 4OH^-(aq) \rightarrow Be(OH)_4^{2-}(aq) + 4H_2O(l)$$
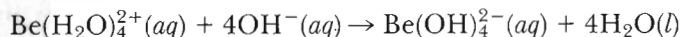
4-2 MAGNESIUM, CALCIUM, STRONTIUM, AND BARIUM FORM IONIC COMPOUNDS INVOLVING M²⁺ IONS

The alkaline earth metals are prepared by electrolysis. Magnesium, calcium, strontium, and barium are prepared by high-temperature electrolysis of the molten chloride; for example,

$$CaCl_2(l) \xrightarrow[\text{high T}]{\text{electrolysis}} Ca(l) + Cl_2(g)$$
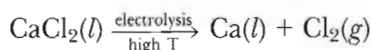
The metals Mg, Ca, Sr, Ba, and Ra are silvery-white in appearance when freshly cut, but tarnish readily in air to form the metal oxide. The free metals have limited commercial use (Table 4-1). The metals are highly electropositive and readily form M^{2+} ions. The alkaline earth $M^{2+}(aq)$ ions are neutral in aqueous solution.

The alkaline earth metals react rapidly with water, but the rates of these reactions are much lower than those for the alkali
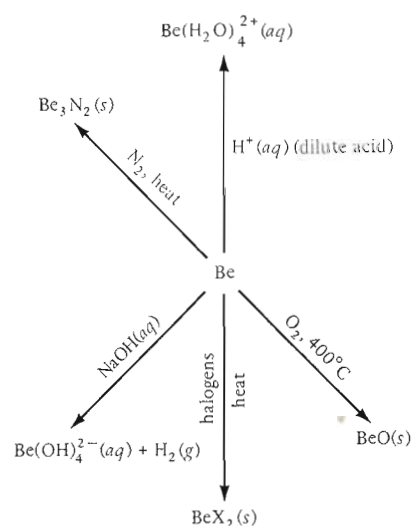
Figure 4-2 Some reactions of beryllium.

metals. Beryllium and magnesium react slowly with water at ordinary temperatures, although hot magnesium reacts violently with water.

The alkaline earth metals burn in oxygen to form the MO oxides, which are ionic solids. Magnesium is used as an incendiary in warfare because of its vigorous reaction with oxygen (Figure 4-3). It burns even more rapidly when sprayed with water and reacts with carbon dioxide via the reaction

$$2Mg(s) + CO_2(g) \rightarrow 2MgO(s) + C(s)$$
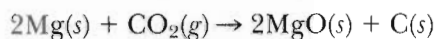
Covering burning magnesium with sand slows the combustion, but the molten magnesium reacts with silicon dioxide (the principal component of sand) to form magnesium oxide:

$$2Mg(l) + SiO_2(s) \rightarrow 2MgO(s) + Si(s)$$
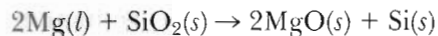
Magnesium ribbon is used in flashbulbs. The brilliant flash is produced by the reaction of magnesium with oxygen.

As with the alkali metals, the alkaline earth metals show an increasing tendency to form peroxides with increasing size. Strontium peroxide, SrO_2, is formed at high oxygen pressure, and barium peroxide, BaO_2, forms readily in air at 500°C.

Except for beryllium, the alkaline earth metals react vigorously with dilute acids:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$
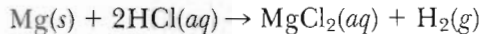
Beryllium reacts slowly with dilute acids.

The alkaline earth metals Mg, Ca, Sr, and Ba react with most of the nonmetals to form ionic binary compounds. Their reactions are summarized in Figure 4-4.

Figure 4-3 Magnesium metal burns in oxygen.
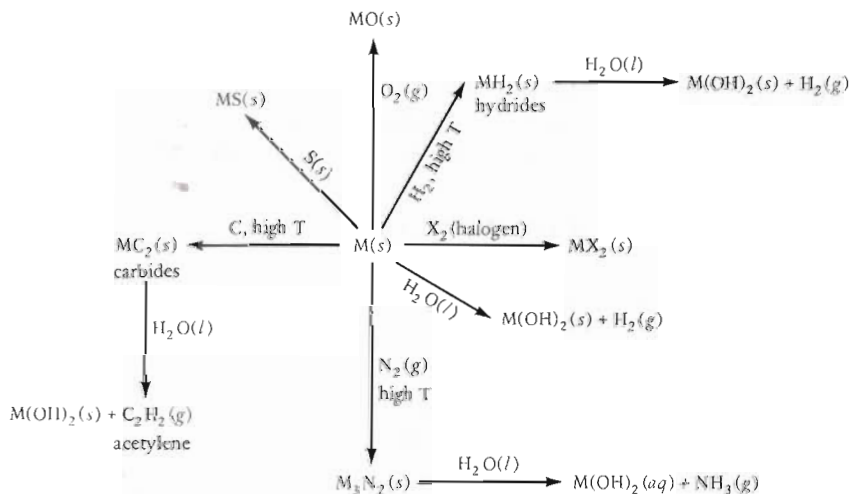
Figure 4-4 Representative reactions of Group 2 metals.

4-3 MAGNESIUM FORMS BOTH IONIC BONDS AND COVALENT BONDS

In addition to forming Mg^{2+} ions, magnesium also exhibits a tendency toward covalent bond formation. In this sense its chemistry differs from calcium, strontium, and barium, but the differences are not as great as those exhibited by beryllium. Covalently bonded organomagnesium halide compounds of the type RMgX (for example, C_2H_5MgBr) are called *Grignard reagents*. They are prepared by the direct reaction of magnesium with an alkyl halide under anhydrous conditions in an electron-donor solvent such as ether. For example,

$$CH_3CH_2Br(ether) + Mg(s) \xrightarrow[ether(l)]{} CH_3CH_2MgBr(ether)$$
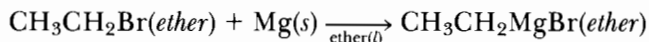
Grignard reagents are used in organic chemistry to synthesize alcohols from carbonyl compounds, which have the general formula

$$\begin{matrix} R \\ \diagdown \\ & C{=}O \\ \diagup \\ R' \end{matrix}$$
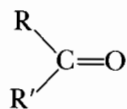
where R and R' may be hydrogen atoms or hydrocarbon groups such as $-CH_3$ (methyl) or $-CH_2CH_3$ (ethyl). The synthesis involves a two-step process.

1. Addition of the Grinard reagent to the carbonyl compound in an ether solution. For example,

$$\begin{matrix} H \\ \diagdown \\ & C{=}O \\ \diagup \\ H \end{matrix} + CH_3CH_2MgCl \xrightarrow{ether} CH_3CH_2 - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - O - Mg - Cl$$
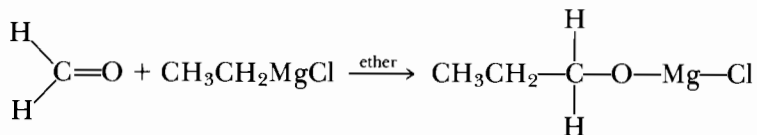
2. The adduct is hydrolyzed in an acidic aqueous solution. For example,

$$CH_3CH_2 - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - O - Mg - Cl + HCl(aq) \longrightarrow$$

$$CH_3CH_2 - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - OH(aq) + MgCl_2(aq)$$
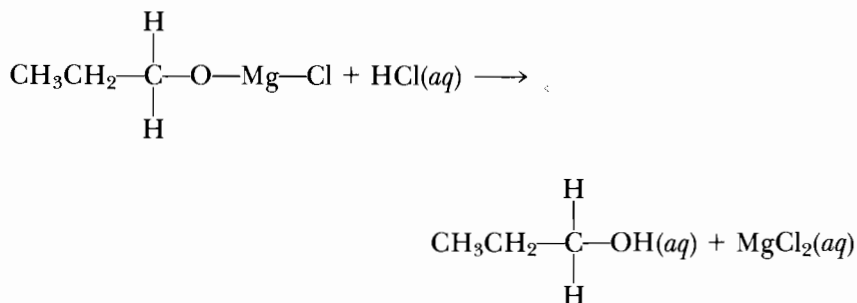
A wide variety of alcohols can be synthesized by the appropriate choice of Grignard reagent and carbonyl compound. Unlike most organic reactions, these reactions often go to completion.

Figure 4-5 Stalactites and stalagmites are produced when calcium carbonate precipitates from ground water. Shown here is the Powerhouse Cave in West Virginia.

4-4 MANY ALKALINE EARTH METAL COMPOUNDS ARE IMPORTANT COMMERCIALLY

Magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$, known as Epsom salt, is used as a cathartic, or purgative. The name Epsom comes from the place where the compound was first discovered in 1695, in a natural spring in Epsom, England. Magnesium hydroxide is only slightly soluble in water, and suspensions of it are sold as the antacid Milk of Magnesia.

Calcium is an essential constituent of bones and teeth, limestone (Figure 4-5), plants, and the shells of marine organisms. The Ca^{2+} ion plays a major role in muscle contraction, vision, and nerve excitation. Calcium oxide, or quicklime, is made by heating limestone:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Calcium oxide is the third ranked industrial chemical; over 35 billion pounds are produced annually in the United States. Large quantities of calcium oxide are used in the steel industry. It is mixed with water to form calcium hydroxide, which is also called *slaked lime:*

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$
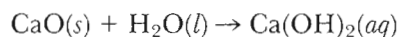
Slaked lime is used to make cement, mortar, and plaster. Plaster of Paris is $CaSO_4 \cdot \frac{1}{2}H_2O$, which combines with water to form gypsum:

$$CaSO_4 \cdot \tfrac{1}{2}H_2O(s) + \tfrac{3}{2}H_2O(l) \rightarrow CaSO_4 \cdot 2H_2O(s)$$

plaster of Paris   gypsum
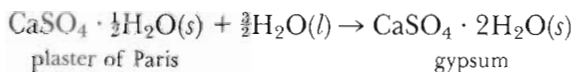
Asbestos is a calcium magnesium silicate with the approximate composition $CaMg_3(SiO_3)_4$. It can resist very high temperatures, but, because small asbestos fibers are a confirmed carcinogen, it is being phased out as a construction material.

Strontium salts produce a brilliant red flame and are used in signal flares and fireworks (Figure 4-6). The radioactive isotope strontium-90, which is produced in atomic bomb explosions, is a major health hazard because it behaves like calcium and incorporates in bone marrow, causing various cancers.

Some commercially useful compounds of the Group 2 elements are listed in Table 4-4.

Figure 4-6 A red signal flare. The red color arises from light emitted by electronically excited strontium atoms.

Table 4-4 Some important compounds of the Group 2 elements

Compound	Uses
beryllium fluoride, $BeF_2(s)$	glass manufacture and nuclear reactors
beryllium oxide, $BeO(s)$	nuclear reactor fuel moderator, electrical insulator
magnesium chloride, $MgCl_2(s)$	fireproofing wood, and disinfectants
magnesium oxide, $MgO(s)$	talcum powder, component of fire bricks; optical instruments
magnesium perchlorate, $Mg(ClO_4)_2(s)$	desiccant
magnesium sulfite, $MgSO_3(s)$	paper pulp manufacture
calcium hydrogen sulfite, $Ca(HSO_3)_2(s)$	germicide, preservative, disinfectant; beer manufacture
calcium carbonate, $CaCO_3(s)$	antacid in wine-making; manufacture of pharmaceuticals
calcium chloride, $CaCl_2(s)$	de-icer on roads, to keep dust down on dirt roads, fire extinguishers
calcium hypochlorite, $Ca(OCl)_2(s)$	bleaching powder, sugar refining, algicide
calcium tartrate, $CaC_4H_4O_6(s)$	fruit and seafood preservative
strontium bromide, $SrBr_2(s)$	sedative and anticonvulsant
strontium hydroxide, $Sr(OH)_2(s)$	sugar refining
strontium nitrate, $Sr(NO_3)_2(s)$	signal flares
strontium sulfide, $SrS(s)$	luminous paints
barium carbonate, $BaCO_3(s)$	rat poison
barium chloride, $BaCl_2(s)$	cardiac stimulant
barium nitrate, $Ba(NO_3)_2(s)$	pyrotechnics (green flame); signal flares
barium selenide, $BaSe(s)$	photocells and semiconductors

TERMS YOU SHOULD KNOW

alkaline earth metals	Grignard reagent	slaked lime
beryl	Epsom salt	

QUESTIONS

4-1. Complete and balance the following equations.
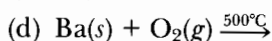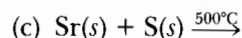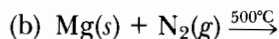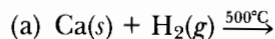
(a) $Ca(s) + H_2(g) \xrightarrow{500°C}$

(b) $Mg(s) + N_2(g) \xrightarrow{500°C}$

(c) $Sr(s) + S(s) \xrightarrow{500°C}$

(d) $Ba(s) + O_2(g) \xrightarrow{500°C}$

4-2. Complete and balance the following equations.

(a) $Ca(s) + H_2O(l) \rightarrow$

(b) $Sr_3N_2(s) + H_2O(l) \rightarrow$

(c) $CaC_2(s) + H_2O(l) \rightarrow$

(d) $Ca(s) + C(s) \xrightarrow{500°C}$

4-3. Complete and balance the following equations.

(a) $Be(s) + HCl(aq) \rightarrow$

(b) $Be(s) + NaOH(aq) \rightarrow$

(c) $Be(s) + N_2(g) \xrightarrow{500°C}$

(d) $Be(s) + O_2(g) \xrightarrow{400°C}$
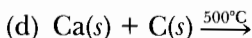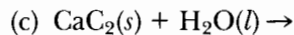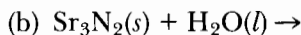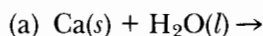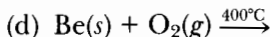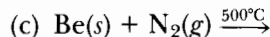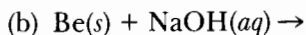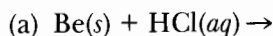
4-4. Burning magnesium, which can occur in automobile fires, should not be attacked with either water or carbon dioxide extinguishers. Why not?

4-5. Unlike the other Group 2 hydroxides, beryllium hydroxide is amphoteric. Write balanced chemical equations for the reaction of $Be(OH)_2$ with $HCl(aq)$ and with $NaOH(aq)$.

4-6. Magnesium hydroxide is only slightly soluble in water, but a suspension of magnesium hydroxide (Milk of Magnesia) in water is used as an antacid.

(a) Write a balanced chemical equation for the neutralization of stomach acid ($HCl(aq)$) by Milk of Magnesia.

(b) Given that stomach acid is about 0.10 M $HCl(aq)$, compute the number of milligrams of $Mg(OH)_2(s)$ required to neutralize 1.0 mL of stomach acid.

4-7. Beryllium is prepared on an industrial scale by the electrolysis of molten $BeCl_2$ or K_2BeF_4 and also by the reduction of BeF_2 with magnesium. Write balanced chemical equations to describe the three processes.

4-8. An old industrial preparation of hydrogen peroxide involves the reaction of oxygen with barium oxide at 500°C to form barium peroxide, followed by the treatment of the peroxide with aqueous acid. Write balanced chemical equations for the process.

4-9. Suggest a method for the preparation of magnesium chloride from magnesium carbonate.

4-10. Suggest a method for the preparation of calcium nitrate from calcium carbonate.

4-11. (a) Use VSEPR theory to predict the structure of beryllium chloride, $BeCl_2$.

(b) Use hybrid orbitals to describe the bonding in $BeCl_2$.

4-12. (a) Use VSEPR theory to predict the shape of the tetrafluoroberyllate(II) ion BeF_4^{2-}.

(b) Use hybrid orbitals to describe the bonding in BeF_4^{2-}.

4-13. The solubilities (in grams per 100 mL of solution) of the alkaline earth hydroxides in water at 20°C are

$Mg(OH)_2$	9×10^{-4}	$Sr(OH)_2$	0.93
$Ca(OH)_2$	0.18	$Ba(OH)_2$	5.8

Calculate the pH of a saturated solution in each case.

4-14. Both $BaCO_3$ and $BaSO_4$ are insoluble in basic solution. In acidic solution, $BaCO_3$ dissolves but $BaSO_4$ does not. Explain.

4-15. Write the formula of the alcohol synthesized from the following combinations:

(a) CH_3CH_2MgBr and $\begin{matrix} H \\ \diagdown \\ C=O \\ \diagup \\ CH_3 \end{matrix}$

(b) CH_3CH_2MgBr and $\begin{matrix} CH_3 \\ \diagdown \\ C=O \\ \diagup \\ CH_3 \end{matrix}$
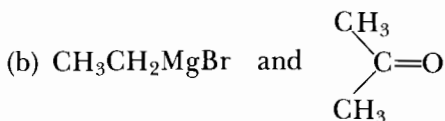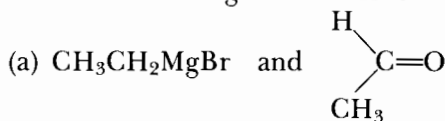
Structures of the Elements

Group 7A, H, O, N exist as diatomic molecules.

1A																	8A
H	2A											3A	4A	5A	6A	7A	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3B	4B	5B	6B	7B	⌐ 8B ¬			1B	2B	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	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	110	111							

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

All metals composed of an atomic lattice. Mostly "close packed."

Hexagonal close-packed crystal structure

Cubic close-packed crystal structure
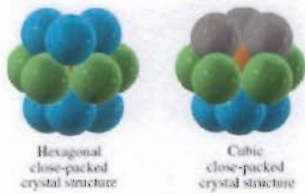
All Noble gases exist as individual discrete atoms.

	7A	8A
3A 4A 5A 6A		1 H
6 C 7 N 8 O	9 F	
	15 P 16 S 17 Cl	
	35 Br	
	53 I	

These elements can exist as discrete molecules.

C, Si, P, S can exist as network or extended solids. Si has the diamond structure.

C, O, P, S have allotropes.

Diamond

Buckyball, C₆₀

Graphite

Oxygen, O₂

Ozone, O₃

White Phosphorus, P₄

Red Phosphorus, chain section

Sulfur, S₈

Sulfur, S₈ chain section

(4)

diamond
sp^3

graphite
sp^2

Fullerene = (sp^2)
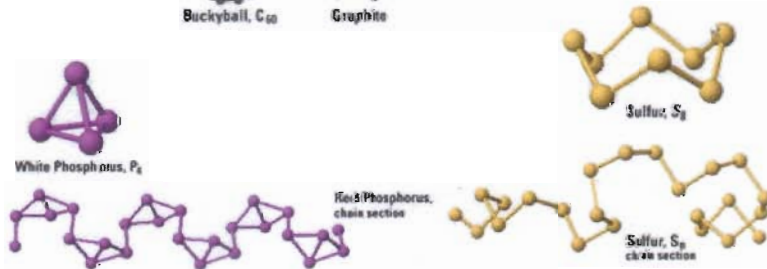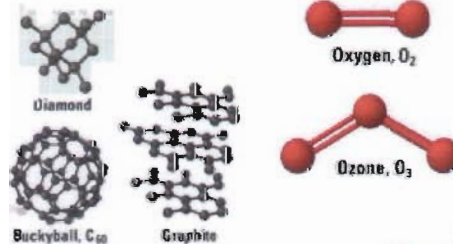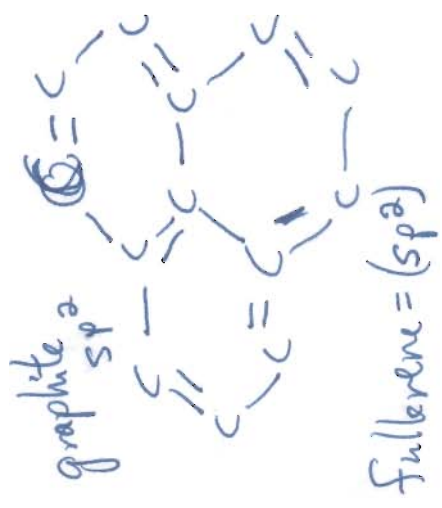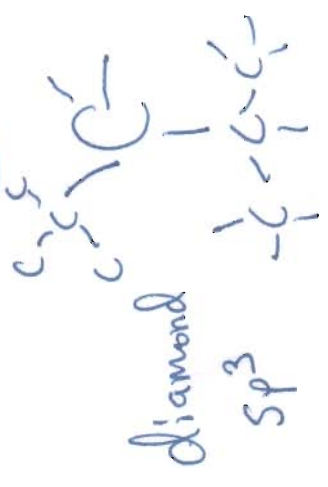
$Si \Rightarrow$ diamond
structure
only
(sp^3)

(5)

$:N \equiv N:$

(6)

$O = O$

$O = O - O$

(7)

$:F - F:$

$Cl - Cl$

$Br - Br$

(8)

$:Ne:$

$:Ar:$

$:Kr:$
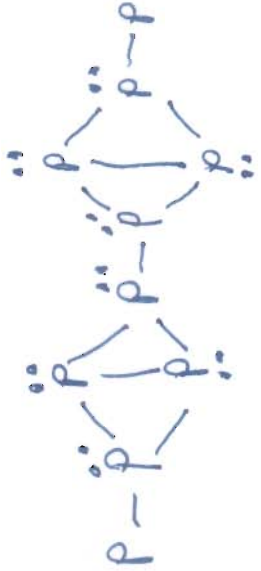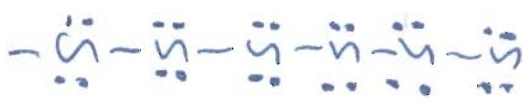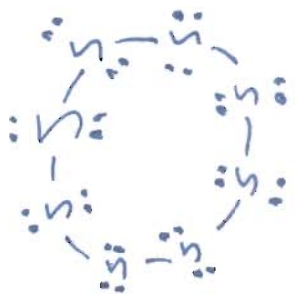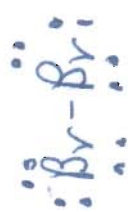
Chem 241: Group 3A

Interesting Examples: All center on electron deficiency of Group 3A atom

Group 3A Hydrides:

AlH_3 and BH_3 react to make AlH_4^- and BH_4^-. Good reducing agents.

Neutral Boron Hydrides: Boranes

simplest is "diborane" B_2H_6: Draw Lewis structure.
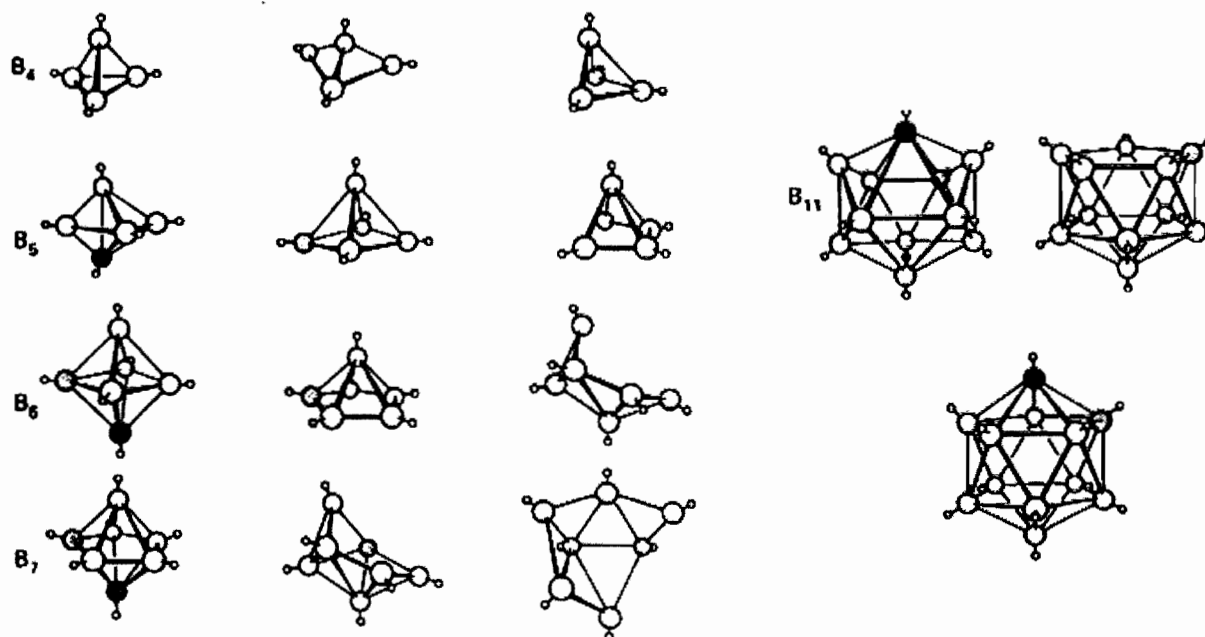
Group 3A Halides:

AlX_3 and BX_3 are "electron deficient," with the central atom having only 6 electrons.

$AlBr_3$ dimerizes to form Al_2Br_6—predict structure and draw a Lewis structure.

How can we tell if BF_3 exists as a monomer or if it exists as a dimer?

S, S₈ on side

Se

P
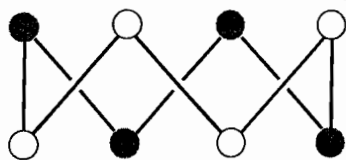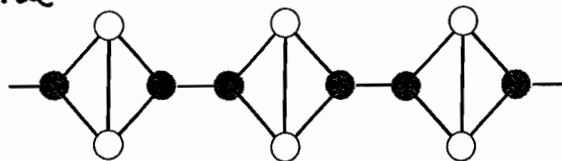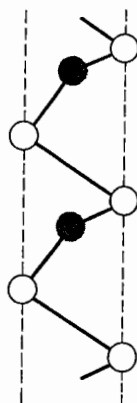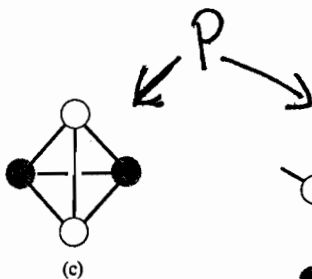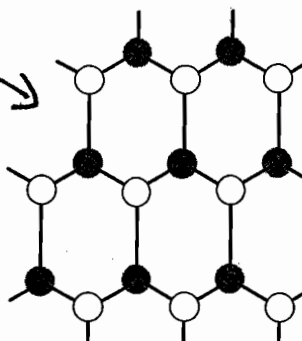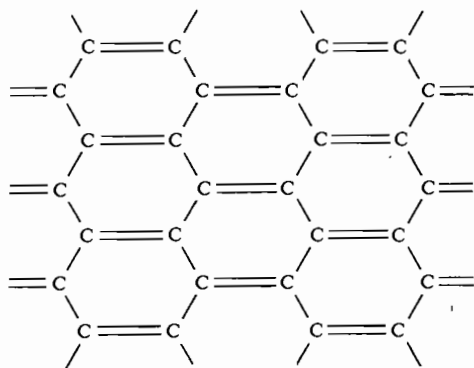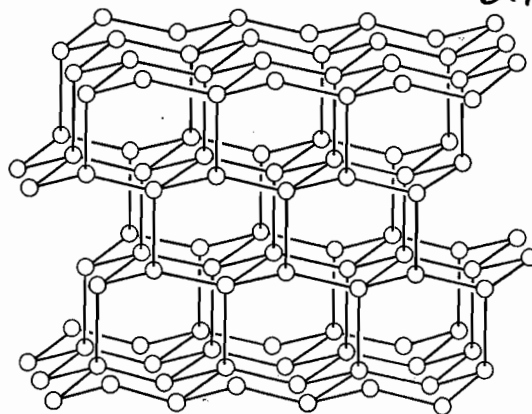
graphite

diamond, Si

Figure 6.2   The structures of some of the allotropes of the nonmetals. Shaded circles represent atoms below the plane of the paper, whereas open circles represent those above the plane of the paper. (a) S_8; (b) the helical structure of gray Se; (c) P_4 (white phosphorus); (d) red phosphorus (in one possible conformation); (e) black phosphorus (rhombohedral form); (f) graphite (one resonance structure); (g) diamond. (f) and (g) adapted from F. A. Cotton and G. Wilkinson, *Basic Inorganic Chemistry*. Copyright © 1976 by John Wiley & Sons, Inc. Reprinted by permission.

4A **5A**
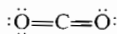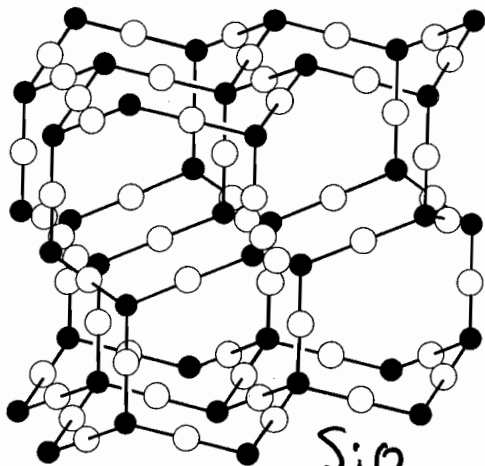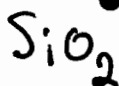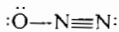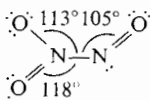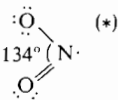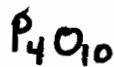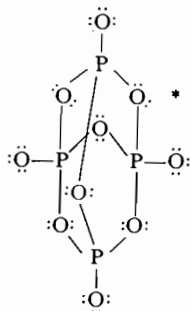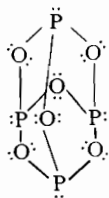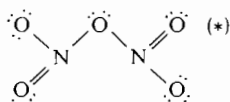
6A

:C≡O:

gas, bp − 190°

:Ö=C=Ö:

:Ö—N≡N:

gas, bp − 88°

·N̈=Ö·

gas, bp − 152°

:Ö—S̈
119° ⟍Ö.

gas, bp − 10°

F—O
103°   ⟍F:

gas, bp − 145°

Cl—O
111°   ⟍Cl:

yellow-red
gas, bp 4°

m. p. 1703°

(a)

SiO_2

:Ö 113°105° :Ö
   N̈—N̈
:Ö 118°   ⟍Ö

gas, dec. 4°

:Ö   (*)
:Ö—S̈
      ⟍Ö.

gaseous form of
volatile solid

:Ö   (*)
:Ö—S̈e
      ⟍Ö.

gaseous form of
volatile solid

:Ö   :Ö
  N̈   N̈
:Ö—   —Ö: (*)

:Ö—S̈e
      ⟍Ö.   (*)

gaseous form of
volatile solid

:Ö (*)
134° (N·
:Ö

brown gas

:Br—Ö:
      ⟍Br:

unstable
gas, bp − 18°

:Ö—Cl·
119°   :Ö

yellow
gas, bp 10°

:Ö   :Ö   :Ö
  Cl 119° Cl
:Ö :Ö   :Ö :Ö

liquid, bp 82°

Xe
:Ö   :Ö.
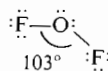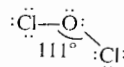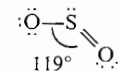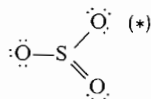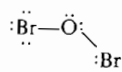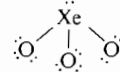
unstable
volatile solid
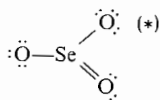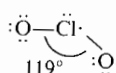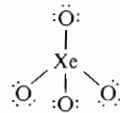
:Ö:
  Xe
:Ö :Ö :Ö.

unstable gas

:Ö:
  Ru
:Ö :Ö :Ö.

solid, mp 25°
bp 100°

P̈
:Ö   :Ö.
  :Ö
:P—Ö:—P:
:Ö: :Ö:
   P̈

:Ö: :Ö:
  S
:Ö: :Ö:
:Ö—S   S—Ö:
:Ö: Ö :Ö:

* :Ö   :Ö   :Ö
   Mn—   —Mn
:Ö :Ö: :Ö :Ö:

unstable green liquid

:Ö:
  Os
:Ö :Ö :Ö.
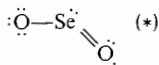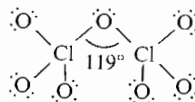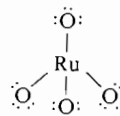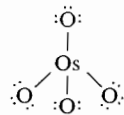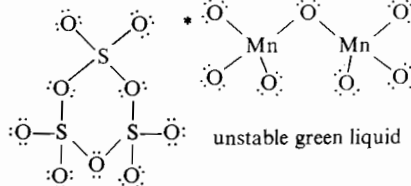
solid, mp 40°
bn 101°

P-Block

Oxides

:Ö:
  P
:Ö   :Ö. *
:Ö—P   P—Ö:
  :Ö:
:Ö: :Ö:
   P
  :Ö:

P_4O_{10}

Se_3O_9

also

As_2O_3

(b)
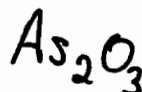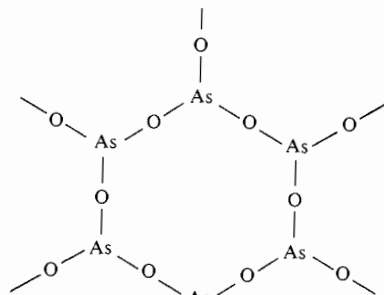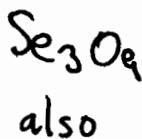
THE GROUP 3 ELEMENTS
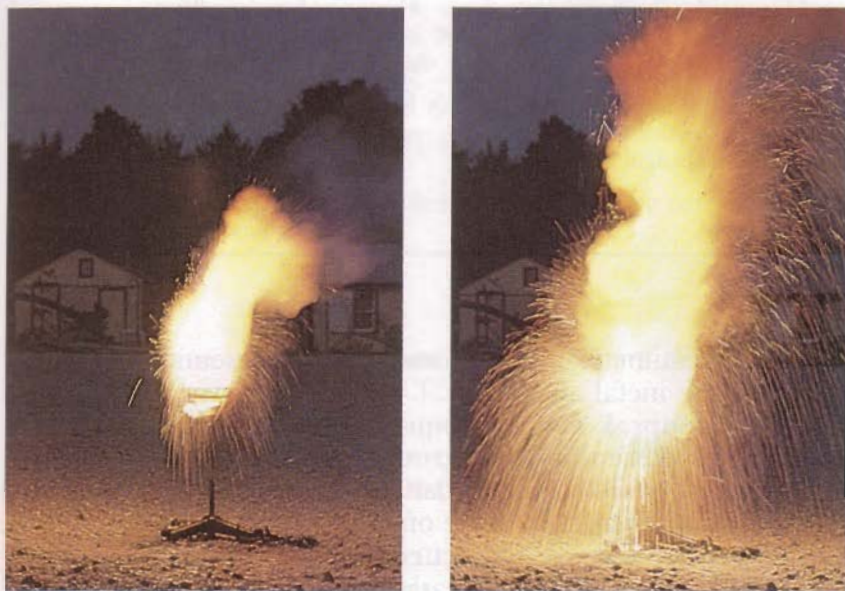
A thermite reaction. As is evident from the figure, thermite reactions are extremely vigorous and highly exothermic. The reaction is driven by the very high stability of the product Al_2O_3.

The Group 3 elements are boron, aluminum, gallium, indium, and thallium. Boron is a semimetal, and the other members of the series are metals, with the metallic character of the elements increasing as we descend the group. The electron configuration of the members of the group is [noble gas]ns^2np^1, and thus the common oxidation states of the Group 3 elements are 0 and +3. The increasing tendency on descending a group to have an oxidation state that is two less than the maximum possible value first appears in Group 3, where In^+ and Tl^+ are significant oxidation states of indium and thallium, respectively.

The chemistry of boron, the first member of the group, differs in many respects from that of the rest of the group.

Table 5-1 The atomic properties of the Group 3 elements

Property	Boron	Aluminum	Gallium	Indium	Thallium
chemical symbol	B	Al	Ga	In	Tl
atomic number	5	13	31	49	81
atomic mass	10.81	26.98154	69.72	114.82	204.37
number of naturally occurring isotopes	2	1	2	2	2
ground-state electron configuration	$[He]2s^22p^1$	$[Ne]3s^23p^1$	$[Ar]3d^{10}4s^24p^1$	$[Kr]4d^{10}5s^25p^1$	$[Xe]4f^{14}5d^{10}6s^26p^1$
atomic radius/pm	85	125	130	155	190
ionic radius M^{3+}/pm	20	51	62	81	95 (Tl^+: 1.44)
sum of the first three ionization energies of $M(g)$/kJ $\cdot$ mol^{-1}	6886	5137	5520	5063	5415
Pauling electronegativity	1.9	1.5	1.6	1.7	1.8

Boron, a semimetal, behaves more like the semimetal silicon than like the metal aluminum.

As in Groups 1 and 2, atomic and ionic radii and density increase on descending the group (Tables 5-1 and 5-2). The enthalpies of fusion (except that for Tl) and vaporization, and the boiling point also decrease on descending the group (Table 5-2). These trends are a direct consequence of the increase in size and mass with increase in atomic number. The electronegativities and standard reduction voltages do not show smooth trends, and the observed variations are not explained easily.

Table 5-2 The physical properties of the Group 3 elements

Property	Boron	Aluminum	Gallium	Indium	Thallium
melting point/°C	2180	660	30	157	304
boiling point/°C	~3650	2467	2250	2070	1457
density at 20°C/g $\cdot$ cm^{-3}	2.35	2.70	5.90	7.30	11.85
$\Delta \overline{H}_{fus}$/kJ $\cdot$ mol^{-1}	23.6	10.5	5.6	3.3	4.3
$\Delta \overline{H}_{vap}$/kJ $\cdot$ mol^{-1}	505	291	270	232	166
E^0/V at 25°C for $M^{3+}(aq) + 3e^- \rightarrow M(s)$	−0.87	−1.66	−0.53	−0.34	+0.72

Table 5-3 Major sources and uses of the Group 3 metals

Metal	Sources	Uses
boron	kernite, $Na_2B_4O_7 \cdot 4H_2O$ borax, $Na_2B_4O_7 \cdot 10H_2O$ colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$	shield for nuclear radiation, and in instruments used for absorbing and detecting neutrons; hardening agent in alloys
aluminum	bauxite, $AlO(OH)$; clays	in aircraft and rockets, utensils, electrical conductors, photography, explosives, fireworks, paint, building decoration, and telescope mirrors
gallium	trace impurity in bauxite and zinc and copper minerals; by-product in the production of aluminum	semiconductors, LEDs, light-emitting diodes, high-temperature heat-transfer fluid
indium	by-product in lead and zinc production	low-melting alloys in safety devices, sprinkler use, transistor manufacture
thallium	by-product from production of other metals	no significant commercial uses

The major sources and commercial uses of the Group 3 elements are given in Table 5-3.

5-1 THE BONDING IN BORON COMPOUNDS IS COVALENT

Boron is a relatively rare element, but *borax* ($Na_2B_4O_7 \cdot 10H_2O$) was known and used thousands of years ago to glaze pottery. Large deposits of the boron minerals *kernite* ($Na_2B_4O_7 \cdot 4H_2O$) and *borax* are found in certain desert regions of California (Figure 5-1). Boron exists in several allotropic forms with rather complex atomic structures, and which are difficult to obtain in high purity. Boron usually occurs as a brown-black powder.

Boron(III) is always covalently bonded; boron forms no simple cations of the type B^{3+}. For example, the boron trihalides, BX_3, are trigonal planar molecules with X—B—X bond angles of 120° as predicted by VSEPR theory (Chapter 11 of the text).

5-2 BX₃ COMPOUNDS ARE LEWIS ACIDS

The boron trihalides are *electron-deficient* compounds whose bonding can be described using sp^2 hybrid orbitals. They have a vacant *p*-orbital perpendicular to the plane of the molecule, and this vacant *p*-orbital can act as an electron acceptor. Thus, the

U.S. Borax

The semimetal boron in crystalline form.

U.S. Borax

Figure 5-1 Aerial view of a U.S. Borax mine in Boron, California, where massive deposits of borax are located.

boron trihalides are *Lewis acids* and are capable of reacting with electron pair donors, or *Lewis bases;* for example,

$$\underset{\text{Lewis base}}{F^-(aq)} + \underset{\text{Lewis acid}}{BF_3(g)} \rightarrow BF_4^-(aq)$$

$$\underset{\text{Lewis base}}{(CH_3)_3N(aq)} + \underset{\text{Lewis acid}}{BCl_3(g)} \rightarrow (CH_3)_3NBCl_3(aq)$$
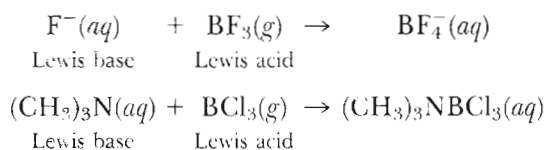
The boron trihalides react with water to form boric acid, $B(OH)_3$, and the hydrohalic acid. For example,

$$BCl_3(g) + 3H_2O(l) \rightarrow B(OH)_3(s) + 3H^+(aq) + 3Cl^-(aq)$$

Boric acid is usually made by adding hydrochloric acid or sulfuric acid to borax:

$$Na_2B_4O_7 \cdot 10H_2O(s) + 2HCl(aq) \rightarrow$$
$$4B(OH)_3(aq) + 5H_2O(l) + 2NaCl(aq)$$
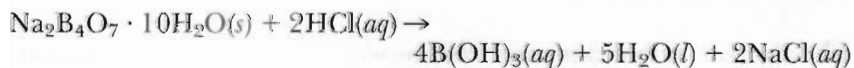
Boric acid is a moderately soluble monoprotic weak acid in water; its formula is usually written as $B(OH)_3$ rather than

H_3BO_3 or $HBO(OH)_2$, because it acts as a Lewis acid by accepting a hydroxide ion rather than by donating a proton:

$$B(OH)_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq) \qquad pK_a = 9.3 \text{ at } 25°C$$
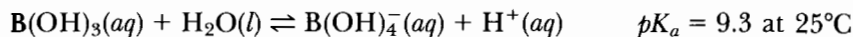
Aqueous solutions of boric acid are used in mouth and eye washes.

The principal oxide of boron, $B_2O_3(s)$, is obtained by heating boric acid:

$$2B(OH)_3(s) \rightarrow B_2O_3(s) + 3H_2O(g)$$

Boron trioxide, commonly known as boric oxide, is a colorless, vitreous substance that is extremely difficult to crystallize. It is used to make heat-resistant glassware such as Pyrex, and as a fire-resistant additive for paints.

5-3 BORON HYDRIDES INVOLVE MULTICENTER BONDS

Boron forms a large number of hydrides. The boron hydrides are volatile, spontaneously flammable in air, and easily hydrolyzed. In Chapter 11 of the text we used VSEPR theory to predict that borane, BH_3, is a symmetrical trigonal planar molecule with 120° bond angles, and in Chapter 12 we described the bonding in BH_3 using sp^2 hybrid orbitals. This molecule is not stable, however, and dimerizes to diborane, B_2H_6:

$$2BH_3(g) \rightleftharpoons B_2H_6(g) \qquad K = 10^5 \text{ atm}^{-1} \text{ at } 25°C$$
$$\Delta H°_{rxn} = -145 \text{ kJ}$$
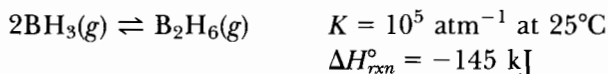
Diborane, which is the simplest boron hydride that can be synthesized in appreciable quantities, can be prepared by reacting sodium borohydride, $NaBH_4$, with sulfuric acid, $H_2SO_4(aq)$:

$$2NaBH_4(aq) + H_2SO_4(aq) \rightleftharpoons B_2H_6(g) + 2H_2(g) + Na_2SO_4(aq)$$
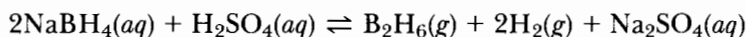
The reaction of B_2H_6 with water is slow enough to enable B_2H_6 to escape from the solution as the gas. Pyrolysis of diborane, in some cases in the presence of H_2, is used to prepare more complex boron hydrides such as B_4H_{10}, B_5H_9, B_6H_{12}, and $B_{10}H_{14}$ and boron-hydride anions such as $B_3H_8^-$ and $B_{12}H_{12}^{2-}$, all of which involve B—H—B bonds (Figure 5-2).

■ Pyrolysis involves the transformation of one substance into another by heat without oxidation.

The bonding in the boranes cannot be explained by the ideas developed in Chapter 12 of the text. For example, the bonding in diborane is not analogous to the bonding in ethane, C_2H_6 (Figures 12-6 and 12-7 of the text); diborane has *two less fewer* valence electrons than ethane. The structure of diborane is shown in Figure 5-3. The bonding can be described in terms of sp^3 hybrid orbitals on the boron atoms. Each of the boron-hydrogen bonds at the ends of the molecule involves an sp^3

B₂H₆

Boron

Hydrogen, terminal

Hydrogen, bridge

B₄H₁₀

B₅H₈

B₅H₉

B₅H₁₁

B₁₀H₁₀²⁻

Figure 5-2 Structures of some boron hydrides.

orbital on the boron atom and the 1*s* orbital on the hydrogen atom. The four terminal B—H bonds use eight of the 12 valence electrons. The bonds in the center of the molecule are quite different. Each of the localized bond orbitals spreads over the two boron atoms and a hydrogen atom and can be described as a combination of an sp^3 orbital from each boron atom and the 1*s* orbital from the hydrogen atom. The resulting bond orbitals are
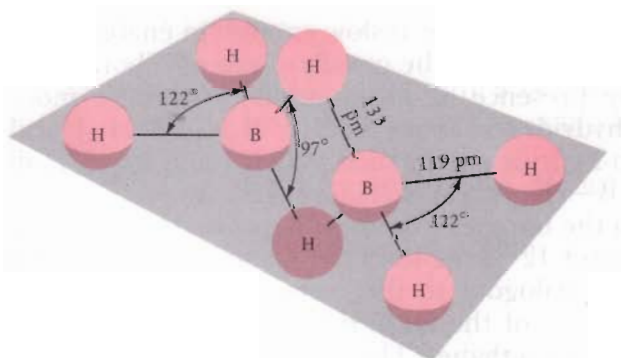
Figure 5-3 The structure of diborane. There are two nonequivalent sets of hydrogen atoms, four lying in a plane with one above and one below the plane.
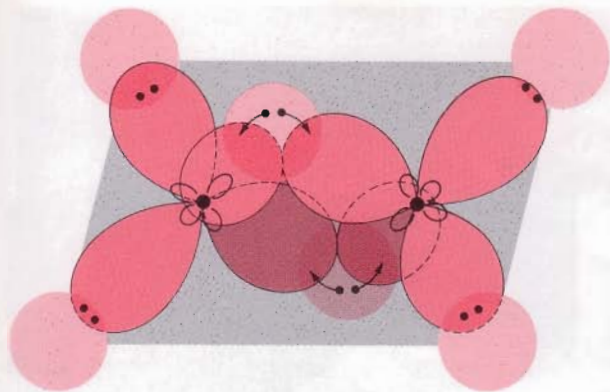
Figure 5-4 An illustration of the bonding orbitals of diborane.

called *three-center bond orbitals;* each one is occupied by two electrons of opposite spin to form a *three-center bond.* Figure 5-4 summarizes the bonding in diborane. The bonding in the higher boranes is more involved than in diborane: Not only are there three-center bonds, but in some there are five-center bonds as well.

5-4 ALUMINUM IS THE MOST ABUNDANT METAL IN THE EARTH'S CRUST

Aluminum is the most abundant metallic element and the third most abundant element in the earth's crust. In addition to its widespread occurrence in silicate minerals, aluminum also is found in enormous deposits of *bauxite,* AlO(OH) (Figure 5-5), which is the chief source of aluminum. The bauxite is refined by the *Bayer process.* The first step is to dissolve the ore in an aqueous sodium hydroxide solution. Bauxite, being amphoteric, dissolves to form sodium aluminate, and some of the sand and silicate rock dissolve to form sodium silicate.

$$2AlO(OH)(s) + 2NaOH(aq) + 2H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$$

$$\underset{\text{sand}}{SiO_2(s)} + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l)$$
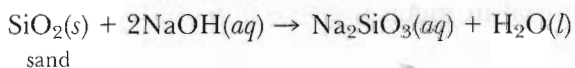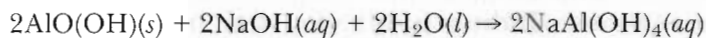
The aluminate-silicate solution is cooled and seeded with AlO(OH) or Al_2O_3, which precipitates $Al(OH)_3$ but leaves the silicate in solution. The resultant $Al(OH)_3$ is allowed to react with HF and NaOH in a lead vessel to obtain cryolite, Na_3AlF_6:

$$6HF(g) + Al(OH)_3(s) + 3NaOH(s) \rightarrow \underset{\text{cryolite}}{Na_3AlF_6(s)} + 6H_2O(g)$$
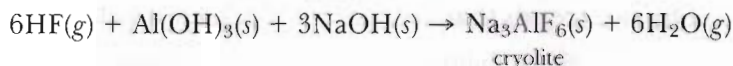
The cryolite is used to obtain aluminum metal by the *Hall process* (Chapter 21 of the text), where a molten mixture of cryolite,

Figure 5-5 Bauxite, a reddish-brown ore, is the principal source of aluminum. Bauxite is heated with coke (the black substance shown) to produce aluminum oxide, a white powder. This is further refined through electrolysis to produce aluminum.

together with CaF_2 and NaF, is electrolyzed at 800 to 1000°C. The other Group 3 metals are also obtained by electrolysis of the appropriate molten halide salt, or by electrolysis of aqueous solutions of their salts.

Aluminum is a light, soft metal that resists corrosion by the formation of a tough, adherent protective layer of the oxide, Al_2O_3. Structural alloys of aluminum for aircraft and automobiles contain silicon, copper, magnesium, and other metals to increase the strength and stiffness of the aluminum. Gallium, indium, and thallium are soft, silvery-white metals. Gallium melts at a temperature less than body temperature (Figure 5-6) and has the widest liquid range (2220°C) of any known substance. Indium is soft enough to find use as a metallic O-ring material in metal high-vacuum fittings.

5-5 THE GROUP 3 OXIDES BECOME INCREASINGLY BASIC ON DESCENDING THE GROUP

The Group 3 metals Al, Ga, In, and Tl exhibit two important trends that are also found to varying degrees in Groups 4, 5, 6, and 7. The two trends that are found on descending Group 3 are

1. A decrease in the stability of a higher oxidation state relative to a lower oxidation state. In the case of the Group 3 metals, we find a decrease in the stability of the M(III) state relative to the M(I) state. Although the trivalent state is important for all Group 3 metals, Tl(I) is also an important oxidation state in the chemistry of thallium.

Figure 5-6 Gallium metal has a melting point of 30°C, so a piece of gallium melts when held in the hand (human body temperature is 37°C). Only two elements are liquids at room temperature (20°C). One is the metal mercury, and the other is the nonmetal bromine.

2. An increase in the metallic character for identical oxidation states. This increase in metallic character is illustrated by an increase in the basicity of the oxides.

Aluminum and gallium are amphoteric; they dissolve in both strong aqueous acids and bases:

$$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$$

$$2Al(s) + 6H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$
<center>aluminate ion</center>
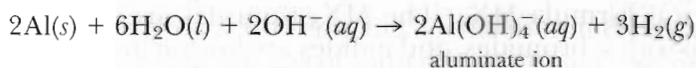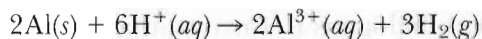
The reaction of aluminum with concentrated aqueous sodium hydroxide is used in the commercial drain cleaner Drāno (Figure 5-7). The heat and gas evolved in the reaction melt the grease and agitate the solid materials blocking the drain, respectively.

The hydroxides and oxides of aluminum and gallium are also amphoteric:

$$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$$

$$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$
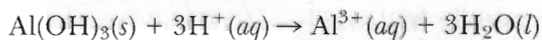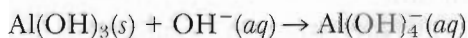
Aluminum oxide, which is commonly called alumina, is an extremely stable compound. This stability is evidenced by the ability of aluminum to reduce many metallic oxides to the corresponding metals in the *thermite reaction* (see Frontispiece). For example,

$$2Al(s) + Cr_2O_3(s) \rightarrow Al_2O_3(s) + 2Cr(s) \qquad \Delta H^\circ_{rxn} = -529 \text{ kJ}$$
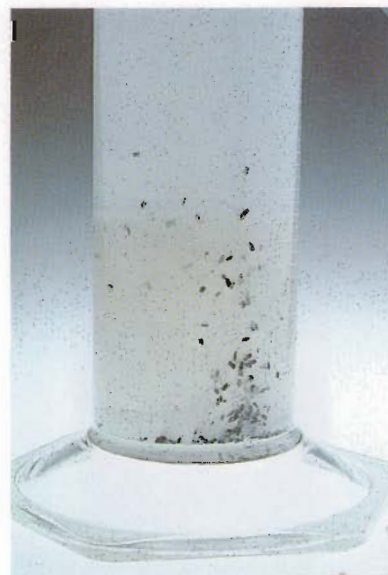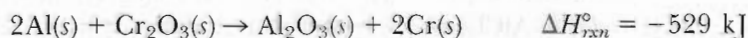
Figure 5-7 Drāno consists of a mixture of pieces of aluminum and NaOH(s). When Drāno is added to water the aluminum reacts with the NaOH(aq) to produce hydrogen gas. The overall process is highly exothermic.
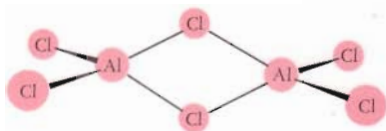
Figure 5-8 The structure of $Al_2Cl_6(g)$. Compare with the structure of diborane (Figure 5-3).

The elements indium (small shiny piece at the left) and thallium (sliced rod showing lustrous metal. The tarnish is due to reaction with air).

Indium and thallium react with aqueous solutions of strong acids, but they are unaffected by strong bases. The oxides and hydroxides of indium and thallium are not amphoteric, but are basic.

5-6 GROUP 3 METALS FORM BOTH IONIC AND COVALENT BONDS

Compounds of the Group 3 metals exhibit both ionic and covalent bonding; however, ionic bonding is somewhat favored. All four metals react with halogens to form compounds with the empirical formula MX_3. The MX_3 fluorides are ionic, whereas the chlorides, bromides, and iodides are low-melting compounds that are dimeric in the vapor state. The halide-bridge structure of the dimer Al_2Cl_6 is shown in Figure 5-8. Note the similarity of the Al_2Cl_6 structure to that of diborane (Figure 5-3).

The $M^{3+}(aq)$ ions of aluminum, gallium, and indium are well-defined cationic species in strongly acidic solutions and undergo acid-dissociation reactions of the type

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(H_2O)_5OH^-(aq) + H^+(aq)$$

$$K = 1.1 \times 10^{-5} \text{ M at } 25°C$$
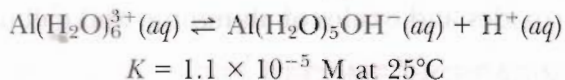
Slow addition of $NaOH(aq)$ to solutions containing $M^{3+}(aq)$ yields the insoluble hydroxides $M(OH)_3(s)$, or hydrated oxides, $M_2O_3 \cdot xH_2O(s)$. Dehydration of the hydroxides or hydrous oxides yields the oxides Al_2O_3 (white), Ga_2O_3 (white), In_2O_3 (yellow), and Tl_2O_3 (brown-black).

The salts $LiAlH_4$ and $LiGaH_4$, which contain the tetrahedral hydride ions MH_4^-, can be prepared from the respective halides and lithium hydride, LiH. For example,
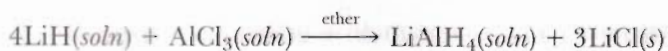
Aluminum hydroxide occurs as a white, flocculent precipitate that is used to clarify water.

$$4LiH(soln) + AlCl_3(soln) \xrightarrow{\text{ether}} LiAlH_4(soln) + 3LiCl(s)$$

Table 5-4 Some important compounds of the Group 3 elements

Compound	Uses
boron trioxide, $B_2O_3(s)$	heat-resistant glassware (Pyrex), fire retardant
boron carbide, $B_4C(s)$	abrasive, wear-resistant tools
boron nitride, $BN(s)$	lubricant, refractory, nose cone windows, cutting tools
aluminum ammonium sulfate, $Al(NH_4)(SO_4)_2(s)$	purification of drinking water, soil acidification, mordant in dyeing
aluminum oxide (alumina), $Al_2O_3(s)$	manufacture of abrasives, refractories, ceramics, spark plugs; artificial gems; absorbing gases and vapors
aluminum borohydride, $Al(BH_4)_3(s)$	reducing agent, rocket fuel component
aluminum hydroxychloride, $AlOHCl_2(s)$	antiperspirant and disinfectant
gallium arsenide, $GaAs(s)$	semiconductors for use in transistors and solar cells
indium oxide, $In_2O_3(s)$	glass manufacture
indium trichloride, $InCl_3(s)$	indium electroplating
thallium(I) oxide, $Tl_2O(s)$	optical glasses and artificial gems
thallium(I) sulfate, $Tl_2SO_4(s)$	rat and ant poison
thallium(I) bromide, $TlBr(s)$, and thallium iodide, $TlI(s)$	crystals for infrared transmitters

These hydrides are useful reducing agents in numerous aprotic solvents, but are violently decomposed by water and occasionally ignite or explode on contact with air.

The M(I) oxidation state of thallium is of major importance in solution. In water at 25°C,

$$Tl^{3+}(aq) + 2e^- \rightleftharpoons Tl^+(aq) \qquad E^0 = +1.25 \text{ V at } 25°C$$
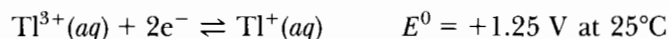
and thus $Tl^{3+}(aq)$ is about as strong an oxidizing agent as oxygen in 1 M aqueous solutions ($E^0 = 1.23$ V). The thallium(I) ion, Tl^+, is in some respects similar to Ag^+, and in other respects it is similar to K^+ and Rb^+. For example, the nitrate and fluoride salts are water-soluble, whereas the chloride, bromide, chromate, and sulfide salts are insoluble in water. Both TlCl and AgCl are white and darken on exposure to light, whereas the hydroxide $TlOH(aq)$ is a moderately soluble strong base. Thallium(I) compounds are extremely poisonous, and even trace amounts can cause complete loss of body hair.

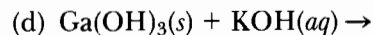Some commercially important Group 3 compounds are given in Table 5-4.
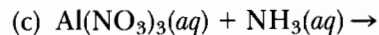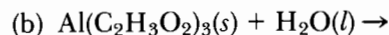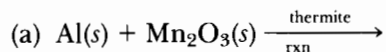
TERMS YOU SHOULD KNOW

borax
electron-deficient compound
Lewis acid
Lewis base
pyrolysis
three-center bond orbitals

three-center bonds
bauxite
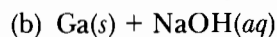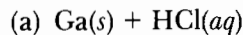Bayer process
Hall process
thermite reaction

QUESTIONS

5-1. Complete and balance the following equations.

(a) $Al(s) + Mn_2O_3(s) \xrightarrow[\text{rxn}]{\text{thermite}}$

(b) $Al(C_2H_3O_2)_3(s) + H_2O(l) \rightarrow$

(c) $Al(NO_3)_3(aq) + NH_3(aq) \rightarrow$

(d) $Ga(OH)_3(s) + KOH(aq) \rightarrow$

5-2. Do the acidities of the oxides of the Group 3 oxides increase or decrease upon descending the group?

5-3. Complete and balance the following equations:

(a) $Ga(s) + HCl(aq)$

(b) $Ga(s) + NaOH(aq)$

5-4. Write chemical equations describing the amphoteric nature of $Al(OH)_3(s)$ and $Ga(OH)_3(s)$.

5-5. The formula for boric acid is often written as $B(OH)_3$ rather than H_3BO_3. A good reason for doing this is because boric acid acts not as a Brønsted-Lowry acid but as a Lewis acid. Write a chemical equation describing the Lewis acid property of an aqueous solution of boric acid.

5-6. Write a balanced chemical equation for the formation of $B_{10}H_{14}$ from B_2H_6.

5-7. Diborane is often prepared by the reaction of boron trifluoride with sodium borohydride, with sodium tetrafluoroborate(III) as the other product. Write a balanced chemical equation for this reaction.

5-8. How many valence electrons are there in (a) $B_3H_8^-$; (b) $B_{10}H_{10}^{2-}$?

5-9. Use VSEPR theory to predict the structures of the following species.

(a) AlF_6^{3-} (b) $Al(OH)_4^-$ (c) $AlOF$
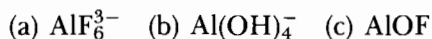
5-10. Use VSEPR theory to predict the structures of the following species.

(a) $GaCl_3$ (b) GaF_2^+ (c) $GaBr_4^-$
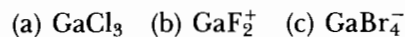
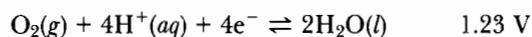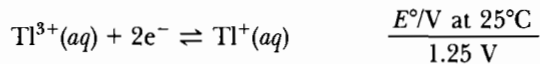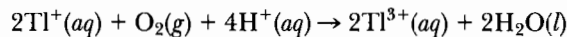**5-11.** Use VSEPR theory to predict the shape of the tetrafluoroborate(III) ion, BF_4^-. Describe the bonding in BF_4^- using hybrid orbitals.

5-12. The structure of tetraborane, B_4H_{10}, is shown in Figure 5-2. Describe the bonding in terms of hybrid orbitals.

5-13. Describe the bonding in $B_3H_8^-$ in terms of hybrid orbitals (see Figure 5-2).

5-14. A mixture of aluminum sulfate and sodium carbonate can be used to clarify water. Write chemical equations to describe this process.

5-15. Use the following data to compute the equilibrium constant at 25°C for the reaction

$$2Tl^+(aq) + O_2(g) + 4H^+(aq) \rightarrow 2Tl^{3+}(aq) + 2H_2O(l)$$

	$E°$/V at 25°C
$Tl^{3+}(aq) + 2e^- \rightleftharpoons Tl^+(aq)$	1.25 V
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.23 V

5-16. In a thermite reaction involving aluminum and Fe_2O_3, so much heat is evolved that the resulting iron is molten. Given the following data, determine if enough heat is evolved in an $Al-Cr_2O_3$ thermite reaction to melt the chromium. Assume (a) that all the heat evolved is absorbed by the products and (b) a 50 percent heat loss.

	m.p./°C	$\overline{C}_p$/J · mol^{-1} · K^{-1}	$\Delta\overline{H}_{fus}$/J · mol^{-1}
Al_2O_3	2054	79.0	—
Cr	1857	23.4	20.5

5-17. The pK_a values for the Group 3 $M^{3+}(aq)$ ions are as follows:

Ion	pK_a at 25°C
$Al^{3+}(aq)$	4.96
$Ga^{3+}(aq)$	2.60
$In^{3+}(aq)$	2.66
$Tl^{3+}(aq)$	1.15

Compute the pH of a 0.10 M aqueous solution of each of these ions.

5-18. The K_{sp} for $Al(OH)_3(s)$ in water at 25°C is 1.3×10^{-33} M^4. Sodium hydroxide is added slowly to 0.10 M $Al(NO_3)_3(aq)$. Compute the pH of the solution at which $Al(OH)_3(s)$ begins to precipitate.

THE GROUP 4 ELEMENTS

The Group 4 elements. From left to right: Carbon (as graphite), silicon, germanium, tin, lead.

The Group 4 elements, carbon, silicon, germanium, tin, and lead, provide the best example of a group in which the first member has properties different from the rest of the group. Carbon is decidedly nonmetallic and differs markedly from the rest of the members of the group, which becomes increasingly metallic with increasing atomic number. The properties of the remaining members vary more smoothly from silicon to lead: Silicon and germanium are semimetals; and tin and lead are metals. As in Group 3, there is a tendency for the elements with higher atomic number to exhibit an oxidation state of two less than the maximum of $+4$. The common oxidation state of silicon and germanium is $+4$, but lead and, to some extent, tin have a common oxidation state of $+2$.

In a West Virginia coal mine this 900 horsepower miner cuts through coal and surrounding rock. Its dual cutting heads have replaceable drill tips composed of silicon carbide.

Carbon is widely distributed in nature both as the free element and in compounds. The great majority of carbon occurs in coal, petroleum, limestone ($CaCO_3$), dolomite ($MgCa(CO_3)_2$), and a few other deposits. Carbon is also a principal element in all living matter, and the study of its compounds forms the vast field of organic chemistry.

Silicon constitutes 28 percent of the mass of the earth's mantle and is the second most abundant element in the mantle, being exceeded only by oxygen. Silicon does not occur as the free element in nature; it occurs primarily as the oxide and in numerous silicates. Most sands are essentially silicon dioxide, and many rocks and minerals are silicate materials. Germanium and tin rank in the range fortieth to fiftieth in elemental abundance. The presence of small amounts of germanium in coal deposits serves as a commercial source of that element. The most important source of tin is the mineral *cassiterite*, SnO_2, from which tin is obtained by reduction with coke. Lead is the most abundant of the heavy metals, its most important ore being *galena*, PbS. The principal sources and commercial uses of the Group 4 elements are given in Table 6-1. Tables 6-2 and 6-3 list the atomic properties and the physical properties of the Group 4 elements.

6-1 DIAMOND AND GRAPHITE ARE ALLOTROPIC FORMS OF CARBON

Solid carbon displays the two important allotropic forms, diamond and graphite (Figure 6-1). Diamond has an extended, covalently bonded tetrahedral structure. Each carbon atom lies

■ Recall that allotropes are two or more forms of an element that differ in their physical or chemical properties.

Table 6-1 Sources and uses of the Group 4 elements

Element	Principal sources	Uses
carbon	coal and petroleum	fuels; production of iron, furnace linings, electrodes (coke); lubricant, fibers, pencils, airframe structures (graphite); decolorizer, air purification, catalyst (activated charcoal); rubber and printing inks (carbon black); drill bits, abrasives (diamond)
silicon	*quartzite* or sand (SiO_2)	steel alloys, silicones, semiconductor in integrated circuits, rectifiers, transistors, solar batteries
germanium	coal ash; by-product of zinc refining	solid-state electronic devices, alloying agent, phosphor, infrared optics
tin	*cassiterite* (SnO_2)	food packaging, tin plate, pewter, bronze, soft solder
lead	*galena* (PbS), *anglesite* ($PbSO_4$), *cerussite* ($PbCO_3$)	storage batteries, solder and low-melting alloys, type metals, ballast, lead shot, cable covering

at the center of a tetrahedron formed by four other carbon atoms (Figure 6-2). The C—C bond distance is 154 pm, which is the same as the C—C bond distance in ethane. The diamond crystal is, in effect, a gigantic molecule. The hardness of diamond is due to the fact that each carbon atom is attached by strong covalent bonds to four other carbon atoms, and thus many covalent bonds must be broken in order to cleave a

Table 6-2 Atomic properties of the Group 4 elements

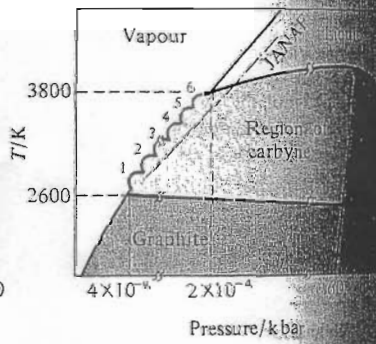| Property	C	Si	Ge	Sn	Pb
atomic number	6	14	32	50	82
atomic mass/amu	12.011	28.0855	72.59	118.69	207.2
number of naturally occurring isotopes	3	3	5	10	4
ground-state electron configuration	[He]$2s^2 2p^2$	[Ne]$3s^2 3p^2$	[Ar]$3d^{10} 4s^2 4p^2$	[Kr]$4d^{10} 5s^2 5p^2$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^2$
atomic radius/pm	70	110	125	145	180
ionization energy/MJ · mol^{-1}					
first	1.09	0.786	0.761	0.708	0.715
second	2.35	1.57	1.53	1.41	1.45
third	4.62	3.23	3.30	2.94	3.08
fourth	6.22	4.36	4.41	3.93	4.08
Pauling electronegativity	2.5	1.8	1.8	1.8	1.8

$c_0/2$ interplanar distance

unit cell
a_0 245.6 pm
c_0 670.8 pm
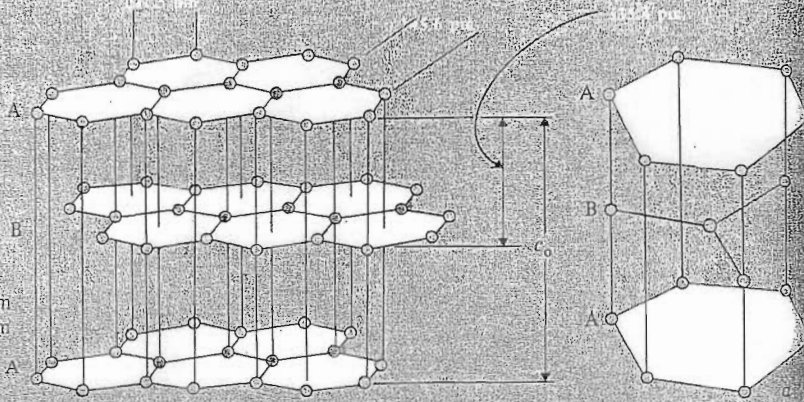
A

B

A

A

B

A'

A

B

C

A

B

C

$a_0 = 245.6$ pm
$c_0 = 3/2\ c_0$ (α-graphite)
i.e. 1006.2 pm
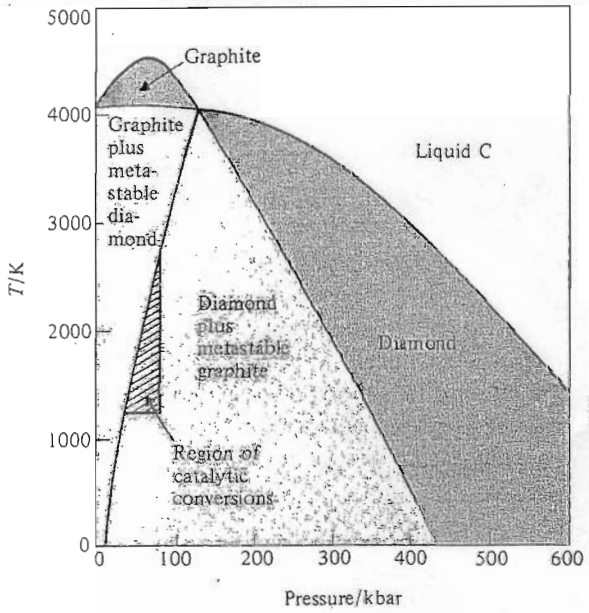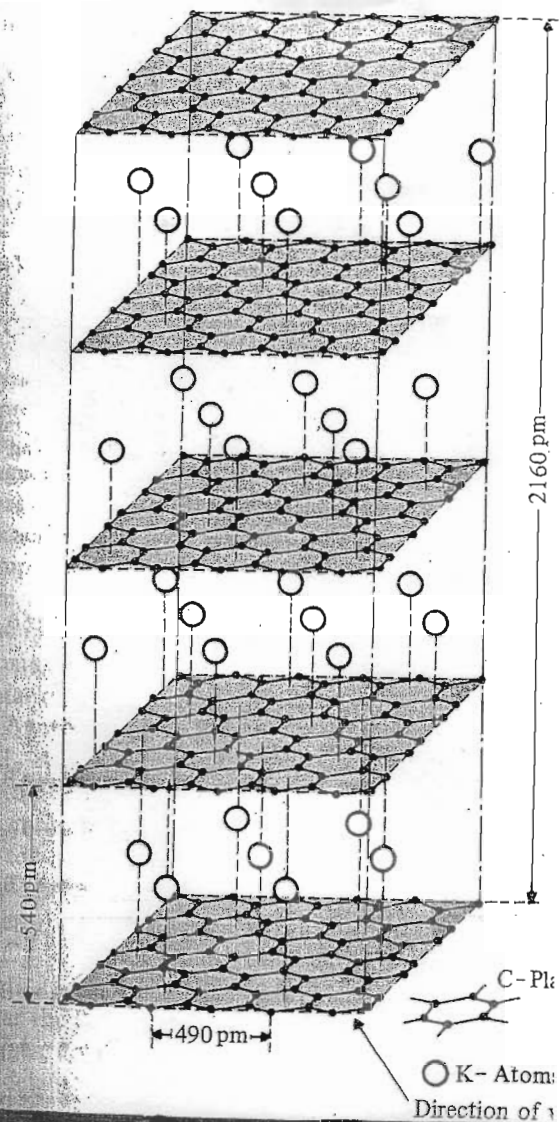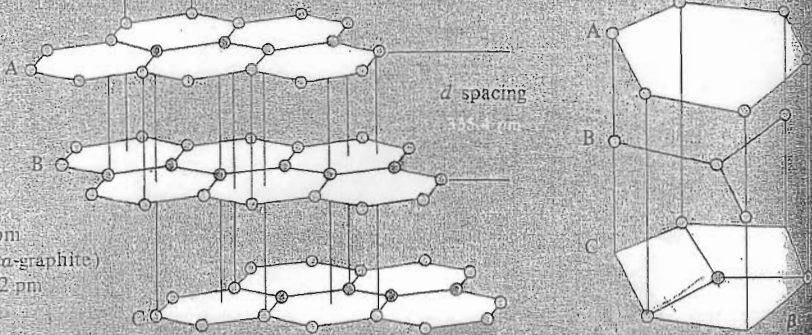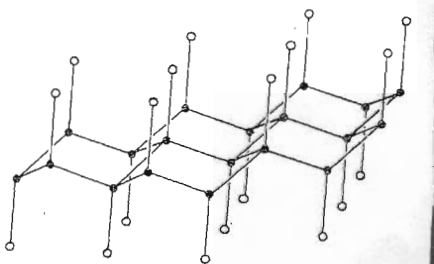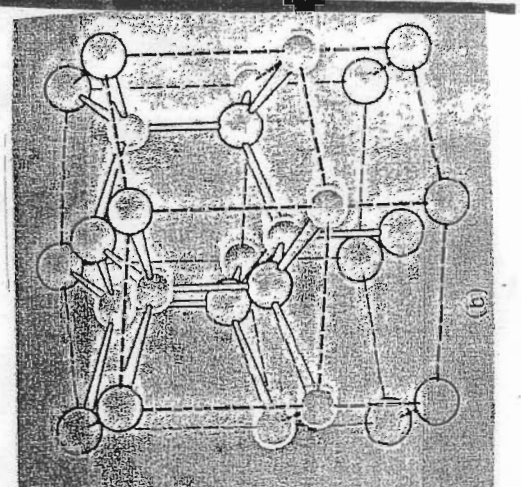
d spacing
335.4 pm

2160 pm

540 pm

490 pm

C- Plane

K- Atoms

Direction of

5000

Graphite

4000

Graphite
plus
meta-
stable
dia-
mond

Liquid C

3000

Diamond
plus
metastable
graphite

Diamond

2000

T/K

1000

Region of
catalytic
conversions

0
0   100   200   300   400   500   600

Pressure/kbar

(a)

Vapour

3800

6
5
4
3
2
1

Region of
carbyne

2600

T/K

Graphite

4×10^{-4} 2×10^{-4}

Pressure/kbar

(b)

ure of CF showing puckered layer lattice of fus
F atoms. The spacing between successive C la
phite 335.4 pm) and the density 2.43 g cm^{-3}
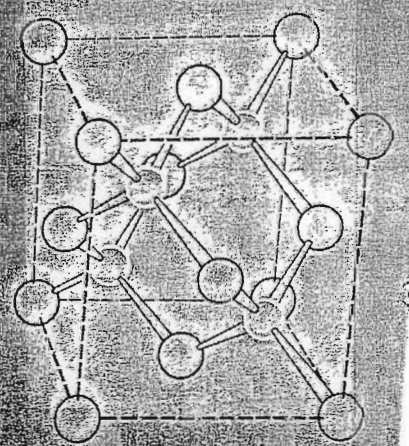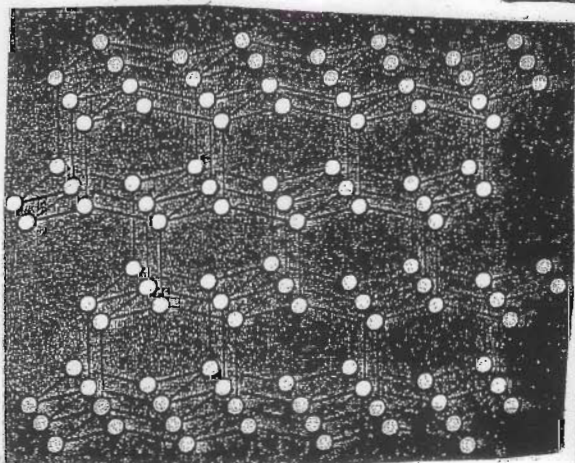
Figure 6-1 Two allotropes of carbon are graphite and diamond.

diamond. Graphite has the unusual layered structure shown in Figure 6-3. The C—C bond distance within a layer is 139 pm, which is close to the C—C bond distance in benzene. The distance between layers is about 340 pm. The bonding within a layer is strong, but the interaction between layers is weak. Therefore, the layers easily slip past each other. This is the molecular basis of the lubricating action of graphite. The "lead" of lead pencils is actually graphite. Layers of the graphite rub off from the pencil onto the paper. Graphite is the stable form at ordinary temperatures and pressures, and diamond is the stable form at high pressures (Figure 13-43 in the text).
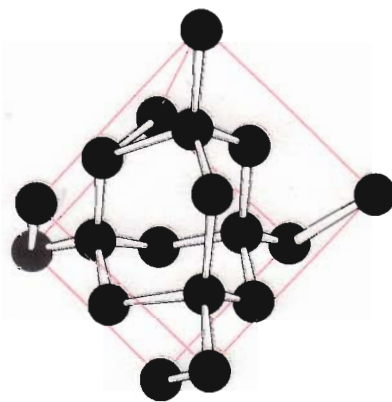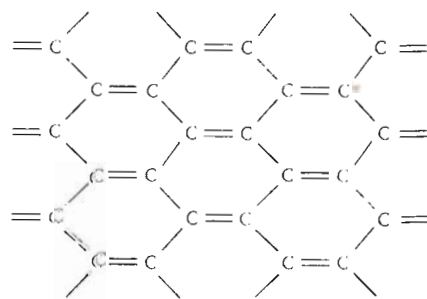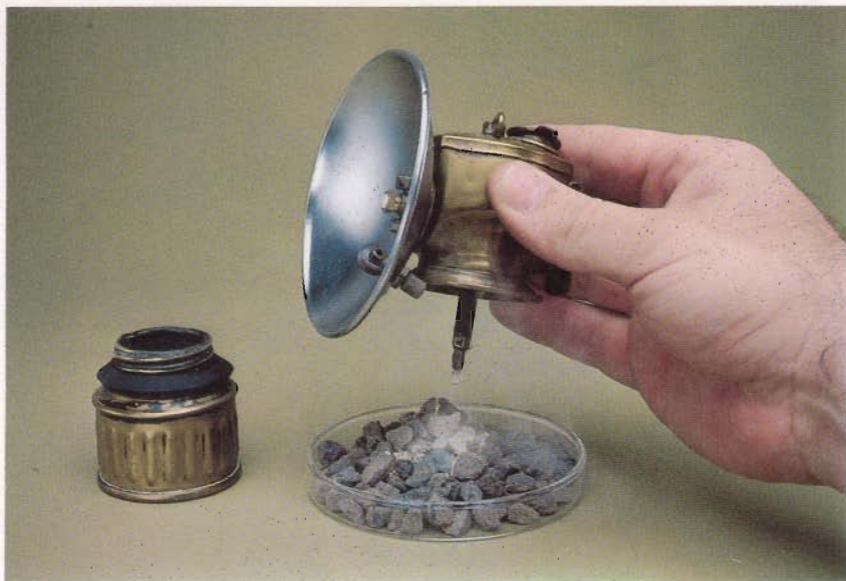

Figure 6-2 The crystalline structure of diamond. Each carbon atom is covalently bonded to four other carbon atoms, forming a tetrahedral network. A diamond crystal is essentially one gigantic molecule.

Table 6-3 Some physical properties of the Group 4 elements

Property	C	Si	Ge	Sn	Pb
melting point/°C		1410	940	232	328
boiling point/°C	sublimes at ~3900	~3000	2850	2620	1750
$\Delta \overline{H}_{fus}$/kJ · mol^{-1}	105	50.2	36.8	6.99	4.77
$\Delta \overline{H}_{vap}$/kJ · mol^{-1}		359	328	296	179
density at 20°C/g · cm^{-3}	2.27 (graphite)	2.33	5.32	7.28 (white)	11.34

Figure 6-3 The layered structure of graphite; each layer resembles a network of benzene rings joined together. The bonding within a layer is covalent and strong. The interaction between layers, however, is due only to London forces and so is relatively weak. Consequently, the layers easily slip past each other, giving graphite its slippery feel. The density of graphite is 2.2 g · cm^{-3}, which is lower than that of diamond (3.5 g · cm^{-3}), reflecting the more open structure of graphite.

Figure 6-4 The reaction of calcium carbide with water yields acetylene gas and calcium hydroxide. The acetylene gas burns in air and is used to provide light in lamps on hats used by spelunkers.

## 6-2 CARBON RANKS SECOND AMONG THE ELEMENTS IN THE NUMBER OF COMPOUNDS FORMED

Carbon forms more compounds than any other element except hydrogen. Most of these compounds are classified as organic compounds, which are discussed in Chapter 25 of the text. Although the classification of compounds into inorganic compounds and organic compounds is artificial, we shall discuss a few of the important "inorganic" compounds of carbon here. Binary compounds in which carbon is combined with less electronegative elements are called carbides. For example, aluminum carbide, Al_4C_3, is made by heating aluminum powder or aluminum oxide with coke in an electric furnace. Aluminum carbide is a yellow crystalline substance with a melting point above 2000°C. It hydrolyzes to produce methane according to

$$Al_4C_3(s) + 12H_2O(l) \rightarrow 4Al(OH)_3(s) + 3CH_4(g)$$
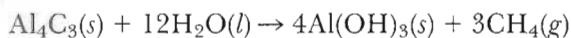
This reaction is used to generate methane in certain metallurgical applications. One of the most important carbides is calcium carbide. It is produced industrially by the reaction of lime (CaO) and coke:

$$CaO(s) + 3C(s) \xrightarrow{2000°C} CaC_2(s) + CO(g)$$
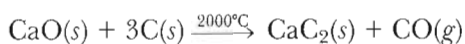
Calcium carbide is a gray-black, hard solid with a melting point over 2000°C. In contrast to aluminum carbide, calcium carbide produces acetylene when it hydrolyzes (Figure 6-4):

$$CaC_2(s) + 2H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(s)$$
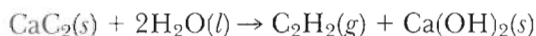
Carbon tetrabromide is a colorless solid, carbon tetrachloride a clear liquid, and carbon tetraiodide a red crystalline solid.

At one time, this reaction represented one of the major sources of acetylene for the chemical industry and for oxyacetylene welding. One other industrially important carbide is silicon carbide, SiC, known also as *carborundum*. Corborundum is one of the hardest known materials and is used as an abrasive for cutting metals and polishing glass. The structure of carborundum is similar to the cubic crystal structure of diamond.

Carbon forms binary compounds with the halogens. Carbon tetrafluoride, CF_4, or tetrafluoromethane, is a colorless, odorless gas that is chemically unreactive. It can be prepared by the direct combination of carbon and fluorine, and also via the reaction

$$SiC(s) + 4F_2(g) \rightarrow SiF_4(g) + CF_4(g)$$
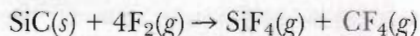
The mixture of gases produced may be separated by passing them through an alkaline solution. The CF_4 does not react, but the SiF_4 hydrolyzes according to

$$SiF_4(g) + 4H_2O(l) \rightarrow Si(OH)_4(s) + 4HF(aq)$$
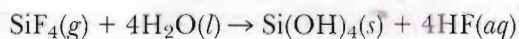
The hydrolysis apparently involves the attack on SiF_4 by H_2O, which can occur via the $3d$ orbitals on silicon. Carbon tetrafluoride has no low-lying d orbitals and thus is unreactive. This difference in reactivity between CF_4 and SiF_4 is typical of carbon and silicon compounds.

Carbon tetrachloride is a colorless liquid with a sweetish, characteristic odor. It was used extensively as a solvent and dry-cleaning agent, but its use has declined because of its toxicity. Carbon tetrabromide is a pale-yellow to colorless solid that is markedly less stable than CF_4 or CCl_4. This trend continues with

carbon tetraiodide, a bright-red crystalline substance with an odor similar to that of iodine. It readily decomposes under heat according to

$$2CI_4(s) \rightarrow 2I_2(s) + C_2I_4(s)$$
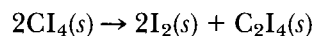
The decreasing stability of the carbon tetrahalides with increasing atomic mass is illustrated nicely by the C—X molar bond enthalpies:

Bond	Bond enthalpy/kJ $\cdot$ mol^{-1}
C—F	439
C—Cl	331
C—Br	276
C—I	213

6-3 CARBON FORMS A NUMBER OF IMPORTANT INORGANIC COMPOUNDS

Carbon has a number of oxides, but only two of them are particularly stable. When carbon is burned in a limited amount of oxygen, carbon monoxide predominates. When an excess of oxygen is used, carbon dioxide results. Carbon monoxide is an odorless, colorless, tasteless gas that burns in oxygen to produce carbon dioxide. It is highly poisonous owing to the fact that it binds to hemoglobin much more strongly than does oxygen. It is used as a fuel and as a reducing agent in metallurgy. Carbon dioxide is an odorless, colorless gas with a faintly acidic taste. When CO_2 is dissolved in water, a small amount of it is converted to carbonic acid, H_2CO_3. At 25°C, we have for the equilibrium constant of the reaction

$$CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq) \qquad K = 1.7 \times 10^{-3}$$

Small amounts of carbon dioxide can be produced by the reaction of carbonates with acids. Over 50 percent of the carbon dioxide produced industrially is used as a refrigerant, either as a liquid or as a solid (Dry Ice), and about 25 percent is used to carbonate soft drinks. The phase diagram of carbon dioxide is discussed in Section 13-11 of the text.

Carbon forms several sulfides, but only one of them, carbon disulfide, CS_2, is stable. Carbon disulfide is a colorless, poisonous, flammable liquid. The purified liquid is said to have a sweet, pleasing odor, but the commonly occurring commercial and reagent grades have an extremely disagreeable odor due to organic impurities. Large quantities of CS_2 are used in the manufacture of rayon, carbon tetrachloride, and cellophane, and as a solvent for a number of substances.

Carbon also forms several important nitrogen-containing compounds. Hydrogen cyanide, HCN, is a colorless, extremely poisonous gas that dissolves in water to form the very weak acid,

hydrocyanic acid (pK_a = 9.32 at 25°C). Salts of hydrocyanic acid, called cyanides, are prepared by direct neutralization. Sodium cyanide, NaCN, is used in the extraction of gold and silver from their ores (Chapter 11), and in the electroplating industry.
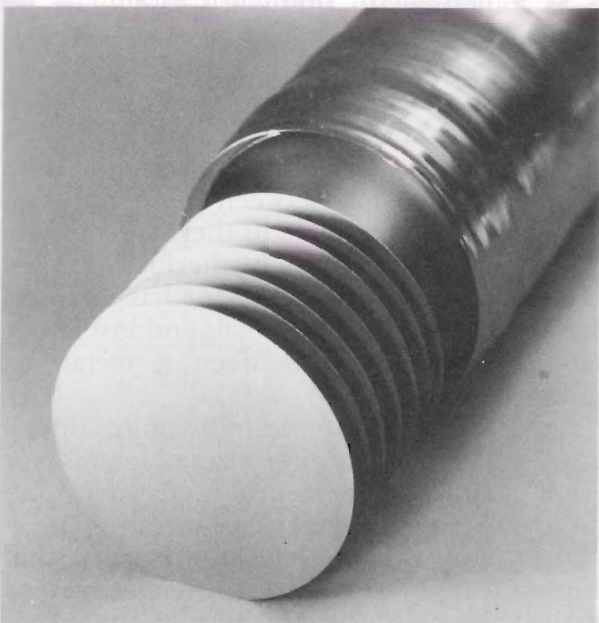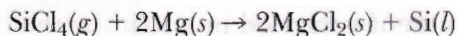
6-4 SILICON IS A SEMIMETAL

Silicon, the most important industrial semimetal, has a gray, metallic luster. Its major use is in the manufacture of transistors. Elemental silicon is made by the high-temperature reduction of silicon dioxide (the major constituent of numerous sands) with carbon:

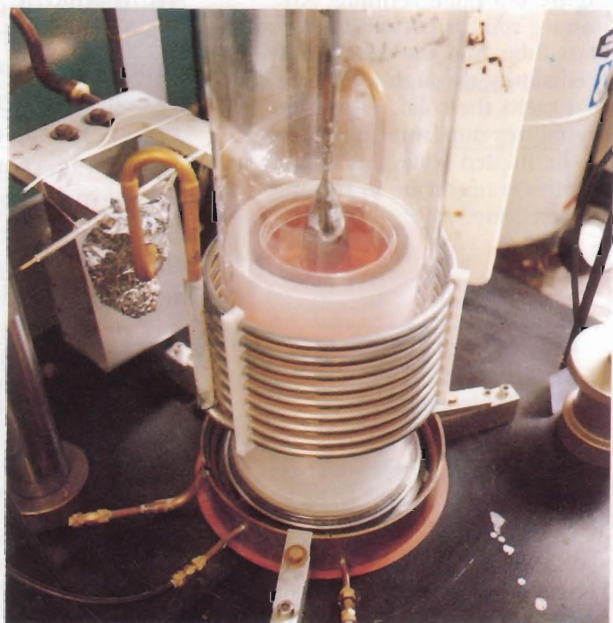$$SiO_2(l) + C(s) \xrightarrow{3000°C} Si(l) + CO_2(g)$$
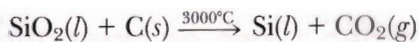
The 98 percent pure silicon prepared by this reaction must be further purified before it can be used to make transistors. It is converted to the liquid silicon tetrachloride by reaction with chlorine:

$$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$$
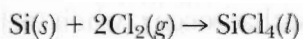
The silicon tetrachloride is further purified by repeated distillation and then converted to silicon by reaction with magnesium:

$$SiCl_4(g) + 2Mg(s) \rightarrow 2MgCl_2(s) + Si(l)$$

■ Amorphous silicon is a solid form of silicon that does not have a crystalline structure. It is used in the fabrication of some solar-energy devices, because of its relatively low cost.


Ultrapure (99.9999 percent) silicon is produced in the form of a cylinder and is then sliced into thin wafers for semiconductor manufacture.

Philips

A germanium crystal is being produced by the zone-refining method. This crystal of ultrapure germanium was grown from a melt.

Lawrence Livermore Lab
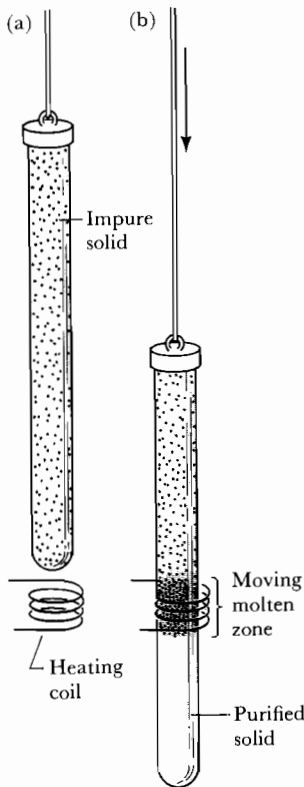
Figure 6-5 Zone refining. An impure solid is packed tightly in a glass tube, and the tube is lowered slowly through a heating coil that melts the solid. Pure solid crystallizes out from the bottom of the melted zone, and the impurities concentrate in moving molten zone.
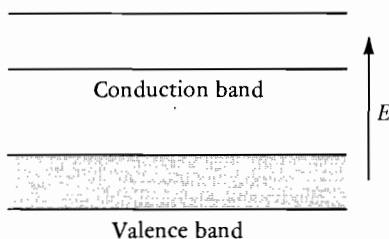
Figure 6-6 When the atoms of a crystal are brought together to form the crystal lattice, the valence orbitals of the atoms combine to form two sets of energy levels, called the valence band and the conduction band.

The resulting silicon is purified still further by a special method of recrystallization called *zone refining*. In this process, solid silicon is packed in a tube that is mounted in a vertical position (Figure 6-5) with an electric heating loop around the base of the tube. The solid near the heating loop is melted by passing a current through the loop, and the tube is then lowered very slowly through the loop. As the melted solid cools slowly in the region of the tube below the heating loop, pure crystals separate out, leaving most of the impurities behind in the moving molten zone. The process can be repeated as often as necessary to achieve the desired purity of the recrystallized solid. Purities up to 99.9999 percent are possible with zone refining.
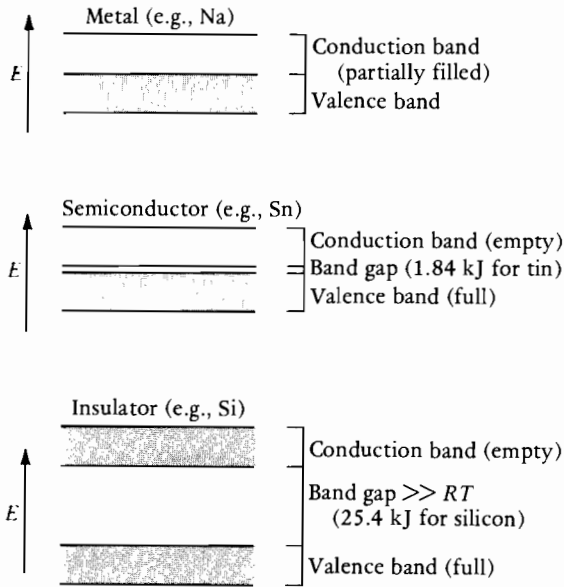
6-5 THERE ARE TWO TYPES OF SEMICONDUCTORS, *n*-TYPE AND *p*-TYPE

In a crystal, there are two sets of energy levels because of the combination of the valence orbitals of all the atoms. These two sets of energy levels are analogous to the bonding and antibonding orbitals that occur when orbitals from just two atoms are combined (Section 12-10 of the text). The lower set of energy levels is called the *valence band* and is occupied by the valence electrons of the atoms. The higher set is called the *conduction band*. Electrons in the conduction band can move readily throughout the crystal (Figure 6-6).

An electric current is carried in a solid by the electrons in the conduction band, which are called the conduction electrons. In an insulator (such as a nonmetal), there are essentially no electrons in the conduction band because the energies there are much higher than the energies in the valence band. Metals are excellent electrical conductors because there is no energy gap between the conduction band and the valence band. The valence electrons in a metal are conduction electrons. In a semiconductor the energy separation between the conduction band and the valence band is comparable to thermal energies, and thus some of the valence electrons can be thermally excited into the conduction band. Thus a semiconductor has electrical properties intermediate between those of metals and insulators. Figure 6-7 illustrates the difference between a metal, an insulator, and a semiconductor.
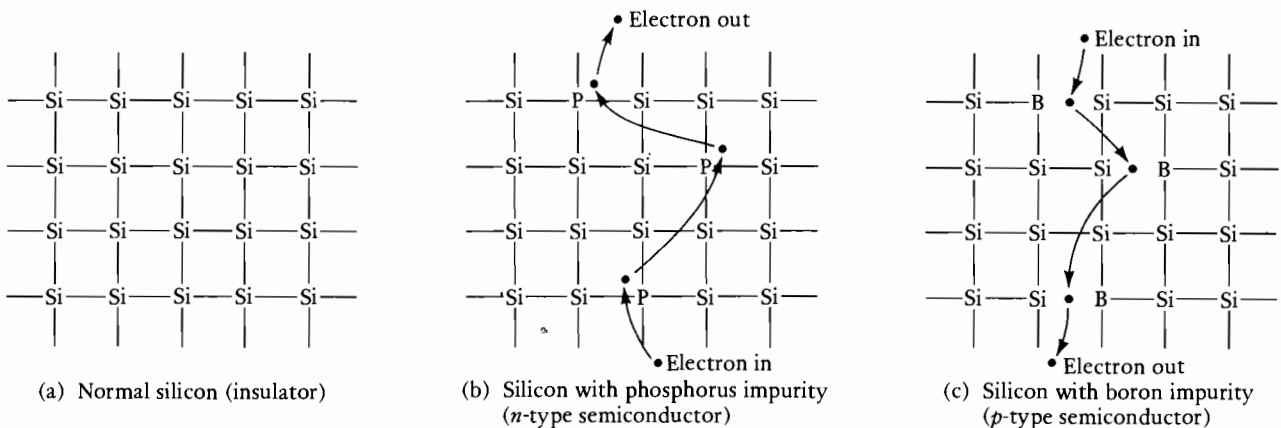
An insulator like silicon can be converted to a semiconductor by addition of selected impurity atoms. For example, an *n*-type (*n* for negative) silicon semiconductor is produced when trace amounts of atoms with five valence electrons, such as phosphorus or antimony, are added to silicon, which has four valence electrons (Figure 6-8a). The excess valence electrons on the impurity atoms, which substitute for some of the silicon atoms in the crystal, become the current carriers in the crystal (Figure 6-8b). A *p*-type (*p* for positive) semiconductor is produced when trace amounts of atoms with three valence electrons, such as boron or indium, are added to silicon. The

Metal (e.g., Na)
E
Conduction band
(partially filled)
Valence band

Semiconductor (e.g., Sn)
E
Conduction band (empty)
Band gap (1.84 kJ for tin)
Valence band (full)

Insulator (e.g., Si)
E
Conduction band (empty)
Band gap $\gg RT$
(25.4 kJ for silicon)
Valence band (full)

Figure 6-7 A comparison of the energy separations between the valence bands (bonding electron energy levels) and conduction bands (accessible energy levels for mobile electrons) of metals, semiconductors, and insulators.

deficiency of valence electrons on the impurity atoms functions as "holes" by means of which electrons can "hop" through the silicon crystal (Figure 6-8c). Because impurity atoms have a major effect on the electrical properties of semiconductors, it is necessary to use extremely pure (≥ 99.9999 percent) silicon and to add precise amounts of impurities of carefully controlled


(a) Normal silicon (insulator)

(b) Silicon with phosphorus impurity
(n-type semiconductor)

(c) Silicon with boron impurity
(p-type semiconductor)

Figure 6-8 Comparison of normal, n-type, and p-type silicon. (a) Silicon has four valence electrons, and each silicon atom forms four 2-electron bonds to other silicon atoms. (b) Phosphorus has five valence electrons, and thus when a phosphorus atom substitutes for an silicon atom in a silicon crystal, there is an unused valence electron on each phosphorus atom that can become a conduction electron. (c) Boron has only three valence electrons, and thus when a boron atom substitutes for a silicon atom in a silicon crystal, there results an electron vacancy (a "hole"). Electrons from the silicon valence bond can move through the crystal by hopping from one vacancy site to another.
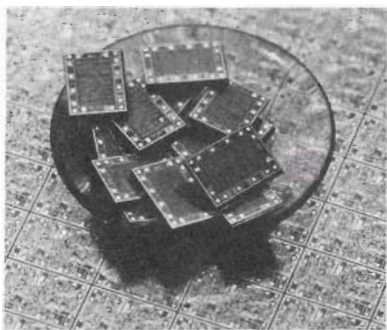
Philips

Computer chips in a contact lens. Each chip may consist of over a million transistors.
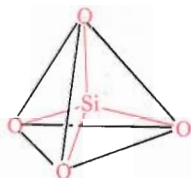
Figure 6-9 The orthosilicate ion, SiO_4^{4-}.

composition to the crystal in order to obtain the desired electrical properties.

It would be difficult to exaggerate the impact of semiconductor devices on modern technology. With their minute size and very low power requirements, these devices have made possible computers with incredible computing, storage, and retrieval capabilities. It is possible to make a computer memory chip with over a million transistors (a transistor is the solid-state equivalent of the now-obsolete vacuum tube) in a space of only 1 mm^2.

6-6 THE MOST COMMON AND IMPORTANT COMPOUNDS OF SILICON INVOLVE OXYGEN

Silicon is fairly unreactive. At ordinary temperatures silicon reacts with the halogens to give tetrahalides and with dilute alkalis to give silicates (SiO_4^{4-}), but it does not react with most acids. Silanes, the silicon hydrides analogous to the hydrocarbons, are much less stable than the corresponding hydrocarbons. Monosilane, SiH_4, and disilane, Si_2H_6, are thermodynamically stable with respect to the elements at room temperature, but the higher silanes decompose spontaneously at room temperature. There are no silicon analogs of ethylene or acetylene, or of unsaturated hydrocarbons in general.

Silicates occur in numerous minerals and in asbestos, mica, and clays. Cement, bricks, tiles, porcelains, glass, and pottery are all made from silicates. All silicates involve silicon-oxygen single bonds, of which there are two types. Terminal —Si—O bonds involve oxygen bonded to silicon and no other atoms, and bridging —Si—O—Si— bonds involve oxygen linking two silicon atoms.

Figure 6-10 The minerals enstatite (right), willemite (rear), spodumene (front), and zircon (left).

The simplest silicate anion is the tetrahedral *orthosilicate* ion, SiO_4^{4-} (Figure 6-9). The SiO_4^{4-} ion is found in the minerals *zircon*, $ZrSiO_4$, and *willemite*, Zn_2SiO_4, and also in sodium silicate, which, when dissolved in water, is called *water glass*, $Na_4SiO_4(aq)$.

The minerals *enstatite*, $MgSiO_3$, and *spodumene*, $LiAl(SiO_3)_2$ (Figure 6-10), are silicates that contain long, straight-chain silicate polyanions involving the SiO_3^{2-} chain unit:

$(SiO_3^{2-})_n$

Figure 6-11 Tetrahedral SiO_4^{4-} units are linked together through oxygen atoms that are shared by tetrahedra to form straight-chain silicate polyanions.

Structures that result from joining many smaller units together are called *polymers*. The straight-chain silicate anions shown in the preceding structure are called silicate polyanions because they result from joining together many silicate anions. The mineral *beryl*, $Be_3Al_2Si_6O_{18}$, contains the cyclic polysilicate anion $Si_6O_{18}^{12-}$ (Figure 6-12a). These cyclic polysilicate anions can themselves be joined together to form polymeric, cyclic

(a)

(b)

(c)

Figure 6-12 (a) The cyclic polysilicate ion $Si_6O_{18}^{12-}$, which occurs in the mineral beryl. Six SiO_4^{4-} tetrahedral units are joined in a ring with the tetrahedra linked by shared oxygen atoms. (b) The cyclic polysilicate ion $Si_6O_{18}^{12-}$ can form a polymeric cyclic network like that shown here. The composition of the cyclic network is $(Si_4O_{11}^{6-})_n$. Asbestos has this structure. (c) Structure of polysilicate sheets composed of $(Si_2O_5^{2-})_n$ subunits. Mica has this structure.

Figure 6-13 Asbestos. The fibrous character of this mineral is a direct consequence of its $(Si_4O_{11}^{6-})_n$ polymeric chains.

Figure 6-14 The ease with which the mineral mica can be separated into thin sheets is a direct consequence of the existence of polymeric silicate sheets with the composition $(Si_2O_5^{2-})_n$.
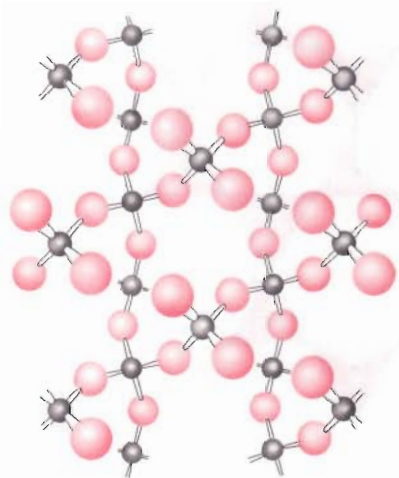
Figure 6-15 The crystalline structure of quartz. Note that each silicon atom is surrounded by four oxygen atoms. The silicon atoms are linked by the oxygen atoms.

polysilicate anions with the composition $(Si_4O_{11}^{6-})_n$ and the structure shown in Figure 6-12(b). The best example of a mineral containing polymeric, cyclic polysilicate chains is *asbestos* (Figure 6-13). The fibrous character of asbestos is a direct consequence of the molecular structure of the $(Si_4O_{11}^{6-})_n$ polymeric chains.

The silicate minerals *mica* and *talc* contain two-dimensional, polymeric silicate sheets with the overall silicate composition $Si_2O_5^{2-}$. The structure of these sheets is illustrated in Figure 6-12(c), and Figure 6-14 shows how mica can easily be fractured into thin sheets. Talc has the composition $Mg_3(OH)_2(Si_2O_5)_2$, whereas micas have a variety of compositions, one example of which is *lepidolite*, $KLi_2Al(Si_2O_5)_2(OH)$. The ease with which mica can be separated into thin sheets and the slippery feel of talcum powder arise from the layered structure of the silicates in these minerals. Some commercially important compounds of silicon are given in Table 6-4.

6-7 MOST GLASSES ARE SILICATES

Quartz is a crystalline material with the composition SiO_2 and the crystalline structure shown in Figure 6-15. When crystalline quartz is melted and then cooled quickly to prevent the formation of crystals, there is formed a disordered three-dimensional array of polymeric chains, sheets, and other three-
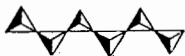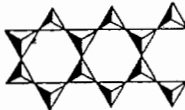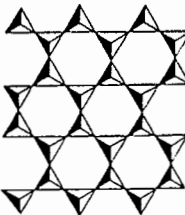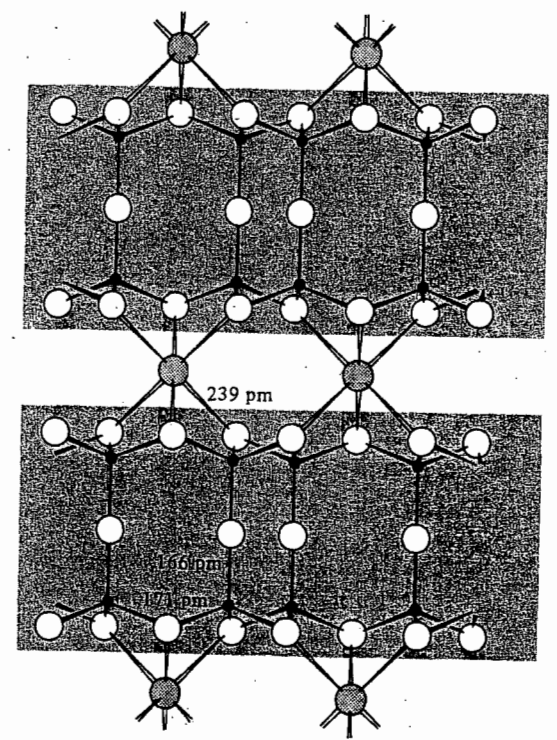
Structure	Formula name		Total O/Si Ratio	O/Si ratio at each nucleus		Charges per Si
				Bridging O	Terminal O	
$\triangle$ = SiO_4	SiO_4^{4-}	Orthosilicate	4	0	4	-4
$\bowtie$	$Si_2O_7^{6-}$	Disilicate	3.5	1	3	-3
	$Si_3O_9^{6-}$	Cyclic silicate	3	2	2	-2
	$Si_6O_{18}^{12-}$	Cyclic silicate	3	2	2	-2
	$(SiO_3^{2-})_n$	Pyroxene (chain silicate)	3	2	2	-2
	$(Si_4O_{11}^{6-})_n$	Amphibole (double chain)	2.75	2.5	1.5	-1.5
	$(Si_4O_{10}^{4-})_n$	Infinite sheet silicate	2.5	3	1	-1
	$(SiO_2)_n$	Silica	2	4	0	0

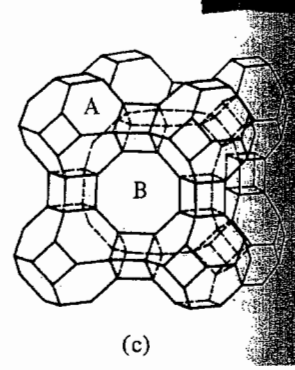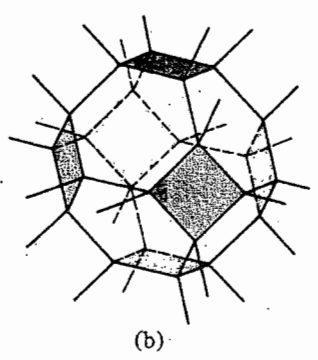**Figure 4.8** Structures of some polysilicates and resulting ratios of oxygen atoms and charge to the

$$[Si_3O_9]^{6-}$$

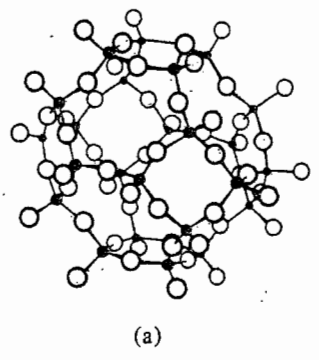Figure 4.7 Schematic and ball-and-stick models of two cyclic polysilicate ions: (a) $Si_3O_9{}^{6-}$; (b) $Si_6O_{18}{}^{12-}$. In the ball-and-stick model, the small closed circles represent Si and the large open circles represent O. In the schematic diagram, each tetrahedron represents the four oxygen atoms coordinated to a silicon atom at the center; bridging oxygens are located at the intersections of neighboring tetrahedra. Reproduced with permission from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, copyright 1984 by Pergamon Press.

$$[Si_6O_{18}]^{12-}$$
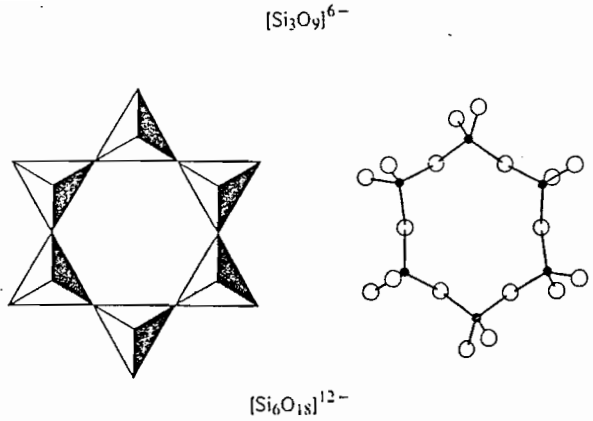
results in a further reduction in both the charge and the number of oxygen atoms per silicon nucleus, as can be seen if we write the simplest formula of this ion as

$[Si_3O_9]^{6-}$

$[Si_4O_{12}]^{8-}$

$[Si_2O_5^{2-}]$ $[Si_4O_{11}^{6-}]$ $[Si_6O_{17}^{10-}]$

$[Si_6O_{18}]^{12-}$

$[Si_8O_{24}]^{16-}$

260	520	460	730	850	730
(1T)	long 2T	short 2T	3T	long 4T	short 4T
(CuGeO$_3$)	Na$_2$SiO$_3$	Ba$_2$Si$_2$O$_6$(ht)	Ca$_3$Si$_3$O$_9$	Ba$_2$Si$_4$O$_8$(OH)$_4$.4H$_2$O	Sr$_2$(VO)$_2$Si$_4$O

239 pm

166 pm
171 pm

● Si(Al)   ○ O   🔘 Ca^{2+}

(a)   (b)   (c)
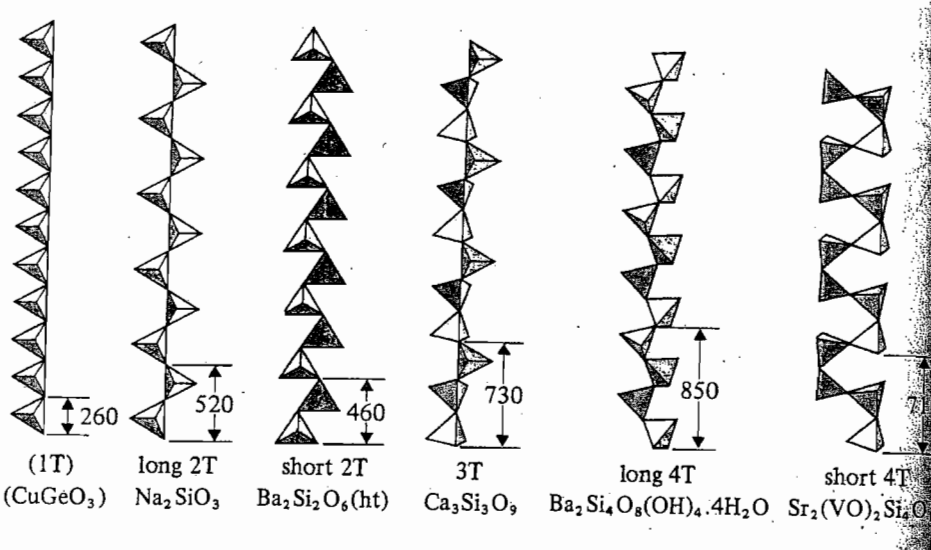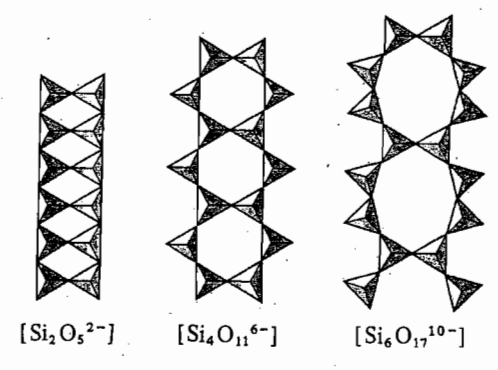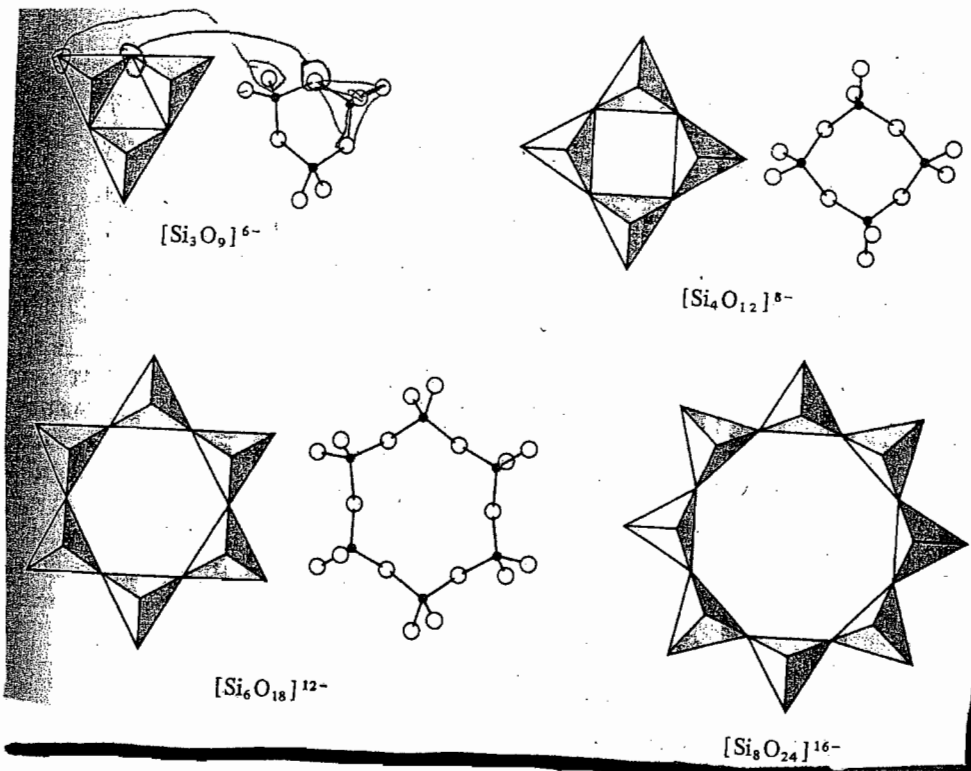
Table 6-4 Some important compounds of silicon

Compound	Uses
fluosilicic acid, $H_2SiF_6(s)$	water fluoridation, sterilizing agent in the brewing industry; hardener in cement and ceramics
sodium silicate, $Na_4SiO_4(s)$	soaps and detergents; silica gels; adhesives; water treatment; sizing of textiles and paper; water-proofing cement; flame retardant, preservative
silicon carbide (carborundum), $SiC(s)$	abrasive for cutting and grinding metals
silicon dioxide (silica), $SiO_2(s)$	glass manufacture, abrasives, refractory material, cement
silicones, $\left(-\overset{\displaystyle R}{\underset{\displaystyle R'}{Si}}-O-\right)_n$	lubricants, adhesives, protective coatings, coolant, waterproofing agent, cosmetics, and many more

dimensional clusters. The resulting material is called quartz glass. All glass consists of a random array of these clusters.

Glass manufacturing is a 10-billion-dollar-per-year industry in the United States. The major component in glass is almost pure quartz sand. Among the other components of glass, soda (Na_2O) comes from soda ash (Na_2CO_3), lime (CaO) comes from limestone ($CaCO_3$), and aluminum oxide comes from feldspars, which have the general formula $M_2O\cdot Al_2O_3\cdot 6SiO_2$, where M is K or Na. All the components of glass are fairly inexpensive chemicals.

A wide variety of glass properties can be produced by varying the glass composition. For example, partial replacement of CaO and Na_2O by B_2O_3 gives a glass that does not expand on heating or contract on cooling and is thus used in making glass utensils meant to be heated. Colored glass is made by adding a few percent of a colored transition metal oxide, such as CoO to make blue "cobalt" glass and Cr_2O_3 to make orange glass. Lead glass, which contains PbO, has attractive optical properties and is used to make decorative, cut-glass articles.

The addition of K_2O increases the hardness of glass and makes it easier to grind to precise shapes. Optical glass contains about 12 percent K_2O. Photochromic eyeglasses have a small amount of added silver chloride dispersed throughout and trapped in the glass. When sunlight strikes this type of glass, the tiny AgCl grains decompose into opaque clusters of silver atoms and chlorine atoms:

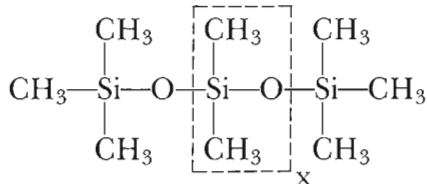$$\underset{\text{clear}}{AgCl} \underset{\text{dark}}{\overset{\text{sunlight}}{\rightleftharpoons}} \underset{\text{opaque}}{Ag + Cl}$$
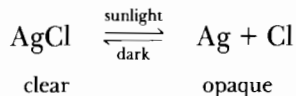
Quartz often forms large, beautiful crystals.

■ Silicon polishes, lubricants, and rubbers are silicon compounds with the following structure (X is variable):

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_X\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3$$

The chlorine atoms are trapped in the crystal lattice, and the silver and chlorine atoms recombine in the dark to form silver chloride, which causes the glass to become clear.

The etching of glass by hydrofluoric acid, HF(aq), is a result of the reaction

$$SiO_2(s) + 6HF(aq) \rightarrow H_2SiF_6(s) + 2H_2O(l)$$
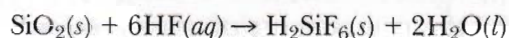
and this reaction is used to "frost" the inside surface of lightbulbs.

Porcelain has a much higher percentage of Al_2O_3 than glass and as a result is a heterogeneous substance. Porcelain is stronger than glass because of this hetereogeneity and is also more chemically resistant than glass. Earthenware is similar in composition to porcelain but is more porous because it is fired at a lower temperature.

6-8 GERMANIUM IS A SEMIMETAL; TIN AND LEAD ARE METALS

Germanium, a semimetal (Figure 6-7), is prepared in a manner similar to that for silicon. The main uses of germanium are in transistor technology and in infrared windows, prisms, and lenses. Germanium is transparent in the infrared.

Tin is found primarily in the mineral *cassiterite,* SnO_2, which occurs in rare but large deposits in Malaysia, China, the U.S.S.R., and the United States. Total U.S. natural reserves of tin are very

The minerals galena and cassiterite.

small. Tin is easily produced by heating SnO_2 with charcoal (carbon) and has been known since prehistoric times. It is used in plating (tin-plated food cans) and in various alloys, including solders, type metal, pewter, bronze, and gun metal. Tin objects are subject to a condition called *tin disease*, which is the conversion of the *white* allotrope of tin to the *gray* allotrope. This conversion occurs slowly below 13°C and results in the brittle gray allotrope of tin. A famous compound of tin is stannous (tin(II)) fluoride, SnF_2, a white crystalline powder that was the first fluoride additive used in toothpaste.

Lead is obtained primarily from the ore *galena*, PbS; commercial deposits occur in over 50 countries. The ore is first roasted in air:

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$
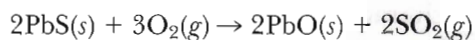
and then reduced by carbon in a blast furnace:

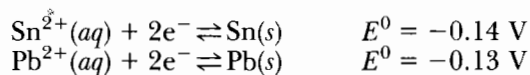$$PbO(s) + CO(g) \rightarrow Pb(l) + CO_2(g)$$
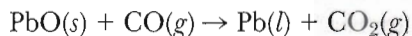
Lead is resistant to corrosion and is used in a variety of alloys. Lead storage batteries constitute the major use of lead. The metal is also used in cable coverings, ammunition, and the synthesis of tetraethyl lead, $(CH_3CH_2)_4Pb$, which is used in leaded gasolines. Lead was once used in paints—$PbCrO_4$ is yellow and Pb_3O_4 is red—but lead salts constitute a serious health hazard, as they are cumulative poisons, and their use in paints has been discontinued. The Romans used lead vessels to store wine and other consumables and to conduct water in lead-lined aqueducts; thus lead poisoning may have had more to do with the collapse of the Roman Empire than any other factor. The use of lead-containing glazes on pottery for food use is now prohibited in the United States.

**Table 6-5 Some important compounds of germanium, tin, and lead**

Compound	Uses
germanium dioxide, $GeO_2(s)$	infrared-transmitting glass, transistors and diodes
tin(IV) oxide, $SnO_2(s)$	white enamels, ceramics and glass, polishing glass and marble, cosmetics
tin(II) chloride, $SnCl_2(s)$	reducing agent in dye manufacture, tin galvanizing, soldering flux
tin(II) fluoride, $SnF_2(s)$	toothpaste additive
tin(IV) chloride, $SnCl_4(s)$	perfume stabilization in soaps, ceramic coatings, manufacture of blueprint paper
lead(II) oxide, $PbO(s)$	glazing pottery and ceramics, lead glass
lead dioxide, $PbO_2(s)$	oxidizing agent, matches, lead-acid storage batteries, pyrotechnics
lead chromate, $PbCrO_4(s)$	yellow-to-red pigments
lead azide, $Pb(N_3)_2(s)$	detonating agent (primer)

The elements germanium, tin, and lead show a steady trend to metallic properties and to increasing stability of the $+2$ oxidation state. The $+2$ oxidation state is of little importance in the chemistry of germanium, but predominates for lead. The ion Pb^{4+} exists only in the solid state as, for example, in PbO_2. Lead has an extensive aqueous solution chemistry as the $Pb^{2+}(aq)$ ion. In addition, the salts of germanium, tin, and lead show increasing ionic character with increasing atomic number. For example, germanium reacts with the halogens upon moderate heating to form covalent tetrahalides of the form GeX_4. Tin forms both dihalides, SnX_2, and tetrahalides, SnX_4, which are also covalent. Lead reacts with the halogens to form dihalides, PbX_2, which have well-defined ionic character.
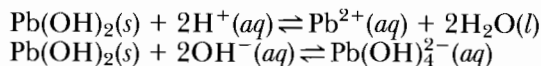
Tin and lead are mild reducing agents in aqueous media:

$$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s) \qquad E^0 = -0.14 \text{ V}$$
$$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s) \qquad E^0 = -0.13 \text{ V}$$

whereas lead(IV) oxide, $PbO_2(s)$, is a fairly strong oxidizing agent in acid solution:

$$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l) \qquad E^0 = 1.46 \text{ V}$$
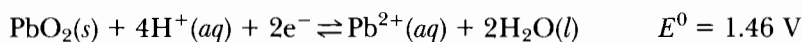
This half-reaction occurs during discharge at the cathode (+ terminal) of the lead storage battery, except that the product is $PbSO_4(s)$ rather than $Pb^{2+}(aq)$.

The oxides become increasingly basic from germanium to lead. The oxide GeO_2 is slightly acidic, whereas the oxides SnO, SnO_2, and PbO and the hydroxides $Sn(OH)_2$ and $Pb(OH)_2$ are amphoteric. For example,

$$Pb(OH)_2(s) + 2H^+(aq) \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$$
$$Pb(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Pb(OH)_4^{2-}(aq)$$

As a consequence, water-insoluble lead(II) salts (except PbS) dissolve readily in strong base.

Tin and lead form a variety of organometallic compounds, such as $(CH_3CH_2)_2Sn$ and $(CH_3CH_2)_4Pb$ (tetraethyllead). Tetraethyllead is used as an antiknock compound in leaded gasolines because it promotes a smooth burning of the fuel, but its use is decreasingly rapidly because of EPA regulations. Table 6-5 lists some of the important compounds of germanium, tin, and lead.
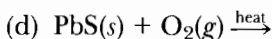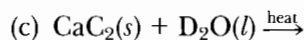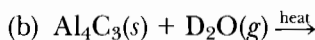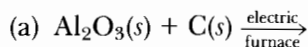
TERMS YOU SHOULD KNOW

cassiterite
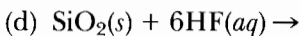galena
allotropes
carborundum
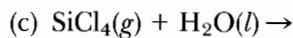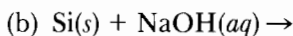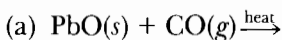zone refining
valence band
conduction band

n-type semiconductor
p-type semiconductor
orthosilicate ion
water glass
polymer
silicones
tin disease

QUESTIONS

6-1. Complete and balance the following equations.

(a) $Al_2O_3(s) + C(s) \xrightarrow[\text{furnace}]{\text{electric}}$

(b) $Al_4C_3(s) + D_2O(g) \xrightarrow{\text{heat}}$

(c) $CaC_2(s) + D_2O(l) \xrightarrow{\text{heat}}$

(d) $PbS(s) + O_2(g) \xrightarrow{\text{heat}}$

6-2. Complete and balance the following equations.

(a) $PbO(s) + CO(g) \xrightarrow{\text{heat}}$
(b) $Si(s) + NaOH(aq) \rightarrow$
(c) $SiCl_4(g) + H_2O(l) \rightarrow$
(d) $SiO_2(s) + 6HF(aq) \rightarrow$

6-3. Do the acidities of the Group 4 oxides increase or decrease with increasing atomic number?

6-4. Write chemical equations describing the amphoteric nature of $Sn(OH)_2$.

6-5. Given that graphite is converted to diamond under high pressures, use Le Châtelier's principle to deduce the relative densities of the two substances.

6-6. Explain on a molecular level why diamond is an extremely hard substance and graphite is slippery. Give applications of these properties.

6-7. Explain on a molecular level why diamond is a poor conductor of electricity and graphite is a good conductor.

6-8. Clean rainwater (as opposed to acid rain) is slightly acidic, with a pH of about 5.6. Explain the acidity of clean rainwater.

6-9. Calcium cyanamide, CaNCN, an important industrial chemical, is produced by the reaction

$$CaC_2(s) + N_2(g) \xrightarrow{1000°C} CaNCN(s) + C(s)$$
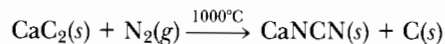
Draw the Lewis formula of the cyanamide ion, and use VSEPR theory to predict its shape.

6-10. Cyanogen, $(CN)_2$, is a colorless, highly toxic gas that is used to synthesize many nitrogen-containing organic compounds. Draw the Lewis formula of cyanogen, and use VSEPR theory to predict its shape.

6-11. Based on analogy with the methods of preparation of other carbides, propose two ways to synthesize silicon carbide, SiC.

6-12. Give two examples (not mentioned in the text) of elements that can be added to make n-type and p-type silicon semiconductors, respectively.

6-13. Discuss and explain the difference in reactivities between the carbon tetrahalides and the silicon tetrahalides.
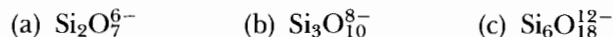
6-14. Determine the oxidation states of the Group 4 elements in the following compounds.
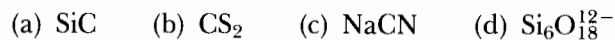
(a) SiC   (b) CS_2 (c) NaCN   (d) $Si_6O_{18}^{12-}$

6-15. Determine the oxidation state(s) of the Group 4 elements in the following compounds.

(a) PbO_2 (c) Al_4C_3
(b) Pb_3O_4 ("red lead")   (d) CaC_2
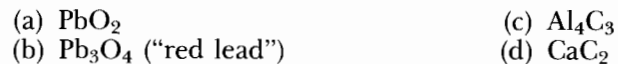
6-16. Draw structures for the following ions.

(a) $Si_2O_7^{6-}$ (b) $Si_3O_{10}^{8-}$ (c) $Si_6O_{18}^{12-}$

6-17. Write the chemical equation that describes the etching of glass by hydrofluoric acid.

6-18. Use VSEPR theory to predict the shapes of (a) $GeBr_4$, (b) $SnCl_2$, (c) GeF_6^{2-}, and (d) SiH_3^-.

6-19. Use hybrid orbitals to describe the bonding in the silanes, SiH_4 and Si_2H_6.

6-20. Write chemical equations describing how tin and lead are obtained from their ores.

6-21. Explain how photochromic glass works.

6-22. Many fine museum pieces and organ pipes made of tin have been ruined because their temperatures were allowed to drop below 13°C for appreciable periods of time. Explain.

6-23. How many kilograms of lead can be obtained from 100 kilograms of galena?

6-24. How many kilograms of tin can be obtained from 100 kilograms of cassiterite?

Lecture Notes: Chem 241: Diamond, Silicones, Computer Chips

At room temperature, graphite is slightly more stable than diamond.

<u>Metastable</u>: kinetically stable, but not thermodynamically stable.

- The larger the activation energy, the slower the reaction rate will be; k will decrease

Why doesn't diamond convert to graphite at room temperature? You would need to shear the diamond along one of its faces and then you would have to break bonds in-between layers and create π-bonds. This would have a large activation energy, and thus would be too slow to observe.

Under pressure, diamond is more stable than graphite. Diamond is more dense than graphite.

<u>Synthetic Diamonds</u>:

- Can use explosions to create high pressure and make diamonds. This method is not efficient and is not used on the industrial scale.

- Can use a catalytic process to create synthetic diamond.

    o Creates a pathway for more favorable intermediate to form.

    o Molten metal is used to form weak carbon-metal bonds. Without the use of a catalyst, a possible mechanism is the breaking of a carbon-carbon π-bond into a double radical (high energy).

    o Graphite and metal are placed in a furnace together and melted at the correct pressure (look on your phase diagram). The graphite dissolved into the metal, and when the carbon precipitates out, it falls out as diamond. Can get metallic impurities.

    o CVD—there is a lot of useful info on the internet.

<u>Silicones</u>: Si-O organic compounds

- Side groups control properties and structures of silicones

  R can be any group, such as H, Me, Et, etc.

$2\ Me_3SiCl + H_2O \rightarrow 2\ HCl + Me_6Si_2O$
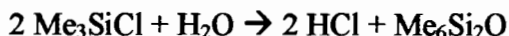
You can make polymers from silicones. By using different groups, you can change the properties of the polymers.

- $Me_3SiCl \rightarrow$ terminal group. This group will cap the polymer
- $Me_2SiCl_2 \rightarrow$ chain forming group. This group can attach two more groups to itself and can form a chain of silicone groups linked together
- $MeSiCl_3 \rightarrow$ branching group. This group can attach 3 silicone groups to itself, which will make a branched polymer.
  - You can control the chain length by adjusting the ratio of Me_2SiCl_2/ Me_3SiCl
  - You can control the degree of cross linking by adjusting the $MeSiCl_3$ concentration

- Relation to physical properties: nonbranched silicones are usually liquid or solid depending on chain length
  - Using more branching groups forms a rubber

<u>Band Theory and Metallic Properties</u>:

If you were to plot Group # vs. Melting point for groups 1A, 2A, and 3B, Cr, Mo, and W would have the highest melting points in each group, and Cr < Mo< W.

- Cr, Mo, and W all have bands that have all of the bonding orbitals filled and none of the antibonding orbitals filled.
- MP of Cr<Mo<W break normal periodic trend expected for MP$\rightarrow$ transition metals don't follow periodic trend.
  - TM bond strength increases and atomic size increases.
    - D-orbital overlap better with large orbitals; they point at each other which leads to stronger pi-bonding.

2

<u>Semiconductors</u>:

- Bulk (aka—III-IV semiconductors)
  - GaAs—silicon structure composed of a 1:1 ratio of Ga:As
    - Band gap has an energy corresponding to red light. (When an electron is promoted to the conductance band, it must gain energy to jump the gap. When it falls back into the valance band, it releases energy in the form of light.)
  - GaP—energy gap is greater than gap in GaAs; emits green light
  - GaN—energy gap is greater than gap in GaP; emits blue light
  - This technology used in LED (Light Emitting Diodes), more efficient and longer lasting than normal light bulbs
    - Can adjust band gap by adjusting ratios of elements in semiconductor.
  - Here is a good website that is worth visiting: http://mrsec.wisc.edu/edetc/LED

- Doping

  - Si is naturally an insulator; add a little bit of Al impurity (~0.1%). Al creates a new band that is slightly above the valance band of Si in terms of energy. Electrons can now be promoted from the valance band of Si and it now conducts.
    - The electron leaves a positive hole in the valance band→ **P-type semiconductor**

<u>Silicon in Semiconductors</u>:

- **Need 10^9:1 silicon vs. impurity in order for silicon to be used as a semiconductor.**
- Use several steps to purify Si
  - $SiO_2 + 2C \rightarrow Si + 2CO$ (~97% purity)
  - $Si + 2Cl_2 \rightarrow SiCl_4$ (g)
  - $SiCl_4 + 2 Zn \rightarrow Si + 2ZnCl_2$
  - Final purification step is **Zone Refining**. Make the Si into a cylinder and slowly heat a small portion of it to melt the Si. When the Si freezes, the impurities are left in the liquid Si.

3

THE GROUP 5 ELEMENTS
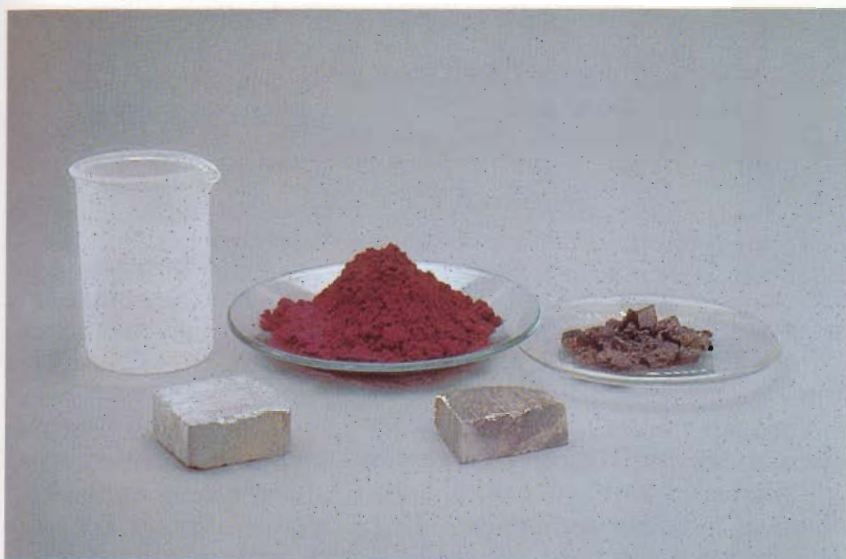
The Group 5 elements. Back row from left to right: Nitrogen, phosphorus, and arsenic. Front row: Antimony and bismuth.

The Group 5 elements are nitrogen, phosphorus, arsenic, antimony, and bismuth. Nitrogen and phosphorus are non-metals, arsenic and antimony are semimetals, and bismuth is a metal. Group 5 nicely illustrates the trend from acidic to basic oxides on descending a group. The oxides of nitrogen, phosphorus, and arsenic are acidic, those of antimony are amphoteric, and bismuth(III) oxide, Bi_2O_3, is basic. There is also an increase in stability of the lower oxidation state with increasing atomic number. Thus, Bi_2O_3 is the only stable oxide of bismuth, whereas the other members of the group also have oxides of the type M_2O_5. The Group 5 family gives us our first opportunity to

Table 7-1 Sources and uses of the Group 5 elements

Element	Principal sources	Uses
nitrogen	fractional distillation of liquid air	production of ammonia (Haber process), inert atmosphere for chemical processes, refrigerant (as liquid)
phosphorus	phosphate rock (impure $Ca_3(PO_4)_2$); apatites $[Ca_{10}F_2(PO_4)_6, Ca_{10}(OH)_2(PO_4)_6]$	manufacture of phosphoric acid, incendiaries, matches, pyrotechnics, smoke bombs
arsenic	*realgar* (As_4S_4), *orpiment* (As_2S_3), *mispickel* (FeAsS), flue dust of copper and lead smelters	doping agent in electronic devices, alloys with lead and copper, special solders
antimony	*stibnite* (Sb_2S_3)	infrared detectors, hardening alloy for lead, antifriction alloys, type metal, tracer bullets
bismuth	*bismuthinite* (Bi_2S_3), *bismite* (Bi_2O_3), by-product of lead, copper, and tin refining	low-melting alloys, pharmaceuticals, cosmetics, permanent magnets

note that the nonmetals of the fourth row, arsenic, selenium and bromine, favor an oxidation state less than their maximum. Thus, although AsF_3, $AsCl_3$, $AsBr_3$, and AsI_3 exist, only AsF_5 is known.

Nitrogen makes up almost 80 percent of the earth's atmosphere, from which it can be obtained by fractional distillation of liquefied air, a method that exploits the difference in the boiling points of nitrogen and oxygen, the principal components of air. The nitrogen can be separated from the oxygen because nitrogen boils at $-196°C$, whereas oxygen boils at $-183°C$. The lack of chemical reactivity of nitrogen accounts for its lack of abundance in mineral form in the earth's crust. The only significant nitrogen-containing minerals are KNO_3 (saltpeter) and $NaNO_3$ (Chile saltpeter). Phosphorus is the twelfth most abundant element in the earth's crust. All its important minerals are phosphates, which are collectively referred to as *phosphate rock.* Both nitrogen and phosphorus occur in all living things, making these two elements essential components of fertilizers. Arsenic, antimony, and bismuth are not particularly abundant. The principal sources and commercial uses of the Group 5 elements are given in Table 7-1.

Tables 7-2 and 7-3 present some atomic and physical properties of the Group 5 elements. Note that atomic size increases and that ionization energy and electronegativity decrease with increasing atomic number.

Table 7-2 Atomic properties of the Group 5 elements

Property	N	P	As	Sb	Bi
atomic number	7	15	33	51	83
atomic mass/amu	14.0067	30.97376	74.9216	121.75	208.9804
number of naturally occurring isotopes	2	1	1	2	1
ground-state electron configuration	$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
atomic radius/pm	65	100	115	145	160
ionization energy/MJ·mol⁻¹					
first	1.40	1.06	0.947	0.834	0.701
second	2.86	1.90	1.70	1.60	1.61
third	4.58	2.91	2.74	2.44	2.47
Pauling electronegativity	3.0	2.1	2.0	1.9	1.8

## 7-1 NITROGEN, N_2, HAS A VERY STRONG TRIPLE BOND

Nitrogen is a colorless, odorless gas that exists as a diatomic molecule, N_2. The most significant property of elemental nitrogen is its lack of chemical reactivity. Nitrogen, as N_2, does not take part in many chemical reactions. The nitrogen molecule is generally unreactive because of the very high bond energy of the triple bond in N_2:

$$N{\equiv}N(g) \rightarrow 2N(g) \qquad \Delta H_{rxn} = 946 \text{ kJ}$$

Although nitrogen compounds are essential nutrients for animals and plants, only a few microorganisms are able to utilize elemental nitrogen directly by converting it to water-soluble compounds of nitrogen. The conversion of nitrogen from the free element to nitrogen compounds is one of the most important problems of modern chemistry and is called *nitrogen fixation.*

Table 7-3 Physical properties of the Group 5 elements

| Property	N_2	P (red)	P (white)	As	Sb	Bi
melting point/°C	−210.0	—	44.1	814	631	271
boiling point/°C	−196.0	416 (sub)	280	613 (sub)	1440	1560
enthalpy of fusion/kJ·mol⁻¹	0.72	—	2.51	21.3	19.8	10.9
enthalpy of vaporization/kJ·mol⁻¹	5.58			—	193	151
density/g·cm⁻³	0.879	2.34	1.82	5.78	6.70	9.80 (rhomb)
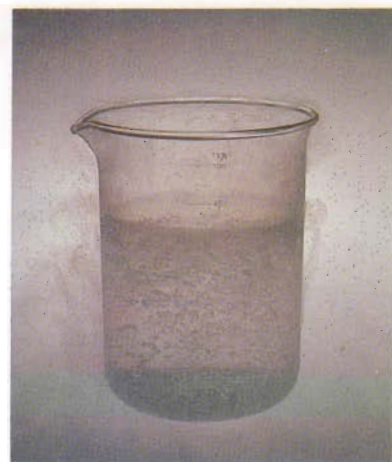
Liquid nitrogen at its boiling point.

7-2 NITROGEN IS THE SECOND-RANKED INDUSTRIAL CHEMICAL

In terms of U.S. industrial production, nitrogen is the second leading chemical. Over 42 billion pounds of pure nitrogen is produced from air each year. Nitrogen is also found in potassium nitrate, KNO_3 (saltpeter), and in sodium nitrate, $NaNO_3$ (Chile saltpeter). Vast deposits of these two nitrates are found in the arid northern region of Chile, where there is insufficient rainfall to wash away these soluble compounds. The Chilean nitrate deposits are about 200 miles long, 20 miles wide, and many feet thick. At one time the economy of Chile was based primarily upon the sale of nitrates for use as fertilizers.

Large quantities of nitrogen are stored and shipped as the liquid in insulated metal cylinders. Smaller quantities are shipped as the gas in heavy-walled steel cylinders. The most convenient source of nitrogen gas in the laboratory is a steel cylinder charged with compressed N_2 gas. An alternative source is to heat an aqueous solution of ammonium nitrite, which thermally decomposes according to the equation

$$NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O(l)$$
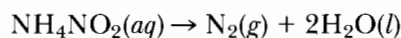
Ammonium nitrite is a potentially explosive solid, and so the aqueous ammonium nitrite solution is made by adding ammonium chloride and sodium nitrite, both stable compounds, to water. Even so, the solution must be heated carefully to avoid an explosion.

Another laboratory preparation of nitrogen is the passage of ammonia gas over hot copper(II) oxide:

$$2NH_3(g) + 3CuO(s) \xrightarrow{400°C} N_2(g) + 3H_2O(g) + 3Cu(s)$$

7-3 MOST NITROGEN IS CONVERTED TO AMMONIA BY THE HABER PROCESS

The inertness of nitrogen toward most other chemical substances makes reactions in which nitrogen combines with other elements economically important. Nitrogen fixation occurs both industrially and in nature. The most important industrial nitrogen-fixation reaction is the *Haber process,* in which nitrogen reacts directly with hydrogen at high pressure and high temperature to form ammonia (Figure 7-1):

$$N_2(g) + 3H_2(g) \xrightarrow[500°C]{300 \text{ atm}} 2NH_3(g)$$
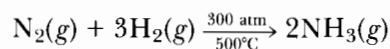
Over 27 billion pounds of ammonia is produced annually in the United States by the Haber process. Rated in terms of pounds produced per year, ammonia is the sixth ranked industrial chemical in the United States.
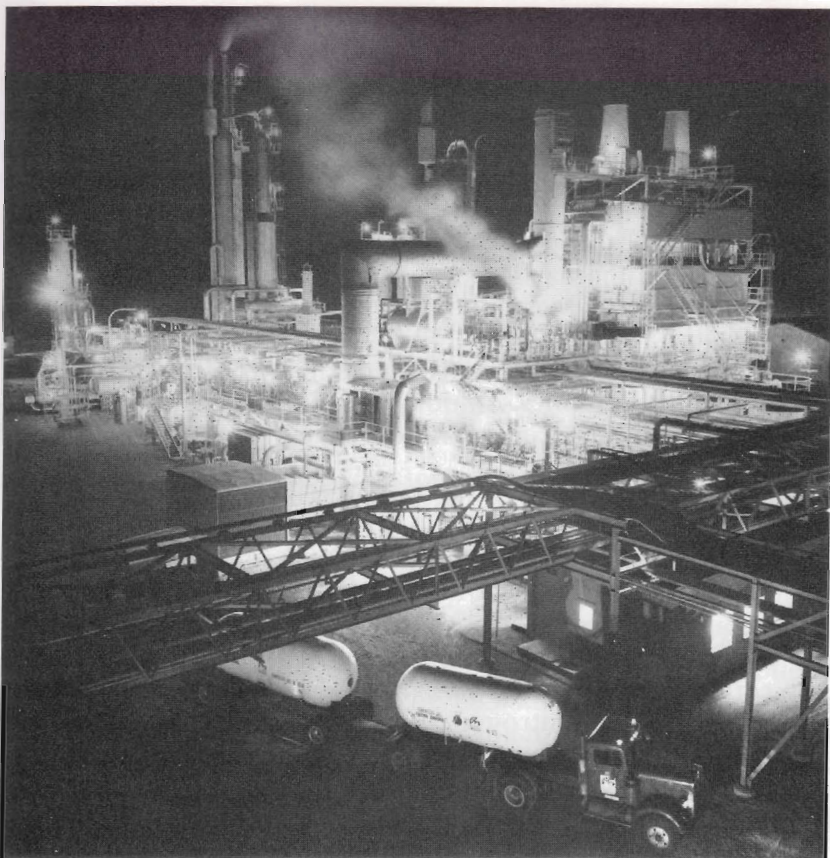
Figure 7-1 An ammonia plant. This plant produces 750 tons of ammonia per day from hydrogen gas and nitrogen gas. The nitrogen comes from air and the hydrogen is obtained from the reaction between methane and steam.

Ammonia is a colorless gas with a sharp, irritating odor. It is the effective agent in some forms of "smelling salts." Unlike nitrogen, ammonia is extremely soluble in water. Household ammonia is about a 2 M solution of NH_3 in water together with a detergent. Ammonia was the first complex molecule to be identified in interstellar space. Ammonia occurs in galactic dust clouds in the Milky Way and, in the solid form, constitutes the rings of Saturn.
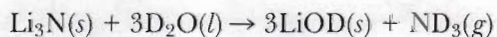
Nitrogen reacts directly with lithium metal at room temperature to form lithium nitride:

$$6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$$
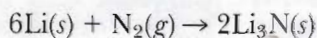
The reddish-black lithium nitride reacts directly with water to form ammonia:

$$Li_3N(s) + 3H_2O(l) \rightarrow 3LiOH(aq) + NH_3(g)$$
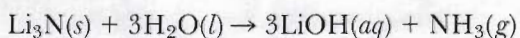
This reaction can be used to prepare deuterated ammonia, ND_3:

$$Li_3N(s) + 3D_2O(l) \rightarrow 3LiOD(s) + ND_3(g)$$

Preparation of ammonia by these reactions is not competitive economically with the Haber process because of the high cost of producing lithium metal.

7-4 FIXED NITROGEN IS A KEY INGREDIENT IN FERTILIZERS

Ammonia is readily soluble in water, binds to many components of soil, and is easily converted to usable plant food. Concentrated aqueous solutions of ammonia or pure liquid ammonia can be sprayed directly into the soil (Figure 7-2). Ammonia is inexpensive and high in nitrogen. The increased growth of plants when fertilized by ammonia is spectacular. Liquid ammonia is toxic and injurious to living tissue, however, and must be handled carefully.

For some purposes it is more convenient to use a solid fertilizer instead of ammonia solutions. For example, ammonia combines directly with sulfuric acid to produce ammonium sulfate:

$$2NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$
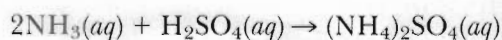
Ammonium sulfate is the most important solid fertilizer in the world. Its annual U.S. production is 4 billion pounds.

The primary fertilizer nutrients are nitrogen, phosphorus, and potassium, and fertilizers are rated by how much of each they contain. For example, a 5-10-5 fertilizer has 5 percent by mass total available nitrogen, 10 percent by mass phosphorus (equivalent to the form P_2O_5), 5 percent by mass potassium (equivalent to the form K_2O), and 80 percent inert ingredients. The production of fertilizers is one of the largest and most important industries in the world.

Figure 7-2 This photo demonstrates the method of spraying ammonia into the soil. Liquid ammonia, called anhydrous ammonia, is used extensively as a fertilizer because it is cheap, high in nitrogen, and easy to apply.

Grant Heilman/Grant Heilman

## 7-5 NITRIC ACID IS PRODUCED BY THE OSTWALD PROCESS

About half of all the ammonia produced is converted to nitric acid by the *Ostwald process*. The first step in this process is the conversion of ammonia to nitrogen oxide:

(1)
$$4NH_3(g) + 5O_2(g) \xrightarrow[825°C]{Pt} 4NO(g) + 6H_2O(g)$$
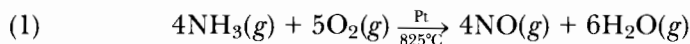
The second step in the Ostwald process involves the oxidation of NO to nitrogen dioxide by reaction with oxygen:

(2)
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

In the final step, the NO_2 is dissolved in water to yield nitric acid:

(3)
$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$
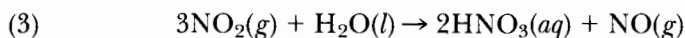
The $NO(g)$ evolved is recycled back to step (2).

Laboratory grade nitric acid is approximately 70 percent HNO_3 by weight with a density of $1.42 \text{ g} \cdot \text{mL}^{-1}$ and a concentration of 16 M (Figure 7-3). The U.S. annual production of nitric acid is over 14 billion pounds, which makes it the eleventh-ranked industrial chemical. Nitric acid is the least expensive potent oxidizing agent and is used in a large number of important chemical processes, including the production of explosives such as trinitrotoluene (TNT), nitroglycerine, and nitrocellulose (gun cotton). It is also used in etching and photoengraving processes to produce grooves in metal surfaces.

DANGER!
CAUSES SEVERE BURNS.
VAPOR EXTREMELY HAZARDOUS.
MAY CAUSE NITROUS GAS POISONING
MAY BE FATAL IF INHALED OR SWALLOWED.
SYMPTOMS OF LUNG INJURY MAY BE DELAYED.
STRONG OXIDIZER.
SPILLAGE MAY CAUSE FIRE OR LIBERATE DANGEROUS GAS.
Do not get in eyes, on skin, on clothing.
Do not breathe vapor
Use only with adequate ventilation.
Wash thoroughly after handling.
Keep from contact with clothing and other combustible materials.
Do not store near combustible materials.
Store in tightly closed containers
Keep out of reach of children

☒ POISON ☒

Call a physician at once.
FIRST AID: In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse.
If inhaled, remove to fresh air. If not breathing give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen
If swallowed, do not give emetics or baking soda. Give tap water, milk of magnesia or eggs beaten with water. Never give anything by mouth to an unconscious person.
In case of spill: Flush immediately with large volumes of water; after washing neutralize residue with soda ash or lime.
In case of fire: Use large quantities of water for extinguishing fire.

Exposure to light causes formation of colored oxides of nitrogen. Store in a cool, dark place.

Allied Corporation
Allied Chemical
Morristown, New Jersey 07960

Allied Chemical
An **ALLIED** Company

Nitric Acid
Code 108-002677
Semiconductor Low Mobile Ion Grade
Meets SEMI specifications.
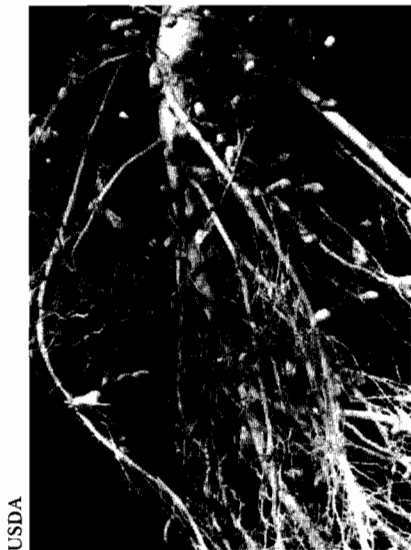For manufacturing use only.
Not for food or drug use.

HNO₃ .... F.W. 63.01
Assay (HNO₃) 70.0-71.0%
Density at 25°C (g/mL) .... 1.42 approx.

NET WT. 7 LBS. (3.18 kg)

108-002677-7-

Allied Chemical Co.

Figure 7-3 Label from a bottle of concentrated nitric acid. Notice that the label contains information on the hazardous properties of the substance.

7-6 CERTAIN BACTERIA CAN FIX NITROGEN

Nitrogen fixation by microorganisms is an important source of plant nutrients. The most common of these nitrogen-fixing bacteria is the *Rhizobium* bacterium, which invades the roots of leguminous plants, such as alfalfa, clover, beans, and peas. The *Rhizobium* forms nodules on the roots of these legumes and has a symbiotic (mutually beneficial) relationship with the plant (Figure 7-4). The plant produces carbohydrates through photosynthesis, and the *Rhizobium* uses the carbohydrate as fuel for fixing the nitrogen, which is incorporated into plant protein. Alfalfa is the most potent nitrogen-fixer, followed by clover, soybeans, other beans, peas, and peanuts. In modern agriculture, crops are rotated, meaning that a nonleguminous crop and a leguminous crop are alternated on one piece of land. The leguminous crop is either harvested, leaving behind nitrogen-rich roots, or plowed into the soil, adding both nitrogen and organic matter. A plowed-back crop of alfalfa may add as much as 400 lb of fixed nitrogen to the soil per acre.

Figure 7-4 Nitrogen-fixing nodules on the roots of a leguminous plant. The nodules contain *Rhizobium,* a soil bacterium that converts atmospheric elemental nitrogen to water-soluble nitrogen compounds.

7-7 NITROGEN FORMS SEVERAL IMPORTANT COMPOUNDS WITH HYDROGEN AND OXYGEN

The most important nitrogen-hydrogen compounds are ammonia, NH_3, hydrazine, N_2H_4, and hydrazoic acid, HN_3. Ammonia is a weak base. The pK_b of the reaction

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
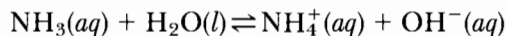
is 4.76 at 25°C. Hydrazine is a colorless, fuming, reactive liquid. It is produced by the *Raschig synthesis,* in which ammonia is reacted with hypochlorite ion (household bleach is sodium hypochlorite in water) in basic solution:

$$2NH_3(aq) + ClO^-(aq) \xrightarrow{OH^-(aq)} N_2H_4(aq) + H_2O(l) + Cl^-(aq)$$

Household bleach should *never* be mixed with household ammonia because extremely toxic and explosive chloramines, such as H_2NCl and $HNCl_2$, are produced as by-products. The reaction of hydrazine with oxygen,

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$$
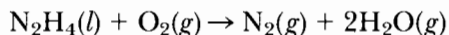
is accompanied by the release of a large amount of energy, and hydrazine and some of its derivatives are used as rocket fuels.

Nitrogen forms a number of oxides, with nitrogen having an oxidation state of +1 through +5 (Table 7-4). Dinitrogen oxide, also known as laughing gas, was once used as a general anesthetic, but its primary use now is as an aerosol and canned whipped cream propellant. Dinitrogen oxide can be produced by a cautious thermal decomposition of NH_4NO_3:

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$$
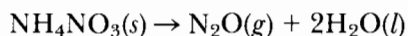
Table 7-4 The principal oxides of nitrogen

Formula	Systematic name	Description
N_2O	dinitrogen oxide (nitrous oxide)	colorless, rather unreactive gas
NO	nitrogen oxide (nitric oxide)	colorless, paramagnetic, reactive gas
N_2O_3	dinitrogen trioxide	dark-blue solid (m.p. $-101°C$); dissociates in gas phase to NO and NO_2
NO_2	nitrogen dioxide	brown, paramagnetic, reactive gas; dimerizes reversibly to N_2O_4
N_2O_4	dinitrogen tetroxide	colorless gas (b.p. $21°C$) dissociates reversibly to NO_2
N_2O_5	dinitrogen pentoxide	colorless, ionic solid; unstable as a gas

Nitrogen oxide is produced in the oxidation of copper by dilute nitric acid:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$
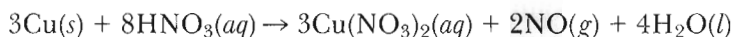
Although $NO(g)$ is colorless, this reaction appears to produce a brown gas if it is run in a vessel that is open to the atmosphere. The brown gas results from the rapid production of nitrogen dioxide by the reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
$$\text{colorless} \qquad\qquad \text{brown}$$
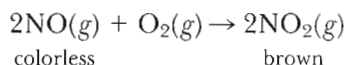
In the gas phase, nitrogen dioxide dimerizes to form dinitrogen tetroxide:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H°_{rxn} = -57.2 \text{ kJ} \cdot \text{mol}^{-1}$$

Because this reaction is exothermic, an increase in temperature results in the formation of more $NO_2(g)$, and hence a more reddish-brown mixture.
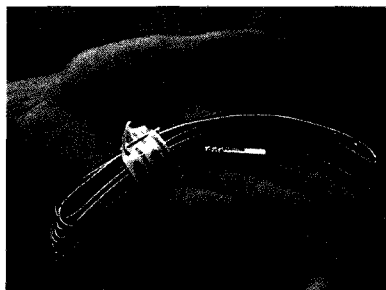
Dinitrogen trioxide can be prepared by the reaction

$$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g) \qquad \Delta H°_{rxn} = -39.7 \text{ kJ} \cdot \text{mol}^{-1}$$

Because the reaction is exothermic, production of $N_2O_3(g)$ is favored at lower temperatures. Dinitrogen trioxide is formally the acid anhydride of nitrous acid, HNO_2, which can be prepared by the reaction of an equimolar mixture of nitrogen oxide and nitrogen dioxide in a basic solution (for example, NaOH):

$$NO(g) + NO_2(g) + 2NaOH(aq) \rightarrow 2NaNO_2(aq) + H_2O(l)$$
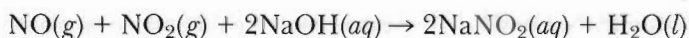
Addition of acid to the resulting solution yields nitrous acid:

$$NO_2^-(aq) + H^+(aq) \rightarrow HNO_2(aq)$$
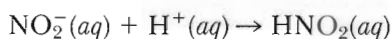
An increase in temperature from 0°C (ice water) to 25°C converts some of the N_2O_4 to NO_2 and results in a darker color for the reaction mixture.
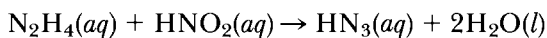
Nitrous acid is a weak acid, with $pK_a = 5.22$ at 25°C.

Salts of nitrous acid are called nitrites. Sodium nitrite, $NaNO_2$, is used as a meat preservative. The nitrite ion combines with the hemoglobin in meat to produce a deep red color. The main problem with the extensive use of nitrites in foods is that the nitrite ion reacts with amines in the body's gastric juices to produce compounds called nitrosamines, such as $(CH_3)_2NNO$, dimethylnitrosamine, which are carcinogenic.

Dinitrogen pentoxide is the anhydride of nitric acid:

$$N_2O_5(s) + H_2O(l) \rightarrow 2HNO_3(aq)$$
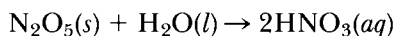
Dinitrogen pentoxide is a rather unstable ionic solid and a powerful oxidizing agent.

The reaction of nitrous acid with hydrazine in acidic solution yields hydrazoic acid:

$$N_2H_4(aq) + HNO_2(aq) \rightarrow HN_3(aq) + 2H_2O(l)$$

Hydrazoic acid is a colorless, toxic liquid and a dangerous explosive. In aqueous solution, HN_3 is a weak acid, with $pK_a = 4.72$ at 25°C. Its lead and mercury salts, $Pb(N_3)_2$ and $Hg(N_3)_2$, which are called *azides,* are used in detonation caps; both compounds are dangerously explosive. Sodium azide, NaN_3, is used as the gas source in automobile air safety bags, which inflate rapidly on impact. Some other commercially important nitrogen-containing compounds are given in Table 7-5.


Detonation ("blasting") caps.

Table 7-5 Some important compounds of nitrogen

Compound	Uses
ammonia, NH_3	fertilizers; manufacture of nitric acid, explosives; synthetic fibers; refrigerant; manufacture of dyes and plastics
nitric acid, HNO_3	manufacture of fertilizers, explosives, lacquers, synthetic fabrics, drugs, and dyes; oxidizing agent; metallurgy; ore flotation
ammonium nitrate, NH_4NO_3	fertilizer, explosives, pyrotechnics, herbicides and insecticides, solid rocket propellant
calcium cyanamide, $CaCN_2$	fertilizer, herbicide, defoliant, hardening of iron and steel
sodium cyanide, $NaCN$	extraction of gold and silver from their ores; electroplating; case-hardening of metals; insecticide; fumigant; manufacture of dyes and pigments; ore flotation

Under ordinary conditions, nitrogen and oxygen do not react with each other. When combined at high pressure and temperature, however, as in the cylinders of an automobile engine, they react to form nitrogen oxide, NO, which then reacts with O_2 to produce nitrogen dioxide. Ordinarily this reaction occurs too slowly at the low concentrations of NO in the atmosphere to account for any significant concentration of $NO_2(g)$, but, for reasons that are not yet understood, the reaction occurs rapidly in sunny, urban atmospheres. Nitrogen dioxide is a red-brown noxious gas that is responsible for the yellow-brown color of smog, first made famous in Los Angeles but now all too common in many urban areas. A concentration of 500 ppm of NO_2 in air is usually fatal; there is some disagreement concerning tolerable levels of NO_2, but they are not higher than 3 to 5 ppm. Levels of NO_2 reach 0.9 ppm in Los Angeles on particularly bad days.
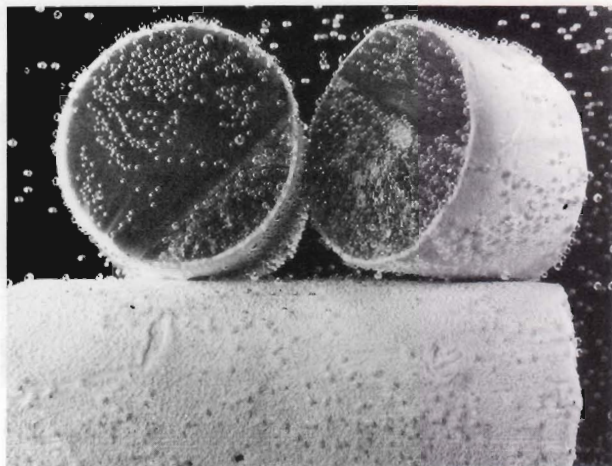
The problem of NO_2 is not so much its primary toxicity but the fact that it is dissociated by radiation to produce atomic oxygen:

$$NO_2(g) \xrightarrow{\text{392-nm light}} NO(g) + O(g)$$
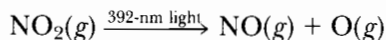
Because the dissociation of the NO_2 is caused by radiation (light), it is called *photodissociation*. The atomic oxygen then reacts with molecular oxygen to produce ozone. These two reactions account for the fact that ozone levels are higher on sunny days than on cloudy days. Ozone in the atmosphere makes up about 90 percent of the general category of pollutants called oxidants, which are now measured continually in many cities. Los Angeles has air pollution alerts when the level of oxidants exceeds 0.35 ppm.

The atomic oxygen produced by the photodissociation of NO_2 also attacks the hydrocarbons introduced into the atmosphere by the incomplete combustion of gasoline and diesel fuel. The reaction of atomic oxygen with hydrocarbons initiates a complicated sequence of chemical reactions. The end products of these reactions are a number of substances that attack living tissue and lead to great discomfort, if not serious disorders. These substances make up what is called *photochemical smog*, which causes eyes to tear and smart, something that people who live in smoggy cities experience often.

The control of photochemical smog requires controlling the emission of its two principal ingredients, NO and hydrocarbons, from automobile exhausts. The Congressional Clean Air Act of 1967, with its amendments in 1970 and 1977, imposed limitations on exhaust emissions. Although there are indications that smog has lessened in some cities, in many others smog and other types of pollution problems are still increasing.

Figure 7-5a White phosphorus is stored in water, as it ignites in air at about 25°C.
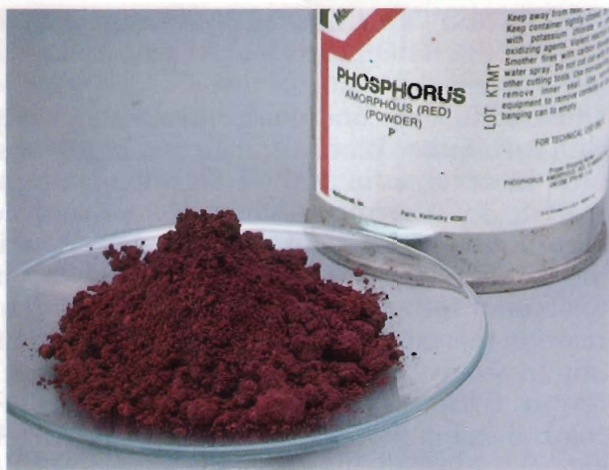
Figure 7-5b Red phosphorus is less reactive than white phosphorus, undergoing the same chemical reactions but at higher temperatures.

Barry Runk/Grant Heilman

7-9 THERE ARE TWO PRINCIPAL ALLOTROPES OF SOLID PHOSPHORUS

There are several allotropic forms of solid phosphorus, the most important of which are *white phosphorus* and *red phosphorus*. White phosphorus is a white, transparent, waxy crystalline solid (Figure 7-5) that often appears pale yellow because of impurities. It is insoluble in water and alcohol but soluble in carbon disulfide. A characteristic property of white phosphorus is its high chemical reactivity. It ignites spontaneously in air at about 25°C. White phosphorus should never be allowed to come into contact with the skin because body temperature (37°C) is sufficient to ignite it spontaneously. Phosphorus burns are extremely painful and slow to heal. In addition, white phosphorus is very poisonous. White phosphorus should always be kept under water and handled with forceps.

When white phosphorus is heated above 250°C in the absence of air, a form called red phosphorus is produced. Red phosphorus is a red to violet powder that is less reactive than white phosphorus. The chemical reactions that the red form undergoes are the same as those of the white form, but they generally occur only at higher temperatures. For example, red phosphorus must be heated to 260°C before it burns in air. The toxicity of red phosphorus is much lower than that of white phosphorus.

White phosphorus consists of tetrahedral P_4 molecules (Figure 7-6), whereas red phosphorus consists of large, random aggregates of phosphorus atoms. The structure of red phosphorus is called *amorphous*, which means that it has no definite shape.

Most of the phosphorus that is produced is used to make phosphoric acid or other phosphorus compounds. Elemental phos-
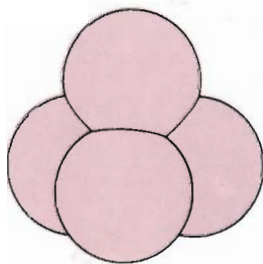
Figure 7-6 White phosphorus consists of tetrahedral P_4 molecules.

phorus, however, is used in the manufacture of pyrotechnics, matches, rat poisons, incendiary shells, smoke bombs, and tracer bullets.

Phosphorus is not found as the free element in nature. The principal sources are the minerals calcium phosphate, hydroxyapatite, (Figure 7-7), fluorapatite, and chlorapatite. These ores collectively are called phosphate rock. Vast phosphate rock deposits occur in the U.S.S.R., in Morocco, and in Florida, Tennessee, and Idaho. An electric furnace is used to obtain phosphorus from phosphate rock. The furnace is charged with powdered phosphate rock, sand (SiO_2), and carbon in the form of coke. The source of heat is an electric current that produces temperatures of over 1000°C. A simplified version of the overall reaction that takes place is

$$2Ca_3(PO_4)_2(s) + 6SiO_2(s) + 10C(s) \rightarrow$$

phosphate rock   sand   coke

$$6CaSiO_3(l) + 10CO(g) + P_4(g)$$
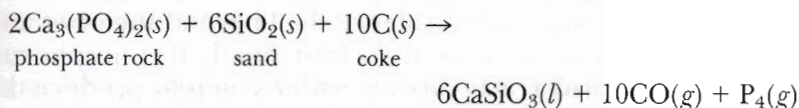
The liquid calcium silicate, $CaSiO_3(l)$, called slag, is tapped off from the bottom of the furnace, and the phosphorus vapor produced solidifies to the white solid when the mixture of $CO(g)$ and $P_4(g)$ is passed through water (carbon monoxide is only very slightly soluble in water).

Although some phosphate rock is used to make elemental phosphorus, most phosphate rock is used in the production of fertilizers. Phosphorus is a required nutrient of all plants, and phosphorus compounds have long been used as fertilizer. In

■ $Ca_3(PO_4)_2$ calcium phosphate
   $Ca_{10}(OH)_2(PO_4)_6$ hydroxyapatite
   $Ca_{10}F_2(PO_4)_6$ fluorapatite
   $Ca_{10}Cl_2(PO_4)_6$ chlorapatite

Bill Tronca/Tom Stack and Assoc.

Figure 7-7 Hydroxyapatite is a common mineral that is found in many areas. It is used in the manufacture of phosphoric acid and phosphate fertilizers.

spite of its great abundance, phosphate rock cannot be used as a fertilizer because, as the name implies, it is insoluble in water. Consequently, plants are not able to assimilate the phosphorus from phosphate rock. To produce a water-soluble source of phosphorus, phosphate rock is reacted with sulfuric acid to produce a water-soluble product called *superphosphate*, $Ca(H_2PO_4)_2$, one of the world's most important fertilizers.
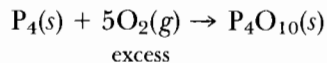
7-10 THE OXIDES OF PHOSPHORUS ARE ACID ANHYDRIDES

The main difference in the chemistries of nitrogen and phosphorus is similar to that between oxygen and sulfur, namely, the availability of $3d$ orbitals on phosphorus. The $3d$ orbitals make possible the expansion of the valence shell beyond the octet and thus the occurrence of more than four bonds to phosphorus.

White phosphorus reacts directly with oxygen to produce the oxides P_4O_6 and P_4O_{10}. With excess phosphorus present, P_4O_6 is formed:

$$P_4(s) \; + \; 3O_2(g) \rightarrow P_4O_6(s)$$
$$\text{excess}$$
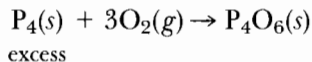
with excess oxygen present, P_4O_{10} is formed:

$$P_4(s) \; + \; 5O_2(g) \rightarrow P_4O_{10}(s)$$
$$\text{excess}$$

The formulas for P_4O_6 and P_4O_{10} are often written P_2O_3 and P_2O_5, respectively. These obsolete (that is, now known to be incorrect) molecular formulas are the basis for the common names phosphorus *tri*oxide and phosphorus *pent*oxide.

It is interesting to compare the structures of P_4O_6 and P_4O_{10} (Figure 7-8). The structure of P_4O_6 is obtained from that of P_4 by inserting an oxygen atom between each pair of adjacent phosphorus atoms; there are six edges on a tetrahedron, and thus a total of six oxygen atoms are required. The structure of P_4O_{10} is obtained from that of P_4O_6 by attaching an additional oxygen atom to each of the four phosphorus atoms.
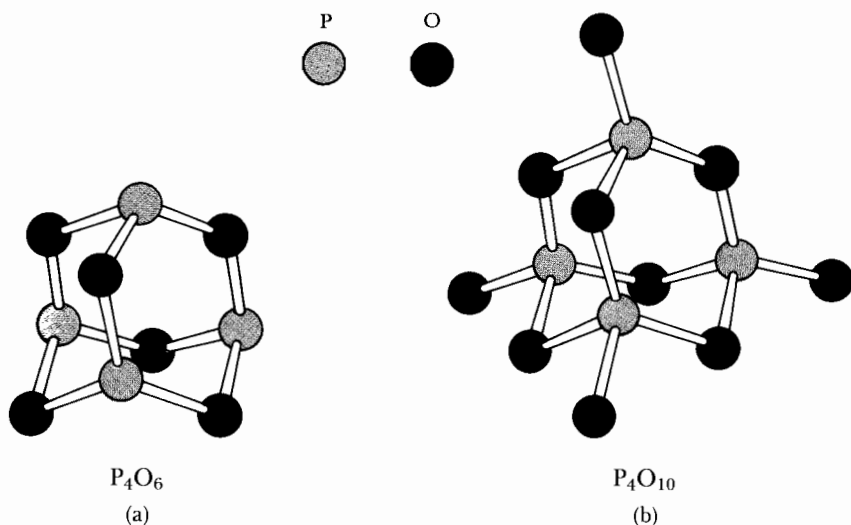
■ P_4O_6 produces a violent explosion when added to hot water.

The phosphorus oxides P_4O_6 and P_4O_{10} react with water to form the phosphorus oxyacids: phosphorous acid, H_3PO_3, and phosphoric acid, H_3PO_4:

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$
$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

Phosphorus pentoxide is a powerful dehydrating agent capable of removing water from concentrated sulfuric acid, which is itself a strong dehydrating agent.

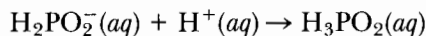$$P_4O_{10}(s) + 6H_2SO_4(l) \rightarrow 4H_3PO_4(l) + 6SO_3(g)$$

Figure 7-8 Structure of P_4O_6 and P_4O_{10}. (a) The P_4O_6 molecule can be viewed as arising from the tetrahedral P_4 molecule when an oxygen atom is inserted between each pair of adjacent phosphorus atoms. (b) The P_4O_{10} molecule can be viewed as arising from P_4O_6 when an oxygen atom is attached to each of the four phosphorus atoms. Note that there are no phosphorus-phosphorus bonds in either P_4O_6 or P_4O_{10}.

Thus phosphorus pentoxide is used as a drying agent in desiccators and dry boxes to remove water vapor.

Hypophosphorous acid, H_3PO_2, is prepared by reacting $P_4(g)$ with a warm aqueous solution of NaOH:

$$P_4(g) + 3OH^-(aq) + 3H_2O(l) \rightarrow 3H_2PO_2^-(aq) + PH_3(g)$$
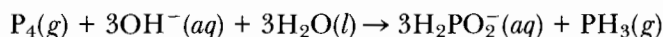
followed by acidification:

$$H_2PO_2^-(aq) + H^+(aq) \rightarrow H_3PO_2(aq)$$

The structures of the phosphate anion, PO_4^{3-}, the phosphite ion, HPO_3^{2-}, and the hypophosphite ion, $H_2PO_2^-$, are
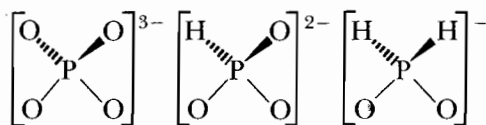
Using VSEPR theory, we predict that these ions are tetrahedral, which is correct.

The hydrogen atoms attached to phosphorus are not dissociable in aqueous solutions. Thus, phosphoric acid, H_3PO_4, is triprotic, phosphorus acid, $H_2(HPO_3)$, is diprotic, and hypophosphorous acid, $H(H_2PO_2)$, is monoprotic. The pK_a values at 25°C are given in Table 7-6.

Phosphoric acid (Figure 7-9) is the ninth ranked industrial chemical, almost 22 billion pounds being produced annually in

Table 7-6 The pK_a values in water at 25°C of phosphorus oxyacids

Acid	pK_{a1}	pK_{a2}	pK_{a3}
H_3PO_4	2.2	7.1	12.4
$H_2(HPO_3)$	1.8	~7	none
$H(H_2PO_2)$	1.2	none	none

Figure 7-9 Phosphoric acid label. Phosphoric acid is sold as a 15 M aqueous solution.

the United States. It is sold in various concentrations. The 85 percent by mass (85 g of H_3PO_4 to 15 g of H_2O) solution is a colorless, syrupy liquid. Laboratory phosphoric acid is sold as an 85% solution, which is equivalent to 15 M.

Phosphoric acid is used extensively in the production of soft drinks, and various of its salts are used in the food industry. For example, the monosodium salt, NaH_2PO_4, is used in a variety of foods to control acidity, and calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, is the acidic ingredient in baking powder. The evolution of carbon dioxide that takes place when baking powder is heated can be represented as

$$\underbrace{Ca(H_2PO_4)_2(s) + 2NaHCO_3(s)}_{\text{in baking powder}} \xrightarrow{300°C}$$

$$2CO_2(g) + 2H_2O(g) + CaHPO_4(s) + Na_2HPO_4(s)$$
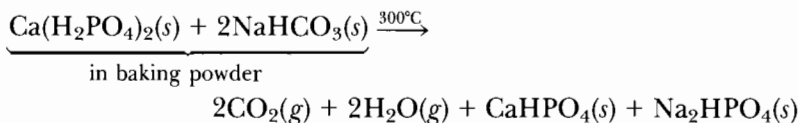
■ Unleavened bread does not contain baking powder and thus does not rise when baked.

The slowly evolving $CO_2(g)$ gets trapped in small gas pockets and thereby causes the cake or bread to rise.

When phosphoric acid is heated gently, pyrophosphoric acid (pyro means heat) is obtained as a result of the elimination of a water molecule from a pair of phosphoric acid molecules:

elimination of water

pyrophosphoric acid, $H_4P_2O_7$
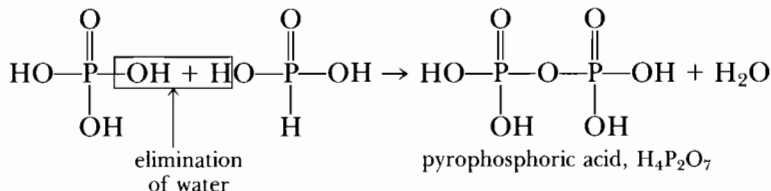
Pyrophosphoric acid is a viscous, syrupy liquid that tends to so-lidify on long standing. In aqueous solution, it slowly reverts to phosphoric acid.

Longer chains of phosphate groups can be formed. The compound sodium tripolyphosphate, $Na_5P_3O_{10}$, used to be the phosphate ingredient of detergents. Its role was to break up and suspend dirt and stains by forming water-soluble complexes with metal ions. (The formation of complexes is discussed in Chapter 23 of the text.) In the 1960s almost all detergents contained phosphates, sometimes as much as 50 percent by mass. It was discovered, however, that the phosphates led to a serious water pollution problem. The enormous quantity of phosphates discharged into rivers and lakes served as a nutrient for the rampant growth of algae and other organisms. When these organisms died, much of the oxygen dissolved in the water was consumed in the d̶e̶c̶a̶y̶ process, thus depleting the water's oxygen supply and destroying the ecological balance. This process is called *eutrophication*. As a result of legislation in the 1970s, phosphates have been eliminated from detergents or their levels have been reduced markedly.

Sodium tripolyphosphate

7-11 PHOSPHORUS FORMS A NUMBER OF BINARY COMPOUNDS
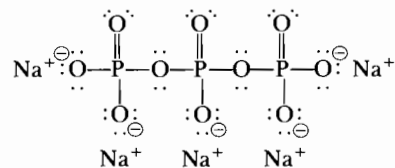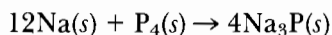
Phosphorus reacts directly with reactive metals, such as sodium and calcium, to form phosphides. A typical reaction is

$$12Na(s) + P_4(s) \rightarrow 4Na_3P(s)$$

Most metal phosphides react vigorously with water to produce phosphine, $PH_3(g)$:

$$Ca_3P_2(s) + 6H_2O(l) \rightarrow 2PH_3(g) + 3Ca(OH)_2(aq)$$
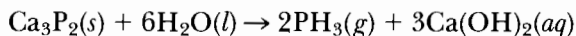
Phosphine has a trigonal pyramidal structure with an H—P—H bond angle of 93.7°. It is a colorless, extremely toxic gas with an offensive odor like that of rotten fish. Unlike ammonia, phosphine does not act as a base toward water, and few phosphonium (PH_4^+) salts are stable. Phosphine can also be prepared by the reaction of white phosphorus with a strong base.

Phosphorus reacts directly with the halogens to form halides of the form PX_3 and PX_5. If an excess of phosphorus is used, then the trihalide is formed. For example,

$$\underset{\text{excess}}{P_4(s)} + 6Cl_2(g) \rightarrow 4PCl_3(l)$$
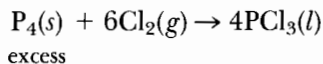
If an excess of halide is used, then the pentahalide is formed:

$$\underset{\text{excess}}{P_4(s)} + 10Cl_2(g) \rightarrow 4PCl_5(s)$$
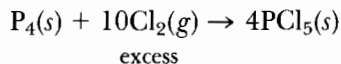
■ Note the similarity of phosphides to nitrides.

■ Phosphine reacts violently with oxygen and the halogens.
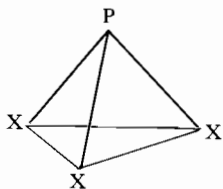
Figure 7-10 The phosphorus trihalides, PX_3, have a trigonal pyramidal structure in the gas phase.
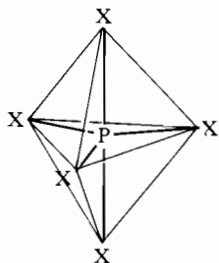
Figure 7-11 The phosphorus pentahalides, PX_5, have a trigonal bipyramidal structure in the gas phase.

Recall from Chapter 11 of the text that phosphorus trihalide molecules in the gas phase have a trigonal pyramidal structure (Figure 7-10) and that phosphorus pentahalide molecules in the gas phase have a trigonal bipyramidal structure (Figure 7-11). Table 7-7 lists the physical states of the various phosphorus halides. Phosphorus halides react vigorously with water. For example,

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$$
$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$$
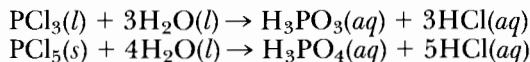
These hydrolysis reactions of PCl_3 and PCl_5 are fairly typical for molecular halides in which the central atom can bond to more atoms. The products are the hydrohalic acid and an oxyacid of the central atom. We encountered reactions of this type earlier (Sections 5-2 and 6-2):

$$BCl_3(g) + 3H_2O(l) \rightarrow B(OH)_3(s) + 3HCl(aq)$$
$$SiF_4(g) + 2H_2O(l) \rightarrow SiO_2(s) + 4HF(aq)$$
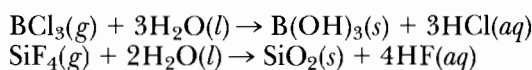
Note that the oxidation state of the central atom does not change in these reactions. The intermediates in these cases are believed to be species such as
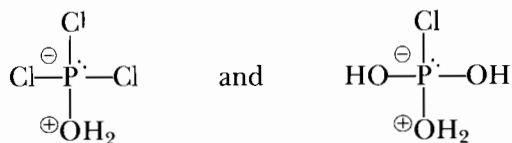
If the central atom has its maximum number of bonds, as in CF_4 or SF_6, such intermediate species cannot form and the halides do not undergo hydrolysis.

Table 7-7 Physical states of the phosphorus halides at room temperature

Halide	Physical state	Molecular description
PF_3	colorless gas	trigonal pyramidal PF_3 molecules
PCl_3	clear, colorless, fuming liquid	trigonal pyramidal PCl_3 molecules
PBr_3	colorless, fuming liquid	trigonal pyramidal PBr_3 molecules
PI_3	red, crystalline, unstable solid	trigonal pyramidal PI_3 molecules
PF_5	colorless gas	trigonal bipyramidal PF_5 molecules
PCl_5	pale-yellow, fuming crystals	$[PCl_4^+][PCl_6^-]$ ion-pairs; PCl_4^+ tetrahedral and PCl_6^- octahedral
PBr_5	yellow, fuming, hygroscopic crystals	$[PBr_4^+]Br^-$ ion-pairs; PBr_4^+ tetrahedral
PI_5	not known	presumably iodine atoms are too large to arrange more than three around a phosphorus atom

When phosphorus is heated with sulfur, the yellow crystalline compound tetraphosphorus trisulfide, P_4S_3, is formed. Matches that can be ignited by striking on any rough surface contain a tip composed of the yellow P_4S_3 on top of a red portion that contains lead dioxide, PbO_2, together with antimony sulfide, Sb_2S_3. Friction causes the P_4S_3 to ignite in air, and the heat produced then initiates a reaction between antimony sulfide and lead dioxide that produces a flame.

Safety matches consist of a mixture of potassium chlorate and antimony sulfide. The match is ignited by striking on a special rough surface composed of a mixture of red phosphorus, glue, and abrasive. The red phosphorus is ignited by friction and in turn ignites the reaction mixture in the matchhead.

7-12 MANY PHOSPHORUS COMPOUNDS ARE IMPORTANT BIOLOGICALLY

Many organic phosphates are potent insecticides that are also highly toxic to humans. These insecticides act by blocking the transmission of electrical signals in the respiratory system, thereby causing paralysis and death by suffocation. Fortunately, such poisons do not last for long in the environment because they are destroyed over a period of several days by reaction with water. An important example of an organophosphorus insecticide is malathion, which was used to combat the Mediterranean fruit fly infestation in California in the summer of 1981. Malathion is toxic to humans, but only at fairly large doses. There is an enzyme in human gastric juice that decomposes malathion (insects lack this enzyme). Thus malathion is most toxic to humans when it is absorbed directly into the bloodstream, as, for example, when it comes into contact with a cut in the skin.

Some commercially important compounds of phosphorus are given in Table 7-8.

$$\begin{array}{c}
CH_3O \\
\qquad\quad S{=}P{-}S{-}CHCOOCH_2CH_3 \\
CH_3O \qquad\qquad\quad CH_2COOCH_2CH_3
\end{array}$$

Malathion
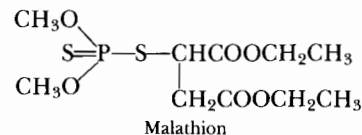
Table 7-8 Some important compounds of phosphorus

Compound	Uses
phosphorus(V) sulfide, P_2S_5	safety matches, oil additive
phosphorus(V) oxide, P_4O_{10}	dehydrating agent
phosphoric acid, H_3PO_4	fertilizers, soaps and detergents, soft drinks, rust-proofing metals, soil stabilizer
sodium phosphates	synthetic detergents, water softeners, leavening agents
calcium phosphates, $CaHPO_4$ and $Ca(H_2PO_4)_2$	fertilizers, poultry and animal feeds
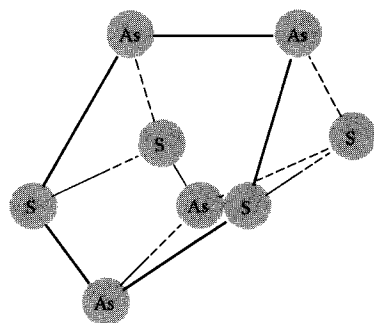
Structure of As_4S_4.

Neither arsenic nor antimony is particularly abundant. Common ores of arsenic are the sulfide minerals *realgar* (As_4S_4) and *orpiment* (As_2S_3), found in Turkey, the U.S.S.R., Eastern Europe, and Nevada. The most important ore of antimony is *stibnite* (Sb_2S_3), which is found in China, South Africa, Mexico, and Bolivia.

The sulfides are converted to the oxides by roasting in air:

$$2As_2S_3(s) + 9O_2(g) \rightarrow 2As_2O_3(s) + 6SO_2(g)$$
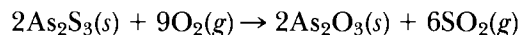
The oxides are reduced to the elements with carbon or hydrogen:

$$2As_2O_3(s) + 3C \rightarrow 3CO_2 + 4As(l)$$
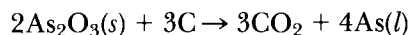
Both arsenic and antimony react directly with the halogens to form trihalides and pentahalides such as AsF_3 and SbF_5.

Like other fourth-row post-transition elements, arsenic has a tendency to favor an oxidation state of two less than the maximum for the group. Thus, although PCl_5 and $SbCl_5$ are stable species, $AsCl_5$ decomposes above $-50°C$. Furthermore, antimony trioxide can be prepared by burning antimony in oxygen, but the pentoxide cannot be produced this way. The relative instability of the $+5$ oxidation state of arsenic means that As_4O_{10} and H_3AsO_4 are strong oxidizing agents.

In conformity with the fact that oxides tend from acidic to basic down any one group in the periodic table, the oxides of arsenic are acidic:

$$As_4O_6(s) + 12NaOH(aq) \rightarrow 4Na_3AsO_3(aq) + 6H_2O(l)$$
<div align="center">sodium arsenite</div>

$$As_4O_{10}(s) + 12NaOH(aq) \rightarrow 4Na_3AsO_4(aq) + 6H_2O(l)$$
<div align="center">sodium arsenate</div>
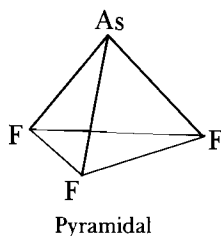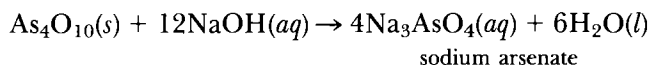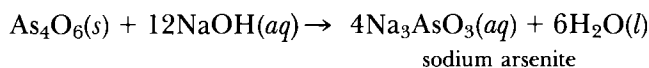
Pyramidal

Arsenic trifluoride has a trigonal pyramidal structure in the gas stage.

and the oxides of antimony are amphoteric:

$$2Sb_2O_3(s) + 6HCl(aq) \rightarrow SbCl_3(s) + 3H_2O(l)$$

$$Sb_2O_3(s) + 6NaOH(aq) \rightarrow 2Na_3SbO_3(aq) + 3H_2O(l)$$
<div align="center">sodium antimonite</div>
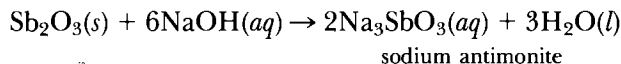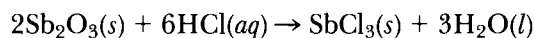
and bismuth(III) oxide is basic:

$$Bi_2O_3(s) + 6HCl(aq) \rightarrow 2BiCl_3(s) + 3H_2O(l)$$

Trigonal bipyramidal

Antimony pentafluoride has a trigonal bipyramidal structure in the gas stage.
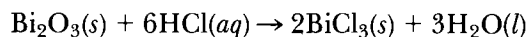
Although arsenic compounds are poisonous, trace amounts of arsenic are essential to the growth of red blood cells in bone marrow, and the average healthy human body contains about 7 milligrams of arsenic.

Antimony is distinctly more metallic in character than arsenic, and numerous alloys contain antimony, which acts to prevent

The minerals orpiment (left), stibnite (center), and realgar (right).

corrosion and to increase the resistance of the alloys to fracturing as a result of thermal shock. Some compounds of arsenic and antimony and their uses are given in Table 7-9.

7-14 BISMUTH IS THE ONLY GROUP 5 METAL

The principal compounds of bismuth contain Bi(III), which is in an oxidation state that is two less than the group number. Bismuth is a pink-white metal that occurs rarely as the free metal.

Table 7-9 Some compounds of arsenic and antimony

Compound	Uses
lead(II) arsenate, $Pb_3(AsO_4)_2(s)$	insecticide
sodium arsenite, $NaAsO_2(s)$	arsenical soap, antiseptic, herbicide, insecticide, fungicide
arsenic(III) oxide, $As_4O_6(s)$	manufacture of glass, insecticide, rodenticide, wood preservative, preparation of many arsenic compounds
antimony trioxide, $Sb_2O_3(s)$	white paint pigment, ceramic opacifier, flame-proofing agent
antimony trichloride, $SbCl_3(s)$	dye mordant, fire-proofing textiles
antimony sulfide, $Sb_2S_3(s)$	vermilion or yellow pigment, pyrotechnics, ruby glass

Table 7-10 Some compounds of bismuth

Compound	Uses
bismuth oxychloride, $BiOCl(s)$	face powder, artificial pearls
bismuth subcarbonate $(BiO)_2CO_3(s)$	ceramic glazes, pharmacology
bismuth subnitrate $BiONO_3(s)$	cosmetics, enamel flux

The most common source of bismuth is the sulfide ore *bismuthinite*, Bi_2S_3.

Bismuth metal is obtained from the ore by roasting it with carbon in air. Bismuth is also obtained as a by-product in lead smelting. Bismuth is used in a variety of alloys, including pewter and low-melting alloys that are used in fire-extinguisher sprinkler-head plugs, electrical fuses, and relief valves for compressed-gas cylinders. Bismuth alloys contract on heating and thus find use in alloys that might otherwise crack because of thermal expansion when subjected to high temperatures.

The oxide Bi_2O_3 is soluble in strongly acidic aqueous solutions (Figure 7-12). The bismuthyl ion, $BiO^+(aq)$, and the bismuthate ion, $BiO_3^-(aq)$, are important in the aqueous-solution chemistry of bismuth. The bismuthyl ion forms insoluble compounds such as $BiOCl$ and $BiO(OH)$, whereas BiO_3^- is a powerful oxidizing agent. Bismuth pentafluoride, BiF_5, is a potent fluorinating agent that transfers fluorine to various compounds and is converted to the trifluoride, BiF_3.

Some bismuth compounds and their major uses are given in Table 7-10.

TERMS YOU SHOULD KNOW

phosphate rock
nitrogen fixation
Haber process
Ostwald process
Raschig synthesis
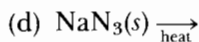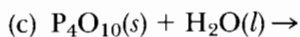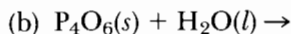
photodissociation
amorphous
superphosphate
eutrophication

Figure 7-12 Bismuth metal and bismuth(III) oxide, Bi_2O_3.

QUESTIONS

7-1. Complete and balance the following equations.

(a) $P_4(s) + O_2(g) \rightarrow$
  excess

(b) $P_4O_6(s) + H_2O(l) \rightarrow$

(c) $P_4O_{10}(s) + H_2O(l) \rightarrow$

(d) $NaN_3(s) \xrightarrow{heat}$

7-2. Complete and balance the following equations.

(a) $N_2O_3(g) + H_2O(l) \rightarrow$ (c) $NH_4NO_3(s) \xrightarrow{heat}$

(b) $N_2O_5(s) + H_2O(l) \rightarrow$ (d) $NH_4NO_2(aq) \xrightarrow{heat}$
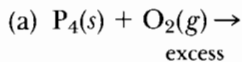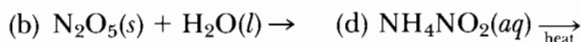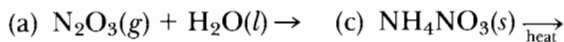
7-3. How could you prepare ammonia starting with air, water, and coke?

7-4. Using D_2O as a source of deuterium, how could you prepare $ND_3(g)$?

7-5. Write a chemical equation for the preparation of hydrazoic acid.

7-6. Write the chemical equation for the preparation of hydrazine by the Raschig process.

7-7. Why do solutions of nitric acid often have a brown-yellow color?

7-8. Why are there no nitrogen pentahalides?

7-9. Write Lewis formulas for the following species (include resonance forms where appropriate).

(a) N_2O_4 (d) H_2N_2

(b) N_2O_3 (e) N_3^-

(c) CN_2^{2-}

7-10. Write Lewis formulas for the following species (include resonance forms where appropriate).

(a) $HONH_2$ (d) N_2O

(b) NO_3^- (e) NO_2

(c) NO_2^-
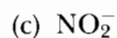
7-11. How could you prepare DCl, using D_2O as a source of deuterium?

7-12. How could you prepare PD_3, using D_2O as a source of deuterium?

7-13. Write chemical equations for the reactions of phosphorus pentoxide with sulfuric acid and with nitric acid.

7-14. Phosphine dissolves in liquid ammonia to give $NH_4^+PH_2^-$. Use VSEPR theory to predict the shape of PH_2^-.

7-15. Use VSEPR theory to predict the shapes of (a) $POCl_3$, (b) PO_4^{3-}, and (c) PCl_6^-.

7-16. When P_4O_{10} and P_4S_{10} are heated in the appropriate proportions above 400°C, $P_4O_6S_4$, a colorless, hygroscopic crystalline substance, is obtained. Using Figure 7-8 as a guide, predict the structure of $P_4O_6S_4$. What about the structure of $P_4O_4S_6$?

7-17. Write chemical equations describing the acidic characters of As_4O_6 and As_4O_{10}, the amphoteric character of Sb_2O_3, and the basic character of Bi_2O_3.

7-18. Use Lewis formulas to show that H_3PO_2 is monobasic, H_3PO_3 is dibasic, and H_3PO_4 is tribasic.

7-19. Predict which of the following molecular halides hydrolyze, and write a balanced equation for those that do.

(a) SF_4 (d) BrF_5

(b) CCl_4 (e) $AsBr_3$

(c) XeF_6

7-20. Use VSEPR theory to predict the structures of the following species.

(a) AsO_3^{3-} (d) $BiCl_3$

(b) AsO_4^{3-} (e) AsF_5

(c) $SbCl_3$
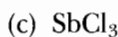
7-21. Suggest why the H—X—H bond angles in NH_3, PH_3, AsH_3, and SbH_3 decrease from 107° for NH_3 to 93° for PH_3, 92° for AsH_3, and 91° for SbH_3.

7-22. For the equilibrium

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H°_{rxn} = -57.2 \text{ kJ}$$
  brown   colorless
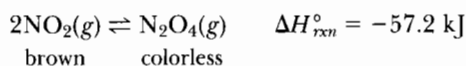
does the reaction mixture become increasingly colored with increasing or decreasing temperature?

7-23. Deuterium chloride gas, DCl(*g*), is prepared in the laboratory by the reaction

$$PCl_3(l) + D_2O(l) \rightarrow DCl(g) + D_3PO_3(l)$$
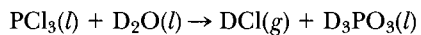
(a) Balance the equation and compute the number of grams of $D_2O(l)$ required to prepare 5.0 mg of DCl(*g*).

(b) Assume that the gas is collected in a 4.0-mL vessel at 20°C and compute the pressure of DCl(*g*) in the vessel.

7-24. Use data in Table 7-6 to compute the pH of the following solutions at 25°C.

(a) 0.10 M $H_3PO_4(aq)$

(b) 0.10 M $H_3PO_3(aq)$

(c) 0.10 M $H_3PO_2(aq)$

THE GROUP 6 ELEMENTS

Although steel wool does not burn in air, it burns vigorously in pure oxygen.

The Group 6 elements are oxygen, sulfur, selenium, tellurium, and polonium. There is a continuous progression in Group 6 from nonmetallic to metallic properties with increasing atomic number. Oxygen, sulfur, and selenium are nonmetals, tellurium is a semimetal, and polonium is a metal. As in other groups, there is a significant difference between the chemical properties of the first member and the second member. Oxygen is limited to two bonds (e.g., H_2O) or occasionally three bonds (e.g., H_3O^+), whereas the other members of the group may uti-

Table 8-1 Sources and uses of the Group 6 elements

Element	Principal sources	Uses
oxygen	fractional distillation of liquid air	blast furnaces; steel production; production of methyl alcohol, acetylene, ethylene oxide, etc.; rocket propellant; sewage treatment; breathing apparatus; many other uses
sulfur	native from underground deposits (Frasch process); natural gas and petroleum by-product	manufacture of sulfuric acid, paper manufacture, rubber vulcanization, drugs and pharmaceuticals, dyes, fungicides, insecticides
selenium	anode muds of the electrolyte refining of copper and lead	photocells, exposure meters, solar cells, xerography, production of ruby-colored glasses and enamels
tellurium	anode muds of the electrolyte refining of copper and lead	alloys to improve machinability of copper and stainless steels, ceramics

lize d orbitals to form compounds such as SF_6 and TeF_6. As in Groups 4 and 5, there is a decrease in thermal stability of the binary hydrogen compounds in going from H_2S to H_2Po. In addition, there is an increasing stability with increasing atomic number of an oxidation state two less than the group number.

Oxygen is the most abundant element on earth and the third most abundant element in the universe, ranking behind hydrogen and helium. Most rocks contain a large amount of combined oxygen. For example, sand is predominantly silicon dioxide (SiO_2) and consists of more than 50 percent oxygen by mass. Almost 90 percent of the mass of the oceans and two thirds of the mass of the human body are oxygen. Air is 21 percent oxygen by volume. We can live weeks without food, days without water, but only minutes without oxygen.

Sulfur is widely distributed in nature, but not usually in sufficient concentration to merit commercial mining. The two most important sources of sulfur are hydrogen sulfide from natural gas and petroleum refining, and elemental sulfur from large salt domes offshore along the Gulf of Mexico. Selenium and tellurium are relatively rare elements. Both elements are found in association with metal sulfide ores, and are obtained commercially as by-products of the refining of copper and lead (Table 8-1). Polonium has no stable isotopes; minute quantities of polonium-210 occur in uranium ores.

Tables 8-2 and 8-3 present some atomic and physical properties of the Group 6 elements. The usual trends with increasing atomic number are evident.

■ Marie Curie was awarded the Nobel Prize in Chemistry in 1911 for the isolation and identification of the element polonium. The element was named in honor of her native country, Poland.

Table 8-2 Atomic properties of the Group 6 elements

Property	O	S	Se	Te	Po
atomic number	8	16	34	52	84
atomic mass/amu	15.9994	32.06	78.96	127.60	(209)
number of naturally occurring isotopes	3	4	6	7	0
ground-state electron configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]3d^{10}4s^2 4p^4$	$[Kr]4d^{10}5s^2 5p^4$	$[Xe]4f^{14}5d^{10}6s^2 6p^4$
atomic radius/pm	60	100	115	140	190
ionization energy/MJ · mol^{-1}					
first	1.31	1.00	0.941	0.869	0.812
second	3.39	2.25	2.05	1.79	—
Pauling electronegativity	3.5	2.5	2.4	2.1	2.0

8-1 THIRTY-FIVE BILLION POUNDS OF OXYGEN ARE SOLD ANNUALLY IN THE UNITED STATES

Oxygen is a colorless, odorless, tasteless gas that exists as a diatomic molecule, O_2. Although colorless in the gaseous state both liquid and solid oxygen are pale blue.

Industrially, oxygen is produced by the fractional distillation of liquid air. Approximately 35 billion pounds of oxygen are sold annually in the United States, making it the fifth most important industrial chemical. The major commercial use of oxygen is in the blast furnaces used to manufacture steel. Oxygen is also used in hospitals, in oxyhydrogen and oxyacetylene torches for welding metals, and to facilitate breathing at high altitudes and under water. Tremendous quantities of oxygen are used directly from air as a reactant in the combustion of hydrocarbon fuels, which supply 93 percent of the energy consumed in the United States. In terms of total usage (pure oxygen and oxygen used directly from air), oxygen is the number two chemical, ranking behind only water.
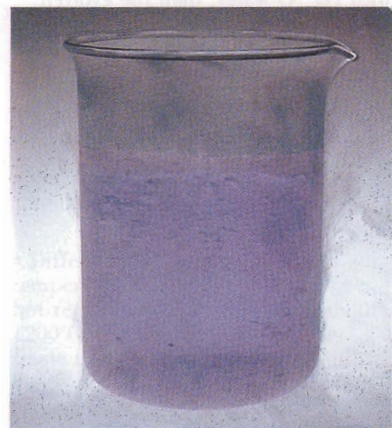
Liquid oxygen.

8-2 OXYGEN IN THE EARTH'S ATMOSPHERE IS PRODUCED BY PHOTOSYNTHESIS

Most of the oxygen in the atmosphere is the result of *photosynthesis*, the process by which green plants combine $CO_2(g)$ and $H_2O(g)$ into carbohydrates and $O_2(g)$ under the influence of visi-

Table 8-3 Some physical properties of the Group 6 elements

Property	O_2	S	Se	Te
melting point/°C	−218.8	115	221	450
boiling point/°C	−183.0	445	685	1009
$\Delta \overline{H}_{fus}$/kJ · mol^{-1}	0.443	1.72	5.44	17.5
$\Delta \overline{H}_{vap}$/kJ · mol^{-1}	6.82	8.37		50.6
density at 20°C/g · cm^{-3}	1.33×10^{-3}	1.96	4.79	6.24

ble light. The carbohydrates appear in the plants as starch, cellulose, and sugars. The reaction is described schematically as

$$CO_2(g) + H_2O(g) \xrightarrow{\text{visible light}} \text{carbohydrate} + O_2(g)$$
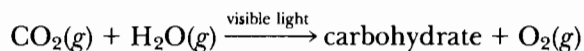
When the carbohydrate is glucose, we have

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$
$$\Delta G^\circ_{rxn} = +2870 \text{ kJ at } 25°C$$
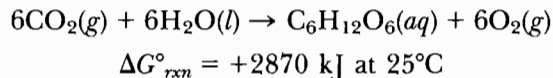
■ The oxygen evolved in photosynthesis reactions arises from the oxygen in the water molecules, as shown by studies with the heavy isotope, ^{18}O. That is, if the photosynthesis reaction is carried out with $H_2{}^{18}O$ water, then the evolved oxygen is $^{18}O_2$, whereas with $C^{18}O_2$, the evolved O_2 has the normal isotopic composition.

The reaction is driven up the Gibbs free energy "hill" ($\Delta G^\circ_{rxn} >> 0$) by the energy obtained from sunlight.

In one year, more than 10^{10} metric tons of carbon is incorporated into carbohydrates by photosynthesis. In the hundreds of millions of years that plant life has existed on earth, photosynthesis has produced much more oxygen than the amount now present in the atmosphere.

8-3 OXYGEN CAN BE PREPARED IN THE LABORATORY BY DECOMPOSITION REACTIONS

A frequently used method for preparing oxygen in the laboratory is the thermal decomposition of potassium chlorate, $KClO_3$. The chemical equation for the reaction is

$$2KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl(s) + 3O_2(g)$$
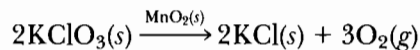
This reaction requires a temperature of about 400°C, but if a small amount of the catalyst manganese dioxide, MnO_2, is added, the reaction occurs rapidly at 250°C. An alternate method for the laboratory preparation of oxygen is to add sodium peroxide, Na_2O_2, to water:

$$2Na_2O_2(s) + 2H_2O(l) \rightarrow 4NaOH(aq) + O_2(g)$$
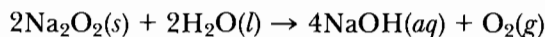
This rapid and convenient reaction does not require heat. However, oxygen also can be prepared by the electrolysis of water (Chapter 2):

$$2H_2O(l) \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)$$
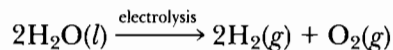
8-4 OXYGEN REACTS DIRECTLY WITH MOST OTHER ELEMENTS

Oxygen is very reactive, and is the second most electronegative element. It reacts directly with all the other elements except the halogens, the noble gases, and some of the less reactive metals to

form a wide variety of compounds. Only fluorine reacts with more elements than oxygen. Compounds containing oxygen constitute 31 of the top 50 industrial chemicals (Appendix A).

Oxygen forms oxides with many elements. Most metals react rather slowly with oxygen at ordinary temperatures but react more rapidly as the temperature is increased. For example, iron, in the form of steel wool, burns vigorously in pure oxygen but does not burn in air (see frontispiece).

Methane, the main constituent of natural gas, burns in oxygen according to the equation

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H^\circ_{rxn} = -802 \text{ kJ}$$
methane
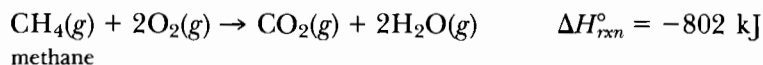
All hydrocarbons burn in oxygen to give carbon dioxide and water. Gasoline is a mixture of hydrocarbons. Using octane, C_8H_{18}, as a typical hydrocarbon in gasoline, we write the combustion of gasoline as

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g) \qquad \Delta H^\circ_{rxn} = -5460 \text{ kJ}$$
octane
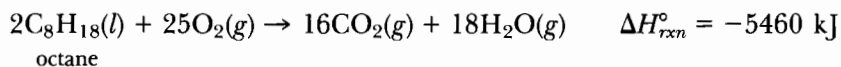
The energy released in reactions of this type is used to power machinery and to produce electricity (Chapter 6 of the text).

A mixture of acetylene and oxygen is burned in the oxyacetylene torch. The chemical equation for the combustion of acetylene is

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$$
acetylene

■ Different flames have different temperatures. The temperature of a hot region of a candle flame is about 1200°C, that of a Bunsen burner flame is about 1800°C, and that of the flame of an oxyacetylene torch is about 2400°C.
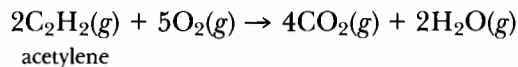
The flame temperature of an oxyacetylene welding torch is about 2400°C, which is sufficient to melt iron and steel. A combustion reaction with which we are all familiar is the burning of a candle. The wax in a candle is composed of long-chain hydrocarbons, such as $C_{20}H_{42}$. The molten wax rises up the wick to the combustion zone the way ink rises in a piece of blotting paper.

8-5 SOME METALS REACT WITH OXYGEN TO YIELD PEROXIDES

Although most metals yield oxides when they react with oxygen, some of the more reactive metals, such as sodium, potassium, and rubidium, yield peroxides and superoxides. Peroxides are compounds in which the negative ion is the peroxide ion, O_2^{2-}, and superoxides are compounds in which the negative ion is the superoxide ion, O_2^-. For example,

$$2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$
sodium peroxide

$$K(s) + O_2(g) \rightarrow KO_2(s)$$
potassium superoxide
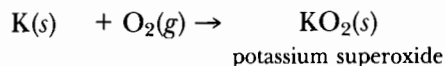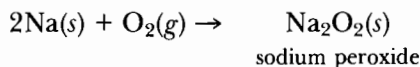
■ The ground state of the oxygen molecule is paramagnetic.

Table 8-4 Comparison of diatomic oxygen species

Species	Molecular-orbital valence electron occupancy	Net number of bonding electrons	Bond length/pm	Bond energy/kJ
O_2^+	$(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(1\pi^*)^1$	5	112	640
O_2	$(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(1\pi^*)^2$	4	121	506
O_2^-	$(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(1\pi^*)^3$	3	126	370
O_2^{2-}	$(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(1\pi^*)^4$	2	149	160

Table 8-5 Commercially available aqueous solutions of hydrogen peroxide

H_2O_2 concentration	Use
3%	antiseptic
6%	hair bleach
30%	industrial and laboratory oxidizing agent
85%	potent oxidizing agent

Table 8-4 gives a comparison of O_2 with the ions O_2^+, O_2^-, and O_2^{2-}.

One of the most important peroxides is hydrogen peroxide, H_2O_2, a colorless, syrupy liquid that explodes violently when heated. Hydrogen peroxide is a strong oxidizing agent that oxidizes a wide variety of organic substances. Dilute aqueous solutions of hydrogen peroxide are fairly safe to use. A 3% aqueous solution is sold in drugstores and used as a mild antiseptic and as a bleach. More concentrated solutions (30%) of hydrogen peroxide are used industrially as a bleaching agent for hair, flour, textile fibers, fats, and oils, in the artificial aging of wines and liquor, and for control of pollution in sewage effluents. Hydrogen peroxide can act as either an oxidizing agent (electron acceptor):

(1) $$2H^+(aq) + H_2O_2(aq) + 2e^- \rightarrow 2H_2O(l)$$

or as a reducing agent (electron donor):

(2) $$H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$$
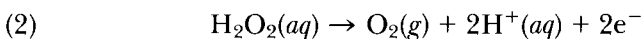
Note that the sum of half-reactions (1) and (2) is

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$
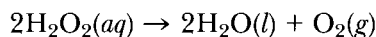
or in other words, hydrogen peroxide self-destructs via a disproportionation (self–oxidation-reduction) reaction.

8-6 OZONE, O_3, IS A POTENT OXIDIZING AGENT

When a spark is passed through oxygen, some of the oxygen is converted to ozone, O_3:

$$3O_2(g) \rightarrow 2O_3(g)$$
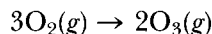
Ozone is a light blue gas at room temperature. It has a sharp, characteristic odor that occurs after electrical storms or near high-voltage generators. Liquid ozone (boiling point $-112°C$) is

a deep blue, explosive liquid. Ozone is so reactive that it cannot be transported safely, but must be generated as needed. Relatively unreactive metals, such as silver and mercury, which do not react with oxygen, react with ozone to form oxides. Ozone is used as a bleaching agent and is being considered as a replacement for chlorine in water treatment because of the environmental problem involving chlorinated hydrocarbons. Ozone is produced in the stratosphere by the photochemical reactions

■ Ozone is one of the strongest known oxidizing agents.

$$O_2(g) \xrightarrow{\lambda < 240\,nm} 2O(g)$$

$$O(g) + O_2(g) \rightarrow O_3(g)$$
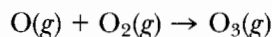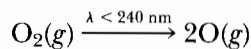
Stratospheric ozone screens out ultraviolet light in the wavelength region 240 to 310 nm via the reaction

$$O_3(g) \xrightarrow{h\nu} O_2(g) + O(g)$$
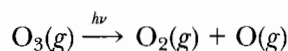
and thereby protects life on earth from destruction by such light.

8-7 SULFUR OCCURS AS THE FREE ELEMENT

Sulfur is a yellow, tasteless, odorless solid that is often found in nature as the free element. Sulfur is essentially insoluble in water but dissolves readily in carbon disulfide, CS_2. It does not react with dilute acids or bases, but it does react with many metals at elevated temperatures to form metal sulfides.

Sulfur, which constitutes only 0.05 percent of the earth's crust, is not one of the most prevalent elements. Yet it is one of the most commercially important ones because it is the starting material for the most important industrial chemical, sulfuric acid.

Prior to 1900, most of the world's supply of sulfur came from Sicily, where sulfur occurs at the surfaces around hot springs and volcanoes. In the early 1900s, however, large subsurface deposits of sulfur were found along the Gulf Coast of the United States. The sulfur occurs in limestone caves, over 1000 feet beneath layers of rock, clay, and quicksand. The recovery of the sulfur from these deposits posed a great technological problem, which was solved by the engineer Herman Frasch. The *Frasch process* (Figure 8-1) uses an arrangement of three concentric pipes (diameters of 1 in., 3 in., and 6 in.) placed in a bore hole that penetrates to the base of the sulfur-bearing calcite ($CaCO_3$) rock formation. Pressurized hot water (180°C) is forced down the space between the 6-in. and 3-in. pipes to melt the sulfur (melting point 119°C). The molten sulfur, which is twice as dense as water, sinks to the bottom of the deposit and is then forced up the space between the 3-in. and 1-in. pipes as a foam by the action of compressed air injected through the innermost pipe. The molten sulfur rises to the surface, where it is pumped into
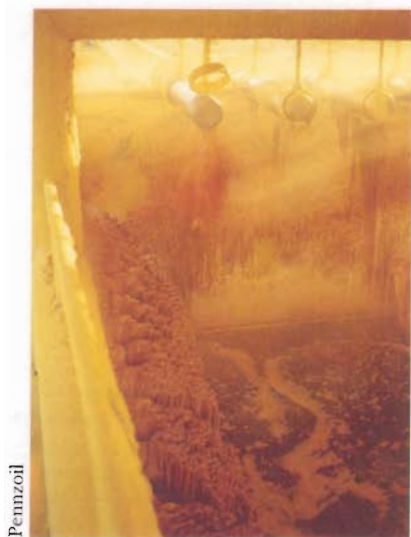
Sulfur with heated hot water and air can be seen surfacing from Culberson Mine in West Texas.
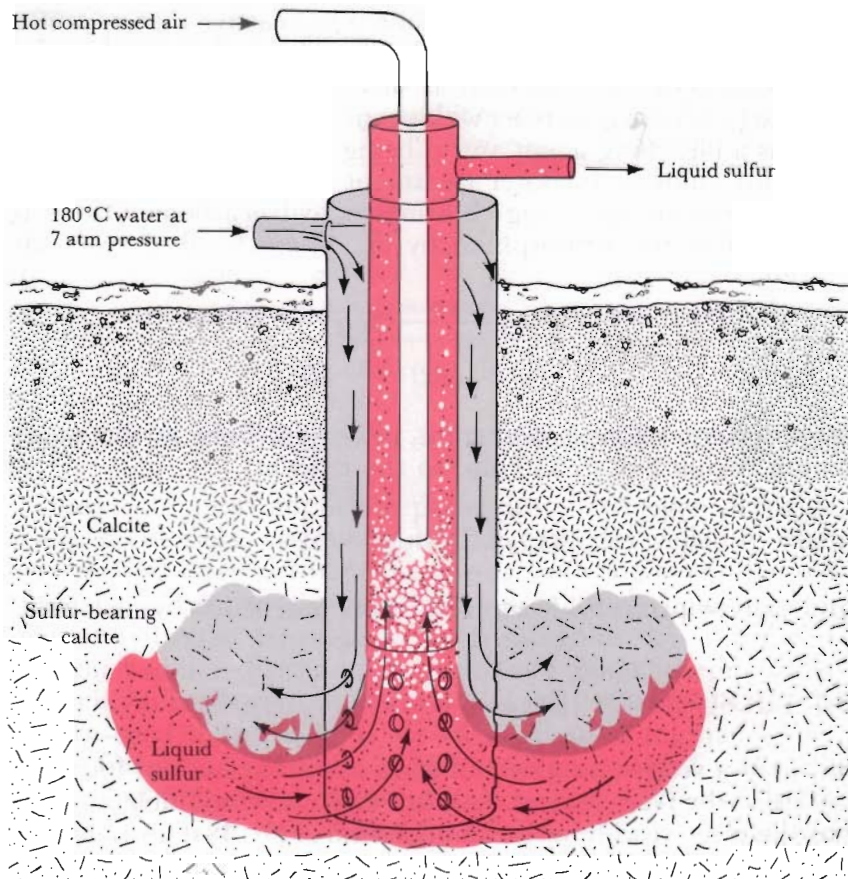
Figure 8-1 The Frasch process for sulfur extraction. Three concentric pipes are sunk into sulfur-bearing calcite rock. Water at 180°C is forced down the outermost pipe to melt the sulfur. Hot compressed air is forced down the innermost pipe and mixes with the molten sulfur, forming a foam of water, air, and sulfur. The mixture rises to the surface through the center pipe. The resulting dried sulfur has a purity of 99.5 percent.

tank cars for shipment or into storage areas. A significant part of the U.S. annual sulfur production of over 10 million metric tons is obtained by the Frasch process from the region around the Gulf of Mexico in Louisiana and Texas (Figure 8-2).

Sulfur is also obtained in increasingly large quantities from the hydrogen sulfide (H_2S) in so-called sour natural gas and from H_2S produced when sulfur is removed from petroleum. Hydrogen sulfide is burned in air to produce sulfur dioxide gas, which is then reacted with additional hydrogen sulfide to produce sulfur:

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g)$$
$$SO_2(g) + 2H_2S(g) \rightarrow 3S(l) + 2H_2O(g)$$
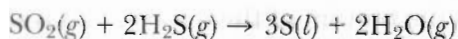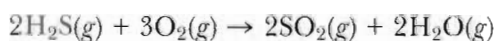
These reactions are also thought to be responsible for the surface deposits of sulfur around hot springs and volcanoes.

Figure 8-2 Sulfur is mined in huge quantities by the Frasch process. It is then formed into huge blocks ready for shipment such as these in Newhall, Texas.

8-8 SULFIDE ORES ARE IMPORTANT SOURCES OF SEVERAL METALS

Deposits of metal sulfides are found in many regions and are valuable ores of the respective metals. Galena (PbS), cinnabar (HgS), and antimony sulfide (Sb_2S_3) are examples of metal sulfides that are ores. In obtaining metals from sulfide ores, the ores are usually *roasted*, meaning that they are heated in an oxygen atmosphere. The roasting of galena is described in Section 6-9.

Iron pyrite, also known as fool's gold, is a famous metal sulfide that has little commercial value. Sulfur is also found in nature in a few insoluble sulfates, such as *gypsum*, $CaSO_4 \cdot 2H_2O$ (calcium sulfate dihydrate) (Figure 8-3), and *barite*, $BaSO_4$.

Sulfur also occurs in many proteins. Hair protein is fairly rich in sulfur. In fact, the formation of a "permanent" wave in hair involves the breaking and remaking of sulfur bonds.

8-9 SULFUR EXISTS AS RINGS OF EIGHT SULFUR ATOMS

Below 96°C sulfur exists as yellow, transparent, *rhombic* crystals, shown in Figure 8-4(a). If rhombic sulfur is heated above 96°C, then it becomes opaque and the crystals expand into *monoclinic* crystals (Figure 8-4(b)). Monoclinic sulfur is the stable form from 96°C to the melting point. The molecular units of the rhombic form are rings containing eight sulfur atoms, S_8 (Figure 8-5). The molecular units of monoclinic sulfur are also S_8 rings, but the rings themselves are arranged differently.

Monoclinic sulfur melts at 119°C to a thin, pale yellow liquid consisting of S_8 rings. Upon heating to about 150°C there is little

■ Cold rhombic sulfur is colorless.

Figure 8-3 Large deposits of gypsum, $CaSO_4 \cdot 2H_2O$, an insoluble mineral, are found in many areas. Left, the dunes of White Sands National Monument in New Mexico are composed of gypsum. Above is a 3-inch cluster of gypsum crystals.

change, but beyond 150°C the liquid sulfur begins to thicken and turns reddish brown. By 200°C, the liquid is so thick that it hardly pours (Figure 8-6). The molecular explanation for this behavior is simple. At about 150°C, thermal agitation causes the S_8 rings to begin to break apart and form chains of sulfur atoms:

(a)
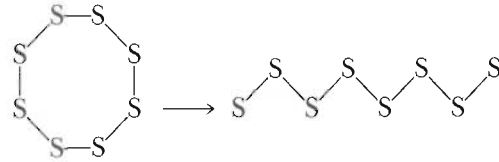
(b)

Figure 8-4 Sulfur occurs as (a) rhombic and (b) monoclinic crystals. Rhombic sulfur is the stable form below 96°C. From 96°C to 119°C (the normal melting point) monoclinic sulfur is the stable form. The terms rhombic and monoclinic are derived from the shape of the crystals.

These chains can then join together to form longer chains, which become entangled in each other and cause the liquid to thicken. Above 250°C, the liquid begins to flow more easily because the thermal agitation is sufficient to begin to break the chains of sulfur atoms. At the boiling point (445°C), liquid sulfur pours freely and the vapor molecules consist mostly of S_8 rings.

If liquid sulfur at about 200°C is placed quickly in cold water (this process is called *quenching*), then a rubbery substance known as plastic sulfur is formed. The material is rubbery because the long, coiled chains of sulfur atoms can straighten out some if they are pulled. As plastic sulfur cools, it slowly becomes hard again as it rearranges itself into the rhombic form.

Figure 8-5 Under most conditions, sulfur exists as eight-membered rings, S_8. The ring is not flat but puckered in such a way that four of the atoms lie in one plane and the other four lie in another plane.

8-10 SULFURIC ACID IS THE LEADING INDUSTRIAL CHEMICAL

By far the most important use of sulfur is in the manufacture of sulfuric acid. Most sulfuric acid is made by the *contact process*. The sulfur is first burned in oxygen to produce sulfur dioxide:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

The sulfur dioxide is then converted to sulfur trioxide in the presence of the catalyst vanadium pentoxide:

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$$

Figure 8-6 Molten sulfur at various temperatures. The change in color and physical properties of liquid sulfur with increasing temperature (120° to about 250°C) is a result of the conversion of eight-membered rings to long chains of sulfur atoms. Above 250°C, the long chains begin to break up into smaller segments and the sulfur is more fluid.

Figure 8-7 Sulfuric acid is sold for laboratory use as an 18 M solution that is 98 percent sulfuric acid and 2 percent water.

The sulfur trioxide is then absorbed into nearly pure liquid sulfuric acid to form *fuming sulfuric acid (oleum)*:

$$H_2SO_4(l) + SO_3(g) \rightarrow H_2S_2O_7(35\% \text{ in } H_2SO_4)$$
$$\text{oleum}$$
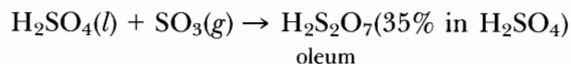
The oleum is then added to water or aqueous sulfuric acid to produce the desired final concentration of aqueous sulfuric acid. Sulfur trioxide cannot be absorbed directly in water because the acid mist of H_2SO_4 that forms is very difficult to condense.

Over 60 billion pounds of sulfuric acid are produced annually in the United States. Commercial-grade sulfuric acid is one of the least expensive chemicals, costing less than 10 cents per pound in bulk quantities. Very large quantities of sulfuric acid are used in the production of fertilizers and numerous industrial chemicals, the petroleum industry, metallurgical processes and synthetic fiber production.

Pure, anhydrous sulfuric acid is a colorless, syrupy liquid that freezes at 10°C and boils at 290°C. The standard laboratory acid is 98 percent H_2SO_4 and 18 M in H_2SO_4 (Figure 8-7). Concentrated sulfuric acid is a powerful dehydrating agent. Gases are sometimes bubbled through it to remove traces of water vapor—provided, of course, that the gases do not react with the acid.

Sulfuric acid is such a strong dehydrating agent that it can remove water from carbohydrates, such as cellulose and sugar, even though these substances contain no free water. If concentrated sulfuric acid is poured over sucrose, $C_{12}H_{22}O_{11}$, then we have the reaction

$$C_{12}H_{22}O_{11}(s) \xrightarrow[\text{H}_2\text{SO}_4\ (98\%)]{} 12C(s) + 11H_2O \text{ (in } H_2SO_4)$$
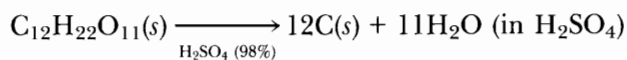
Figure 8-8 Concentrated (98%) sulfuric acid is a powerful dehydrating agent capable of converting sucrose to carbon.

This impressive reaction is shown in Figure 8-8. Similar reactions are responsible for the destructive action of concentrated sulfuric acid on wood, paper, and skin.

The high boiling point and strength of sulfuric acid are the basis of its use in the production of other acids. For example, dry hydrogen chloride gas is produced by the reaction of sodium chloride with sulfuric acid:

$$2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl(g)$$
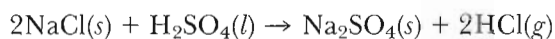
The high boiling point of the sulfuric acid allows the $HCl(g)$ to be driven off by heating. The $HCl(g)$ is then added to water to produce hydrochloric acid. Note that this reaction is a double replacement reaction driven by the removal of a gaseous product from the reaction mixture.

8-11 SULFUR FORMS SEVERAL WIDELY USED COMPOUNDS

Most metal sulfides react with strong acids to produce the foul-smelling, very poisonous gas, hydrogen sulfide. For example,

$$ZnS(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2S(g)$$
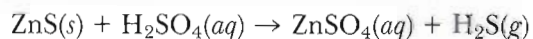
Hydrogen sulfide is detectable by smell at low concentrations, but at high concentrations H_2S readily saturates the olfactory sense and the presence of the gas cannot be detected by smell.

Trace amounts of hydrogen sulfide occur naturally in the atmosphere due to volcanic activity and the decay of organic matter. In fact, the presence of hydrogen sulfide in the atmosphere is demonstrated by the tarnishing of silver. In the presence of

Silver sulfide is a black, insoluble solid that appears as a dark tarnish on the surface of silver.

Table 8-6 Some compounds of sulfur

Compound	Uses
sulfuric acid, $H_2SO_4(l)$	manufacture of fertilizers, dyes, explosives, steel, and other acids; petroleum industry; metallurgy; plastics
sulfur dioxide, $SO_2(g)$	disinfectant in the food and brewing industries; bleaching agent for paper, textiles, oils, etc.; fumigant, preservative
aluminum sulfate, $Al_2(SO_4)_3(s)$	leather tanning; sizing paper; fire-proofing and water-proofing cloth; clarifying agent for oils and fats; water treatment; decolorizer and deodorizer; antiperspirants
ammonium sulfate, $(NH_4)_2SO_4(s)$	fertilizer; water treatment; fire-proofing fabrics; tanning; food additive
sodium sulfate, $Na_2SO_4(s)$	manufacture of paper and glass; textiles; dyes; ceramic glazes; pharmaceuticals; solar heat storage (as the decahydrate, called Glauber's salt)
carbon disulfide, $CS_2(l)$	production of rayon, carbon tetrachloride, cellophanes, soil disinfectants; solvent

oxygen, silver reacts with hydrogen sulfide according to the reaction

$$4Ag(s) + 2H_2S(g) + O_2(g) \rightarrow \underset{\text{black}}{2Ag_2S(s)} + 2H_2O(l)$$
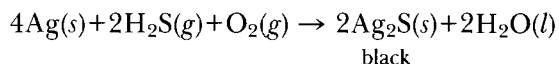
Hydrogen sulfide is a very weak diprotic acid in water ($pK_{a1} = 7$, $pK_{a2} = 13$, at 25°C), and thus the sulfide ion $S^{2-}(aq)$ has a high affinity for protons in water. This is the reason why metal sulfides, most of which are insoluble in water, dissolve readily in aqueous solutions of strong acids, as illustrated previously for ZnS. Hydrogen sulfide is an important reagent in various qualitative analysis schemes in which metal ions are selectively removed from solution as insoluble metal sulfides (Section 19-13 of the text).

The organosulfur compound thioacetamide, CH_3CSNH_2, is now often used in qualitative analysis schemes as a controlled source of hydrogen sulfide, which is generated by heating a solution of thioacetamide:

$$CH_3\overset{\|}{\underset{S}{C}}NH_2(aq) + 2H_2O(l) \xrightarrow{60°C} CH_3COO^-(aq) + NH_4^+(aq) + H_2S(aq)$$

$$CH_3 \diagdown \overset{NH_2}{\diagup}$$
$$\underset{S}{\overset{\|}{C}}$$
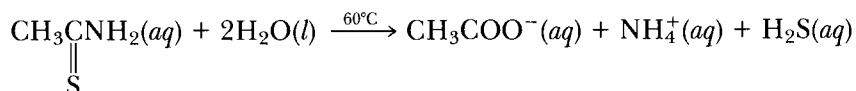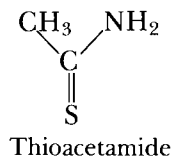
Thioacetamide

By using thioacetamide it is possible to keep the H_2S content of laboratory air below harmful levels.

Sulfur burns in oxygen to form sulfur dioxide, a colorless gas with a characteristic choking odor. A pressure of 3 atm is sufficient to liquefy sulfur dioxide at 20°C. At one time SO_2 was used in industrial refrigeration units, but the unpleasant odor and toxicity brought on its replacement by Freons.

Most sulfur dioxide is used to make sulfuric acid, but some is used as a bleaching agent in the manufacture of paper products, oils and starch, and as a food additive to inhibit browning. Large quantities are used in the wine industry as a fungicide for grapevines and as an antioxidant for wines.

Sulfur dioxide is very soluble in water; over 200 g of sulfur dioxide dissolve in one liter of water. Some of the sulfur dioxide reacts with the water to form sulfurous acid:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$
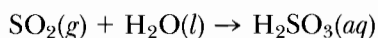
but most of its exists in solution as $SO_2(aq)$.

The salts of sulfurous acid are called sulfites. For example, if sodium hydroxide is added to an aqueous solution of sulfur dioxide, then sodium sulfite is formed according to the equation

$$2NaOH(aq) + H_2SO_3(aq) \rightarrow \underset{\text{sodium sulfite}}{Na_2SO_3(aq)} + 2H_2O(l)$$
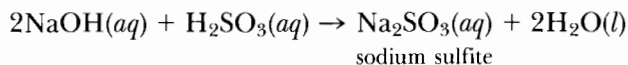
The sulfite ion is a mild reducing agent that is used in the textile and paper industries to destroy excess chlorine, which is used as a bleaching agent:

$$Cl_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2Cl^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$$
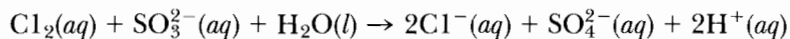
Sodium sulfite is used occasionally as a preservative, especially for dehydrated fruits. The sulfite ion acts as a fungicide; however, it imparts a characteristic sulfur dioxide odor and taste to the food.

The thiosulfate ion is produced when an aqueous solution of a metal sulfite, such as $Na_2SO_3(aq)$, is boiled in the presence of solid sulfur:

- The designation thio denotes the replacement of an oxygen atom by a sulfur atom.

$$S(s) + SO_3^{2-}(aq) \rightarrow \underset{\text{thiosulfate}}{S_2O_3^{2-}(aq)}$$

The thiosulfite ion has a tetrahedral structure. Note that the two sulfur atoms in $S_2O_3^{2-}$ are not equivalent. The structure is analogous to that of sulfate ion with one of the oxygen atoms replaced by a sulfur ion. Thiosulfate ion is used extensively as "hypo" ($Na_2S_2O_3 \cdot 5H_2O$) in black-and-white photography (Section 11-6). Thiosulfate ion is a moderately strong reducing agent that reacts with aqueous iodine or triiodide ion (I_3^-) to form tetrathionate ion, $S_4O_6^{2-}(aq)$:

$$2S_2O_3^{2-}(aq) + I_3^-(aq) \rightarrow \underset{\text{tetrathionate}}{S_4O_6^{2-}(aq)} + 3I^-(aq)$$

This reaction is used in the analytical determination of triiodide ion, which is produced by the action of many mild oxidizing agents on $I^-(aq)$.

8-12 OXIDES OF SULFUR ARE MAJOR POLLUTANTS OF THE ATMOSPHERE

Two oxides of sulfur, SO_2 and SO_3, are major atmospheric pollutants in industrial and urban areas. Most coal and petroleum contain some sulfur, which becomes SO_2 when burned. Concentrations of SO_2 as low as 0.1 to 0.2 ppm can be incapacitating to persons suffering from respiratory conditions such as emphysema and asthma. Although SO_2 is not easily oxidized to SO_3, the presence of dust particles and other particulate matter or ultraviolet radiation facilitates the conversion. The SO_3 then reacts with water vapor to form a very fine sulfuric acid mist. Such a mist is also produced in automobile catalytic converters. Both sulfuric acid and sulfurous acid, H_2SO_3, which arises from the reaction

$$SO_2(g) + H_2O(g) \rightarrow H_2SO_3(\text{mist})$$
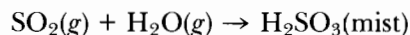
produce acid rain, which is rain that is up to 1000 times more acidic than normal rain. Acid rain occurs commonly in northern Europe and in the northeastern United States and Canada. Many lakes in these regions are so acidic as a result of acid rain that the fish life is disappearing.

Acid rain has a devastating effect on limestone and marble, both of which contain $CaCO_3$. The reaction that occurs is

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

The formation of powdered calcium sulfate breaks down the limestone or marble structure. The decomposition of carbonates by acid rain is a major cause of the deterioration of the ancient buildings and monuments of Europe.

There have been three major disasters attributed to air polluted with oxides of sulfur. In 1952, a gray fog highly polluted with oxides of sulfur settled over London for several days and was reportedly responsible for 4000 deaths. Such a *London fog,* as it is now called, also caused hundreds of deaths in Donora, Pennsylvania, in 1948 and along the Meuse Valley in Belgium in 1930.

Several methods can be used to control the amount of SO_2 introduced into the atmosphere. One obvious way is to burn low-sulfur coal and petroleum. Nigerian oil and some Middle East oil is low in sulfur, whereas Venezuelan oil is high on sulfur. In general, coal from east of the Mississippi River is higher in sulfur than western coal. One method for removing SO_2 from fossil fuel combustion products involves passing the effluent gases through a device called a *scrubber,* where the gases are sprayed

The elements tellurium (left) and selenium (right).

with an aqueous suspension of calcium oxide (lime). The scrubbing eliminates most of the SO_2 but produces large amounts of $CaSO_3$ and $CaSO_4$ that must be disposed of.

8-13 SELENIUM AND TELLURIUM BEHAVE LIKE SULFUR

Selenium is found in the rare minerals *crooksite* and *clausthalite*, and tellurium occurs rarely as the free element or as the telluride of gold ($AuTe_2$) and other metals. The major commercial source of selenium and tellurium is the anode muds produced in the electrolytic refining of impure copper metal obtained from copper sulfide ores. Selenium occurs in several allotropic forms including a metallic gray hexagonal form and as deep-red, monoclinic crystals, which are composed of cyclic Se_8 molecules, analogous to S_8. Pure crystalline tellurium is very brittle and has a silvery-white metallic luster. Both selenium and tellurium are p-type semiconductors and are used to fabricate various photoelectric and solid-state electronic devices. Selenium is used in photocells, solar cells, and rectifiers (AC to DC current converters), and in xerography. Bismuth-tellurium semiconductors are used in thermoelectric coolers that can remove energy as heat from a liquid when an electric current is passed through the device immersed in the liquid.

The chemistries of selenium and tellurium are similar to that of sulfur in that they behave essentially like nonmetals in forming covalently bonded compounds. However, as is normally found on descending a group, there is an increase in metallic character, and tellurium has a very slight metallic character, whereas polonium is a metal. Thus, like sulfur, selenium and tellurium form hydrides and oxides analogous to H_2S, SO_2, and SO_3.

Table 8-7 Some important compounds of selenium and tellurium

Compound	Uses
cadmium selenide, CdSe(s)	produce ruby-colored glass, ceramics, and enamels
selenium dioxide, SeO$_2$(s)	antioxidant in lubricating oils
selenium sulfide, SeS(s)	medicated shampoos (treatment of seborrhea)
tungsten selenide, WSe$_2$(s)	as a solid lubricant for vacuum and elevated-temperature applications
cadmium telluride, CdTe(s)	semiconductors, phosphors, infrared-transmitting material
tellurium dioxide, TeO$_2$(s)	tinting glass

■ Selenium sulfide is an ingredient in several anti-dandruff shampoos.

Most metallic elements react directly with Se and Te to form compounds like those obtained in the analogous reactions with sulfur. Thus we have Na$_2$Se, CaTe, and FeTe. The reactions of selenium and tellurium with nonmetals are also analogous to those of sulfur, as seen in the reactions

$$Se(s) + 2Cl_2(g) \rightarrow SeCl_4(l)$$

$$Te(s) + \underset{\text{excess}}{3F_2(g)} \rightarrow TeF_6(g)$$

$$Se(s) + O_2(g) \rightarrow SeO_2(g)$$
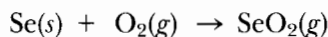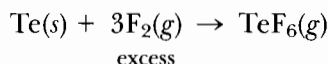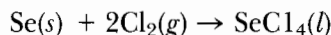
Like arsenic, selenium shows a reluctance to be oxidized to its maximum oxidation state. For example, unlike SO$_3$ and TeO$_3$, SeO$_3$ is thermally unstable with respect to SeO$_2$:

$$SeO_3(s) \rightarrow SeO_2(s) + \tfrac{1}{2}O_2(g) \qquad \Delta H^\circ_{rxn} = -58.5 \text{ kJ}$$
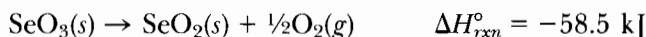
The acids H$_2$SeO$_3$ (selenous acid) and H$_2$SeO$_4$ (selenic acid) are prepared by dissolving SeO$_2$ and SeO$_3$, respectively, in water. These acids are analogous to sulfurous acid and sulfuric acid, respectively. However, TeO$_2$ is insoluble in water, and telluric acid is not at all like sulfuric acid. Its formula is Te(OH)$_6$, and it is a very weak acid (pK_a ~7 at 25°C).

Some compounds of selenium and tellurium are given in Table 8-7.

TERMS YOU SHOULD KNOW

photosynthesis
ozone layer
Frasch process
roasting of ores

quenching
contact process
oleum (fuming sulfuric acid)

QUESTIONS

8-1. What is the source of most of the oxygen in the earth's atmosphere?

8-2. Give two methods used to produce small quantities of oxygen in the laboratory.

8-3. What is the heat-producing reaction of an oxyacetylene torch?

8-4. The alkali superoxides react with CO_2 according to

$$4MO_2(s) + 2CO_2(g) \rightarrow 2M_2CO_3(s) + 3O_2(g)$$
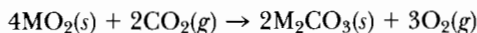
Suggest an application of this reaction.

8-5. Outline by means of balanced chemical equations a method for the preparation of $D_2O_2(aq)$.

8-6. It has been determined that in the oxidation of H_2O_2 in aqueous solution by MnO_4^-, Ce^{4+}, and other strong oxidizing agents, the $O_2(g)$ produced comes entirely from the H_2O_2, and not from water. How could this be determined?

8-7. Describe the Frasch process.

8-8. Describe what happens at various stages when sulfur (initially in the rhombic form) is heated slowly from 90°C to 450°C.

8-9. Describe, using balanced chemical equations, the contact process for the manufacture of sulfuric acid.

8-10. Why would it be unwise to attempt to increase the acidity of the soil around plants by adding concentrated sulfuric acid?

8-11. The gas inside some tennis balls is about 50 percent SF_6 and 50 percent air. Such balls retain their bounce longer than balls charged solely with air. Suggest an explanation based on molecular size for this observation.

8-12. There are two known isomers of S_2F_2 with significantly different sulfur-sulfur bond lengths. Propose structures for the two isomers, draw the Lewis formulas.

8-13. Draw a Lewis formula for disulfuric acid, $H_2S_2O_7$ (there is an S—O—S linkage).

8-14. Draw a Lewis formula for peroxomonosulfuric acid, H_2SO_5. This acid is also known as Caro's acid.

8-15. Write the chemical equation for the analytical determination of iodine by thiosulfate.

8-16. Write a chemical equation for the tarnishing of silver.

8-17. Write the chemical equations for the reactions that account for the yellow deposits of sulfur that occur near many hot springs.

8-18. Explain why the bond angles in H_2O, H_2S, H_2Se, and H_2Te decrease from 104.5° for water to 92° for H_2S, 91° for H_2Se, and 90° for H_2Te.

8-19. The compounds SF_4 and SF_6 are both very unstable with respect to reaction with water, as shown by the following ΔG_{rxn}° values.

(a) $SF_4(g) + 2H_2O(l) \rightarrow SO_2(aq) + 4HF(aq)$
$$\Delta G_{rxn}^\circ = -282 \text{ kJ}$$

(b) $SF_6(g) + 4H_2O(l) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) +$
$$6HF(aq) \qquad \Delta G_{rxn}^\circ = -472 \text{ kJ}$$
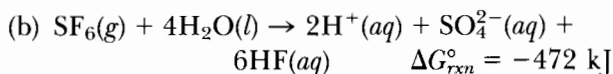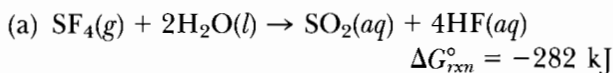
Although $SF_4(g)$ reacts rapidly with water $SF_6(g)$ does not, being inert even to hot $NaOH(aq)$ or $HNO_3(aq)$. Consider the bonding in the two molecules, and offer an explanation for the observed difference in reactivities.

8-20. Given the thermodynamic data, $\Delta \overline{G}_f^\circ[SF_4(g)] = -731.3$ $kJ \cdot mol^{-1}$ and $\Delta \overline{G}_f^\circ[SF_6(g)] = -1105.3$ $kJ \cdot mol^{-1}$ at 25°C, calculate the equilibrium constant of the reaction

$$SF_4(g) + F_2(g) \rightleftharpoons SF_6(g)$$
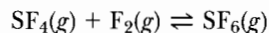
Given that $\Delta H_{rxn}^\circ = -434.1$ kJ at 25°C, is the production of SF_6 more favored at high or low temperatures?

8-21. A 35.0-mL sample of $I_3^-(aq)$ requires 28.5 mL of 0.150 M $Na_2S_2O_3(aq)$ to react with all the $I_3^-(aq)$. Calculate the concentration of $I_3^-(aq)$ in the sample.

8-22. The concentration of ozone in oxygen-ozone mixtures can be determined by passing the gas mixture into a buffered $KI(aq)$ solution. The O_3 oxidizes $I^-(aq)$ to $I_3^-(aq)$:

$$O_3(g) + 3I^-(aq) \rightarrow O_2(g) + I_3^-(aq) + 2OH^-(aq)$$
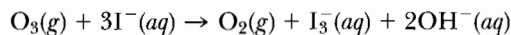
The concentration of $I_3^-(aq)$ formed is then determined by titration with $Na_2S_2O_3(aq)$. Given that

22.50 mL of 0.0100 M $Na_2S_2O_3(aq)$ are required to titrate the $I_3^-(aq)$ in a 50.0-mL sample of $KI(aq)$ that was equilibrated with a $O_2 + O_3$ sample, compute the moles of O_3 in the sample.

8-23. Atmospheric SO_2 can be determined by reaction with $H_2O_2(aq)$:

$$H_2O_2(aq) + SO_2(g) \rightarrow H_2SO_4(aq)$$
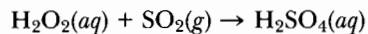
followed by titration of the $H_2SO_4(aq)$ produced. Given that 18.50 mL of 0.0250 M NaOH was required to neutralize the $H_2SO_4(aq)$ in a 50.0-mL $H_2O_2(aq)$ sample that was equilibrated with a sample of air containing SO_2, compute the moles of SO_2 in the air sample.

THE HALOGENS
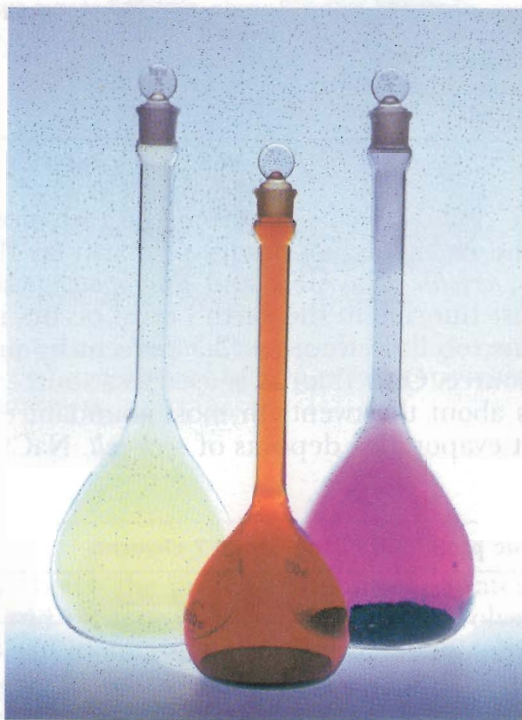
Chlorine, bromine, and iodine.

The Group 7 elements, fluorine, chlorine, bromine, iodine, and astatine, are collectively called the *halogens*. At 25°C, fluorine is a pale yellow gas, chlorine is a green-yellow gas, bromine is a dark red liquid, and iodine is a gray-violet solid. There are no stable isotopes of astatine, all of them being radioactive. All the halogens have a pungent, irritating odor and are very poisonous. The elements exist as reactive diatomic molecules, with their reactivity decreasing with increasing atomic number.

The halogens react directly with most metals and many nonmetals. Because of the reactivity of the halogens, they do not occur as the free elements in nature; they occur primarily as

▪ Halogen means salt former.

Table 9-1 Sources and uses of the Group 7 elements

Element	Principal sources	Uses
fluorine	*fluorspar*, $CaF_2(s)$	production of UF_6 for the nuclear industry, production of fluorocarbons
chlorine	*halite*, $NaCl(s)$, *sylvite*, $KCl(s)$, seawater	production of organic compounds, water purification, bleaches, flame-retardant compounds, dyes, textiles, insecticides, plastics
bromine	natural brines, salt lakes and salt beds	production of ethylene dibromide (a lead scavenger in antiknock gasoline), production of pesticides, fire-retardant materials, photography, dyestuffs
iodine	brines associated with certain oil well drillings, Chilean deposits of saltpeter, seaweeds	production of organic compounds, iodized salt and tincture of iodine

halide (F^-, Cl^-, Br^-, I^-) salts. Fluorine, the 13th most abundant element in the earth's crust, occurs primarily as the minerals *fluorite*, CaF_2, *cryolite*, Na_3AlF_6, and *fluorapatite*, $Ca_{10}F_2(PO_4)_6$. Although most fluorine in the earth's crust occurs in fluorapatite, it contains too little fluorine (3.5 percent by mass) to be a commercial source. Only fluorite is used as a source of fluorine.

Chlorine is about the twentieth most abundant element and occurs in vast evaporative deposits of *rock salt*, NaCl, and *sylvite*,

Table 9-2 Atomic properties of the Group 7 elements

Property	Fluorine	Chlorine	Bromine	Iodine
atomic number	9	17	35	53
atomic mass/amu	18.998403	35.453	79.904	126.9045
number of naturally occurring isotopes	1	2	2	1
ground-state electron configuration	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar]3d^{10}4s^2 4p^5$	$[Kr]4d^{10}5s^2 5p^5$
atomic radius/pm	71	99	114	133
ionic radius/pm	136	181	195	216
bond length of X_2/pm	142	198	228	266
bond enthalpy of X_2/kJ $\cdot$ mol^{-1}	155	243	192	150
ionization energy/MJ $\cdot$ mol^{-1}	1.68	1.26	1.14	1.01
electronegativity	4.0	3.2	3.0	2.7

F (71 pm)/ F⁻ (136 pm) F₂ (142 pm)

Cl (99 pm)/Cl⁻ (181 pm) Cl₂ (198 pm)

Br (114 pm)/ Br⁻ (195 pm) Br₂ (228 pm)

I (133 pm)/ I⁻ (216 pm) I₂ (266 pm)
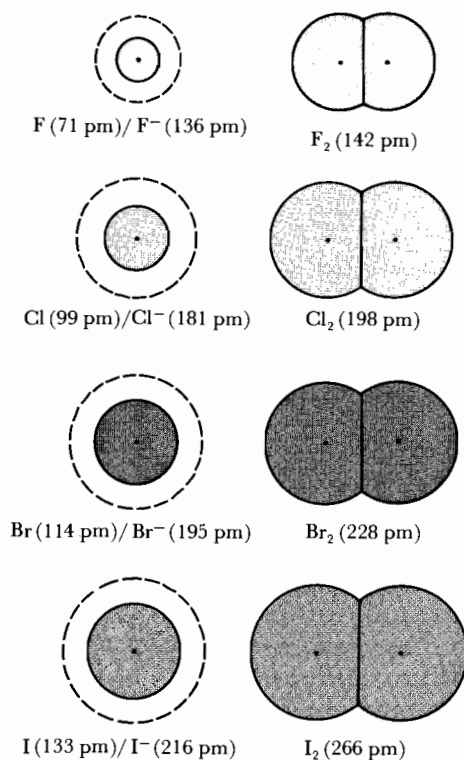
Figure 9-1 Relative sizes of neutral halogen atoms (single spheres), halide ions (dashed circles), and diatomic halogen molecules (attached pairs). Distances are in picometers.

KCl, as well as being the principal anion in seawater. The chlorine is recovered from its chloride salts by electrolysis. Bromine is only about half as abundant as chlorine. Although seawater is a potentially inexhaustible source of bromine, it is presently obtained commercially from certain natural brines and salt lakes.

Iodine is the rarest of the halogens and is about half as abundant as bromine. The principal source of iodine was once the Chilean nitrate beds, which contain a fair amount of $Ca(IO_3)_2$, but this source has been replaced by brines associated with oil wells in Louisiana and California and subterranean brines in Michigan and Oklahoma. Since World War II, however, Japan has been the world's leading producer of iodine. Table 9-1 summarizes the principal sources and commercial uses of the halogens.

The halogens serve as a good example of the variation of atomic and physical properties with atomic number. Their atomic and ionic radii and molecular bond lengths increase (Figure 9-1) and their ionization energies, electronegativities, and bond enthalpies decrease with increasing atomic number (Table 9-2). The melting points and boiling points and the values of ΔH_{fus} and ΔH_{vap} increase while the values of the standard re-

Table 9-3 Some physical properties of the Group 7 elements

Property	F_2	Cl_2	Br_2	I_2
melting point/°C	-219.6	-101.0	-7.2	113.5
boiling point/°C	-183.1	-34.6	58.8	184.4
$\Delta\overline{H}_{fus}$/kJ $\cdot$ mol^{-1}	0.510	6.41	10.6	15.5
$\Delta\overline{H}_{vap}$/kJ $\cdot$ mol^{-1}	6.54	20.4	29.5	41.9
density at 20°C/g $\cdot$ cm^{-3}	1.58×10^{-3}	2.98×10^{-3}	3.103	4.660
E^0/V at 25°C for $\frac{1}{2}X_2 + e^- \rightarrow X^-(aq)$	2.87	1.36	1.07	0.54

duction voltages decrease with increasing atomic number (Table 9-3).

Fluorine, the first member of the halogens, is the most reactive element. Although there are some important differences between the chemical properties of fluorine and the rest of the halogens, the halogens are about as uniform in their chemical properties as are the Group 1 metals. The small size of a fluorine atom and its high electronegativity account for its special properties. Fluorine is the strongest known oxidizing agent, and consequently there are no known positive oxidation states of fluorine. The only known oxidation states of fluorine are 0 and -1. For example, unlike the other halogens, fluorine forms no oxyacids. Like arsenic and selenium, bromine shows a reluctance to reach its maximum oxidation state of $+7$. For instance, perbromates, BrO_4^-, were not prepared until about 1970, and BrO_4^- is a stronger oxidizing agent than either ClO_4^- or IO_4^-.

9-1 FLUORINE IS THE MOST REACTIVE ELEMENT

Fluorine is a pale-yellow, corrosive gas that is the strongest oxidizing agent known and the most reactive of all the elements. It reacts directly, and in most cases vigorously, with all the elements except helium and neon. The extremely corrosive nature of fluorine is shown by its reactions with glass, ceramics, and carbon; even water burns vigorously in fluorine:

$$2F_2(g) + H_2O(g) \rightarrow OF_2(g) + 2HF(g)$$
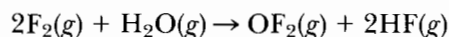
Many of the known noble-gas compounds are fluorides, such as XeF_2, XeF_4, and XeF_6.

Because of its high electronegativity, fluorine is capable of stabilizing unusually high oxidation states of other elements. Some examples are

OF_2 O(II) AgF_2 Ag(II) IF_7 I(VII)
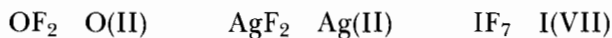
■ Fluorine is the most electronegative element.

The high reactivity of fluorine is a consequence of the low F—F bond energy (139 kJ $\cdot$ mol^{-1}) and the high X—F bond energies (~ 500 kJ $\cdot$ mol^{-1}) to other elements. For example, the reaction

$$H_2(g) + F_2(g) \rightarrow 2HF(g) \qquad \Delta H^\circ_{rxn} = -536 \text{ kJ}$$
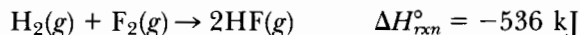
is highly exothermic and produces a flame temperature of over $6000°C$, which is the highest known chemical flame temperature, being approximately equal to the surface temperature of the Sun.

Because of its extreme reactivity, elemental fluorine wasn't isolated until 1886. Elemental fluorine is obtained by the electrolysis of hydrogen fluoride dissolved in molten potassium fluoride:

■ The French chemist Henri Moissan, who first isolated fluorine, received the 1906 Nobel Prize in Chemistry for his work.

$$2HF \text{ (}in \text{ } KF \text{ } melt\text{)} \xrightarrow{\text{electrolysis}} H_2(g) + F_2(g)$$
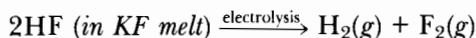
The modern method of producing F_2 is essentially a variation of the method first used by Moisson. Prior to World War II, there was no commercial production of fluorine. The atomic bomb project required huge quantities of fluorine for the production of uranium hexafluoride, UF_6, a gaseous compound that is used in the separation of uranium-235 from uranium-238. It is uranium-235 that is used in nuclear devices. The production of uranium hexafluoride for the preparation of fuel for nuclear power plants is today a major commercial use of fluorine.

■ $^{235}UF_6$ is separated from $^{238}UF_6$ by gaseous effusion. The lighter $^{235}UF_6$ effuses more rapidly than does the heavier $^{238}UF_6$.

Hydrogen fluoride is used in petroleum refining and in the production of fluorocarbon polymers, such as Teflon and Freons. It is also used to etch, or "frost," glass for light bulbs and decorative glassware via the reaction

$$SiO_2(s) + 6HF(aq) \rightarrow H_2SiF_6(s) + 2H_2O(l)$$
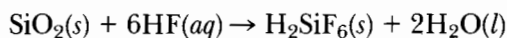
Because hydrofluoric acid, $HF(aq)$, dissolves glass via this reaction, it must be stored in plastic bottles.

Various fluorides, such as tin(II) fluoride, SnF_2, and sodium monofluorophosphate, Na_2PO_3F, are used as toothpaste additives, and sodium fluoride is added to some municipal water supplies to aid in the prevention of tooth decay. Ordinary tooth enamel is hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$. If low concentrations of fluoride ion are added to the diets of children, then a substantial amount of the tooth enamel formed will consist of fluorapatite, $Ca_{10}F_2(PO_4)_6$, which is much harder and less affected by acidic substances than hydroxyapatite. Consequently, fluorapatite is more resistant to tooth decay than is hydroxyapatite. The use of fluoride has decreased the incidence of tooth decay among children markedly over the past 30 years.

■ Tin(II) fluoride is also known as stannous fluoride.

Many organofluoride compounds are used as refrigerants. Two common ones are dichlorodifluoromethane (Freon 12), CCl_2F_2, which is used in automobile air conditioners, and chlorodifluoromethane (Freon 21), $CHClF_2$, which is used in home air conditioners. Fluorocarbons have displaced refriger-

Table 9-4 Some important compounds of fluorine

Compound	Uses
hydrogen fluoride, HF(g)	catalyst in the petroleum industry; refining of uranium; etching glass; pickling stainless steel; gasoline production
boron trifluoride, BF₃(g)	catalyst for many organic reactions; soldering fluxes; measurement of neutron intensities
sulfur hexafluoride, SF₆(g)	gaseous electrical insulator in high-voltage generators and radar wave guides
sodium hexaflouroaluminate(III) (*cryolite*), Na₃AlF₆(s)	production of aluminum; electrical insulation; polishes; ceramics; insecticide

This submerged mouse is breathing oxygen dissolved in a liquid fluorocarbon. The solubility of oxygen in this liquid is so great that the mouse is able to breath by absorbing oxygen from the oxygen-containing fluorocarbon that fills its lungs. When the mouse is removed from the liquid, the fluorocarbon vaporizes from its lungs and normal breathing resumes.

ants such as ammonia and sulfur dioxide in refrigerators because of their much lower toxicity and greater chemical stability. Some commercially important fluorine compounds are given in Table 9-4.

9-2 CHLORINE IS OBTAINED FROM CHLORIDES BY ELECTROLYSIS

Chlorine is a green-yellow, poisonous, corrosive gas that is prepared commercially by the electrolysis of either brines or molten rock salt:

$$2NaCl(l) \xrightarrow{\text{electrolysis}} 2Na(l) + Cl_2(g)$$

molten rock salt

About 10 million metric tons of chlorine are produced annually in the United States, making it the eighth ranked chemical in terms of production. It is prepared on a laboratory scale by heating a mixture of hydrochloric acid and manganese dioxide:

$$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$$
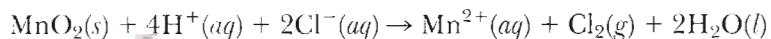
This reaction was used by the Swedish chemist Karl Scheele in 1774 in the first laboratory preparation of Cl₂.

Chlorine is very reactive, combining directly with most other elements with notable exceptions being carbon, nitrogen, and oxygen. Chlorine burns in hydrogen to form hydrogen chloride:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$
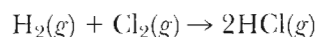
This reaction is used to prepare very pure HCl(g). Mixtures of H₂(g) and Cl₂(g) are explosive when exposed to light.

Many metals react directly with chlorine to form ionic chlorides:

$$Zn(s) + Cl_2(g) \rightarrow ZnCl_2(s)$$
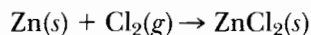
and nonmetals react with chlorine to form covalent chlorides:
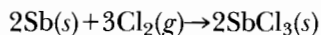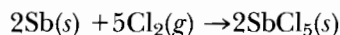
$$2Sb(s) + 3Cl_2(g) \rightarrow 2SbCl_3(s)$$
$$\text{excess}$$
$$2Sb(s) + 5Cl_2(g) \rightarrow 2SbCl_5(s)$$
$$\text{excess}$$

Chlorine is a strong oxidizing agent:

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \qquad E^0 = +1.36 \text{ V}$$

as illustrated by the following reactions:

$$Cl_2(g) + H_2S(aq) \rightarrow 2HCl(aq) + S(s)$$
$$Cl_2(aq) + 2Fe^{2+}(aq) \rightarrow 2Cl^-(aq) + 2Fe^{3+}(aq)$$
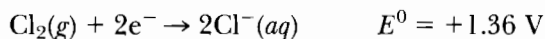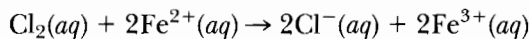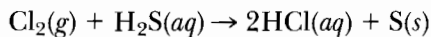
Most chlorine produced in the United States is used as a bleaching agent in the pulp and paper industry. It is also used extensively as a germicide in water purification and in the production of insecticides (DDT and chlordane) and herbicides (2,4-D).

Many chlorinated hydrocarbons present a serious health hazard to humans and other mammals, fishes, and birds. Such compounds are not biodegradable and, because of their high solubility in nonpolar solvents, accumulate in fatty tissues, where their presence may lead to irreversible liver damage and, in some cases, cancer. They also tend to work their way up the food chain to humans in increasing concentrations. Chlorinated hydrocarbons can be absorbed directly through the skin. An especially insidious group of chlorinated hydrocarbons are the carcinogenic PCBs, *poly*chlorinated *bi*phenyls. PCBs are inexpensive, nonflammable, very stable compounds with excellent insulation properties and, as a consequence, were once widely used in transformers and capacitors on electric power lines. The discovery of the health hazards of PCBs has led to an extensive effort to remove them from power grids. Table 9-5 lists some compounds of chlorine and their major uses.

9-3 BROMINE AND IODINE ARE OBTAINED BY OXIDATION OF BROMIDES AND IODIDES WITH CHLORINE

Bromine is a dense, red-brown, corrosive liquid with a very pungent odor. It attacks skin and tissue and produces painful, slow-healing sores. Bromine vapor and solutions of bromine in nonpolar solvents are red (Figures 9-2 and 9-3).

Table 9-5 Some important compounds of chlorine

Compound	Uses
hydrochloric acid, $HCl(g)$	ore refining; metallurgy; boiler-scale removal; food processing; oil and gas well treatment; general acid
sodium chloride, $NaCl(s)$	source of many sodium and chlorine compounds; food preservative; manufacture of soaps and dyes; ceramic glazes; home water softeners; highway de-icing; food seasoning; curing of hides; metallurgy
calcium chloride, $CaCl_2(s)$	drying agent; dust control on roads; paper and pulp industry; refrigeration brines; fireproofing fabrics; wood preservative; sizing and finishing cotton fabrics
potassium chlorate, $KClO_3(s)$	oxidizing agent; explosives; matches; textile printing; pyrotechnics; bleaching agent; manufacture of aniline dyes
calcium hypochlorite, $Ca(ClO)_2(s)$	algicide; bactericide; deodorant; swimming pool disinfectant; fungicide; bleaching agent for paper and textiles
sodium hypochlorite, $NaClO(s)$	bleaching agent for paper and textiles; water purification; swimming pool disinfectant; fungicide; laundry agent

The major source of bromine in the United States is from brines that contain bromide ions. The pH of the brine is adjusted to 3.5, and chlorine is added; the chlorine oxidizes bromide ion to bromine, which is swept out of the brine with a current of air:
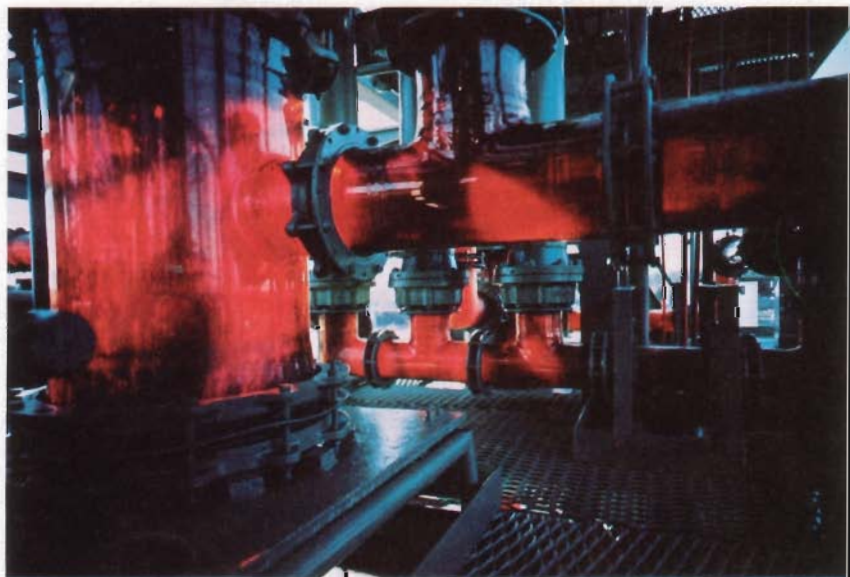
Figure 9-2 Bromine processing plant. The red color is produced by the bromine gas.

Table 9-6 Some important compounds of bromine

Compound	Uses
sodium bromide, NaBr(s)	photography; sedative
potassium bromide, KBr(s)	gelatin bromide; photographic papers and plates; lithography; special soaps; infrared spectroscopic prisms
potassium bromate, $KBrO_3(s)$	oxidizing agent; food additive; permanent wave compound
silver bromide, AgBr(s)	photographic film and plates; photochromic glass
calcium bromide, $CaBr_2(s)$	photography; medicine; desiccant; food preservative; fire retardant

$$2Br^-(aq) + Cl_2(aq) \xrightarrow{pH\,=\,3.5} 2Cl^-(aq) + Br_2(aq)$$
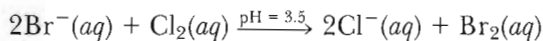
About 1 kg of bromine can be obtained from 15,000 L of seawater. About 200,000 metric tons of bromine were produced in the United States during 1980.

Bromine is used to prepare a wide variety of metal bromide and organobromide compounds. Its major uses are in the production of dibromoethane, $BrCH_2CH_2Br$, which is added to leaded gasolines as a lead scavenger, and in the production of silver bromide emulsions for black-and-white photographic films. Bromine is also used as a fumigant and in the synthesis of fire retardants, dyes, and pharmaceuticals, especially sedatives. Table 9-6 lists some important compounds of bromine.

Solid iodine is dark gray in color with a slight metallic luster. Iodine gas and solutions of iodine in nonpolar solvents such as carbon tetrachloride are a beautiful purple color (Figure 9-4); solutions of iodine in water and alcohols are brown as a result of the specific polar interactions between I_2 and the —O—H bond.

Iodide ion is present in seawater and is assimilated and concentrated by many marine animals and by seaweed. Certain seaweeds are an especially rich source of iodine. The iodide ion in seaweed is converted to iodine by oxidation with chlorine.

Iodine is the only halogen to occur naturally in a positive oxidation state as in the Chilean iodate deposits. The free element is obtained by reduction of IO_3^- and IO_4^- with sodium hydrogen sulfite:

$$2IO_3^-(aq) + 5HSO_3^-(aq) \rightarrow I_2(aq) + 5SO_4^{2-}(aq) + 3H^+(aq) + H_2O(l)$$
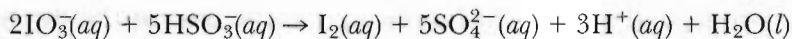
Iodine is not very soluble in pure water, but is very soluble in an aqueous KI solution. The increased solubility in KI (aq) is due to the formation of a linear, colorless tri-iodide species (Figure 9-4):

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K = 700M^{-1} \text{ at } 25°C$$
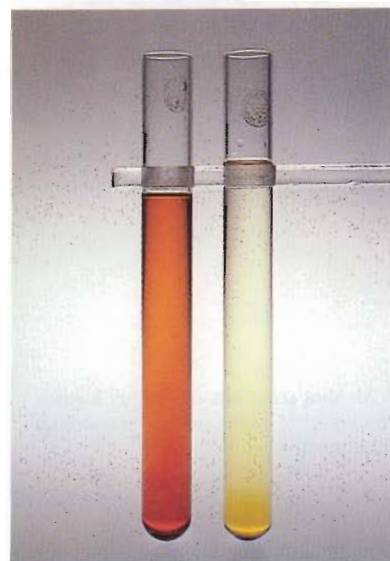
Figure 9-3 Bromine dissolved in carbon tetrachloride (left) and in water (right).

Figure 9-4 Various solutions of iodine. Left, I_2 dissolved in CCl_4. Center left, I_2 dissolved in KI(*aq*). Center right, I_2 dissolved with water. Right, I_2 dissolved in KI(aq) with starch added to the solution.

Table 9-7 Some important compounds of iodine

Compound	Uses
sodium iodide, NaI(*s*)	photography; feed additive; cloud seeding
potassium iodide, KI(*s*)	photographic emulsions; dietary supplement; infrared optics
silver iodide, AgI(*s*)	photography; cloud seeding
sodium iodate, NaIO₃(*s*)	disinfectant; antiseptic; feed additive

The presence of very low concentrations of aqueous tri-iodide can be detected by adding starch to the solution. The tri-iodide ion combines with starch to form a brilliant deep-blue species (Figure 9-4).

Iodide ion is essential for the proper functioning of the human thyroid gland, which is located in the base of the throat. Iodide deficiency manifests itself as the disease *goiter*, which causes an enlargement of the thyroid gland. Small quantities of potassium iodide are added to ordinary table salt, which is then marketed as iodized salt.

Table 9-7 lists some commercially important compounds of iodine.

■ Alcohol solutions of iodine, known as *tincture of iodine,* were once used as an antiseptic.

The halogens form hydrogen halides of composition HX, where X represents a halogen. Except for HI, and to some extent for HBr, the hydrogen halides can be prepared by the reaction of concentrated sulfuric acid with the corresponding alkali metal halide, which produces gaseous HX. For example,

$$2NaCl(s) + H_2SO_4(conc) \rightarrow Na_2SO_4(s) + 2HCl(g)$$
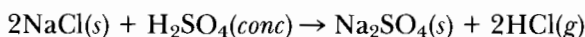
The reaction occurs because hydrogen chloride is much less soluble in water and more volatile than sulfuric acid. A major commercial preparation of HCl is as a by-product in the chlorination of hydrocarbons, for example,

$$CH_3CH_3(g) + Cl_2(g) \rightarrow CH_3CH_2Cl(g) + HCl(g)$$

■ About 5 billion pounds of hydrochloric acid are produced annually in the United States.
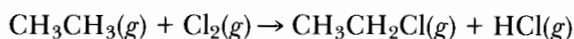
Hydrogen chloride can also be prepared on a laboratory scale by the vigorous reaction of PCl_5 with water:

$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(g)$$
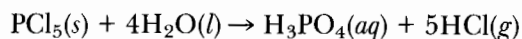
Hydrogen bromide is prepared industrially by direct reaction of hydrogen and bromine at elevated temperature in the presence of a platinum catalyst:

$$H_2(g) + Br_2(g) \overset{Pt}{\rightarrow} 2HBr(g)$$
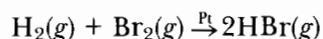
Hydrogen iodide is oxidized to iodine by concentrated sulfuric acid and thus must be prepared by a different method. One method is the reaction of iodine with hydrazine:

$$2I_2(s) + N_2H_4(aq) \rightarrow 4HI(aq) + N_2(g)$$
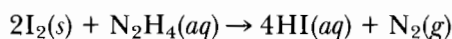
The molar bond enthalpies of the hydrogen halides decrease with increasing atomic number, as shown in Table 9-8. In water, HCl, HBr, and HI are all strong acids, and HF is a weak acid:

Table 9-8 The hydrogen halide molar bond enthalpies

Hydrogen halide	Molar bond enthalpy/kJ · mol^{-1}
HF	569
HCl	431
HBr	368
HI	297

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad K = 7 \times 10^{-4} \text{ M at } 25°C$$
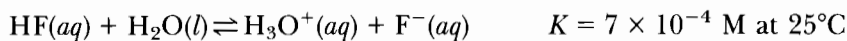
Hydrogen fluoride is a weak acid because of the very strong H—F bond. Because fluoride has the highest electronegativity of any element, fluorine forms the strongest hydrogen bonds. The strong hydrogen-bonding property of fluorine is seen in the formation of the linear *bifluoride* ion:

$$HF(aq) + F^-(aq) \rightleftharpoons F{-}H{-}F^-(aq) \qquad K = 5 \text{ M}^{-1} \text{ at } 25°C$$
$$\text{bifluoride}$$
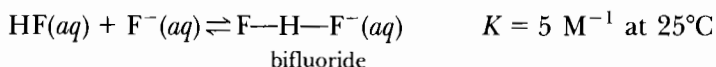
and also by the formation of polymeric hydrogen fluorides such as $(HF)_2$ and $(HF)_6$, which are cyclic molecules.

The molecule $(HF)_6$ is cyclic. Note the hydrogen bonds.

9-5 THE HALOGENS FORM NUMEROUS COMPOUNDS WITH OXYGEN-HALOGEN BONDS

The best known and most important oxygen-halogen compounds are the halogen oxyacids. The halogens form a series of oxyacids in which the oxidation state of the halogen atom can be +1, +3, +5, or +7. For example, the oxyacids of chlorine are

HClO	hypochlorous acid	+1
$HClO_2$	chlorous acid	+3
$HClO_3$	chloric acid	+5
$HClO_4$	perchloric acid	+7

The numbers after the names give the oxidation state of the chlorine in the acid. The Lewis formulas for these acids are
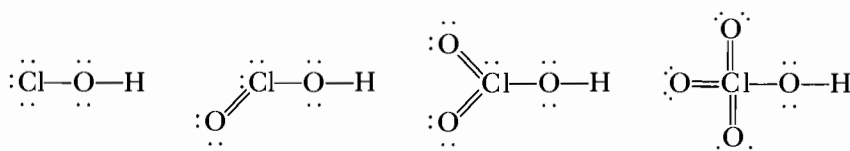
Notice that in each case the hydrogen is attached to an oxygen atom. The anions of the chlorine oxyacids are

ClO^-	hypochlorite
ClO_2^-	chlorite
ClO_3^-	chlorate
ClO_4^-	perchlorate

The shapes of these ions are predicted correctly by VSEPR theory (Chapter 11 of the text) and are shown in Figure 9-5. Table 9-9 gives the known halogen oxyacids and their anions. Note that there are no oxyacids of fluorine.

When Cl_2, Br_2, or I_2 is dissolved in aqueous alkaline solution, the following type of disproportionation reaction occurs:

Table 9-9 The halogen oxyacids and their pK_a values in water at 25°C

Halogen oxidation state	Cl acid pK_a	Br acid pK_a	I acid pK_a	Acid name	Salt
+1	HClO, 7.49	HBrO, 8.68	HIO, 11	hypohalous	hypohalite
+3	$HClO_2$, 1.96	—	—	halous	halite
+5	$HClO_3$, strong	$HBrO_3$, strong	HIO_3, 0.8	halic	halate
+7	$HClO_4$, strong	$HBrO_4$, strong	HIO_4, strong H_5IO_6, 3.3, 6.7	perhalic	perhalate

$$Cl_2(g) + 2OH^-(aq) \rightleftharpoons Cl^-(aq) + ClO^-(aq) + H_2O(l)$$
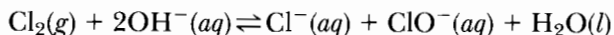
A solution of $NaClO(aq)$ is a bleaching agent, and many household bleaches are a 5.25% aqueous solution of sodium hypochlorite. Commercially, solutions of $NaClO$ are manufactured by the electrolysis of cold aqueous solutions of sodium chloride:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad \text{anode}$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad \text{cathode}$$
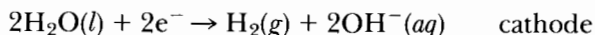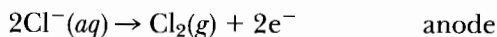
The products of the two electrode reactions are allowed to mix, producing $ClO^-(aq)$ by the above reaction. Sodium hypochlorite is also employed as a disinfectant and deodorant in water supplies and sewage disposals.

Hypohalite ions decompose in basic solution via reactions of the type

$$3IO^-(aq) \xrightarrow{OH^-} 2I^-(aq) + IO_3^-(aq)$$
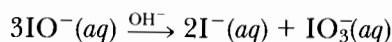
The analogous reaction with $ClO^-(aq)$ is slow, which makes it possible to use hypochlorite as a bleach in basic solutions. The rate of decomposition of $ClO^-(aq)$, $IO^-(aq)$, and $BrO^-(aq)$ in hot alkaline aqueous solution is sufficiently fast that when Cl_2, Br_2, or I_2 is dissolved in basic solution and the resulting solution is heated to 60°C, the following type of reaction goes essentially to completion:

$$3Br_2(aq) + 6OH^-(aq) \xrightarrow{60°C} 5Br^-(aq) + BrO_3^-(aq) + 3H_2O(l)$$

Chlorates, bromates, and iodates also can be prepared by the reaction of the appropriate halogen with concentrated nitric acid or hydrogen peroxide or (commercially) by electrolysis of the halide. For example, the reaction for the oxidation of I_2 by H_2O_2 is

$$I_2(s) + 5H_2O_2(aq) \rightarrow 2IO_3^-(aq) + 4H_2O(l) + 2H^+(aq)$$
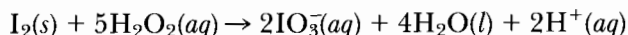
Perchlorate and periodate are prepared by the electrochemical oxidation of chlorate and iodate, respectively. For example,

$$ClO_3^-(aq) + H_2O(l) \xrightarrow{\text{electrolysis}} ClO_4^-(aq) + 2H^+(aq) + 2e^-$$
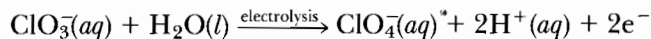
The perchlorate is obtained from the electrolyzed cell solution by adding potassium chloride in order to precipitate potassium perchlorate, which is only moderately soluble in water. Perchloric acid, $HClO_4$, also can be obtained from the electrolyzed solution containing perchlorate by adding sulfuric acid and then distilling. The distillation is very dangerous and often results in a violent explosion. Concentrated perchloric acid should not be allowed to come into contact with reducing agents, such as organic matter, because of the extreme danger of a violent explo-
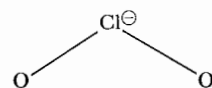
Bent
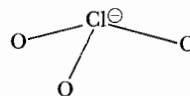
Trigonal pyramidal
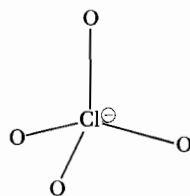
Tetrahedral

Figure 9-5 The shapes of the oxyacid anions of chlorine.

sion. Solutions containing perchlorates should not be evaporated because of their treacherously explosive nature. Perchlorates are used in explosives, solid rocket fuels, and matches.

When potassium chlorate, $KClO_3$, is mixed with concentrated sulfuric acid and the reducing agent oxalic acid, $H_2C_2O_4$, gaseous chlorine dioxide, ClO_2, is produced:

$$2H^+(aq) + 2ClO_3^-(aq) + H_2C_2O_4(aq) \rightarrow 2ClO_2(g) + 2CO_2(g) + 2H_2O(l)$$
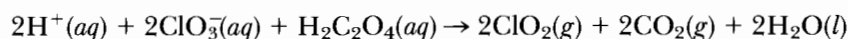
Chlorine dioxide is a yellow, violently explosive gas, which acts as a powerful oxidizing agent. Sodium chlorite is prepared on a commercial scale from chlorine dioxide via the reaction

$$4NaOH(aq) + Ca(OH)_2(aq) + C(s) + 4ClO_2(g) \rightarrow$$
$$4NaClO_2(aq) + CaCO_3(s) + 3H_2O(l)$$
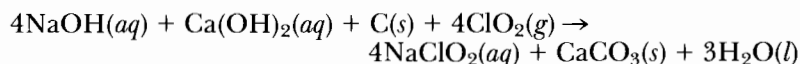
Sodium chlorite is a strong oxidizing agent that is used in the pulp and textile industries.

9-6 INTERHALOGENS ARE COMPOUNDS CONTAINING TWO OR MORE DIFFERENT TYPES OF HALOGENS

The *interhalogen compounds* are binary compounds involving two different halogens. The known interhalogens are listed in Table 9-10. The structures of all the interhalogens are predicted correctly using VSEPR theory (Chapter 11 of the text). The interhalogens are prepared by the direct combination of the elements under appropriate experimental conditions. For example, ClF may be prepared by direct combination of the elements at a temperature of 220° to 250°C. Chlorine trifluoride, ClF_3, is also formed in the reaction, and the ClF and ClF_3 may be separated by distillation.

Most of the diatomic interhalogens disproportionate. For example, BrF disproportionates according to

$$3BrF(g) \rightleftharpoons BrF_3(g) + Br_2(l)$$

The interhalogens are all rather reactive and are strong oxidizing agents. They react with most elements to produce a mixture of halides. They react readily with water, and in some cases (for example, BrF_5) explosively.

Several polyatomic halide and interhalogen ions are known. The linear, triatomic halogen anions such as $I_3^-(aq)$ and $ICl_2^-(aq)$ are formed in reactions of the type

$$ICl(aq) + Cl^-(aq) \rightleftharpoons ICl_2^-(aq) \qquad K = 1.7 \times 10^2 \text{ M}^{-1} \text{ at } 25°C$$

Interhalogen polyhalide ions such as ICl_4^- (square planar) and BrF_6^- (octahedral) are prepared from the neutral interhalogens using reactions of the type

$$CsCl(s) + ICl_3(g) \rightarrow CsICl_4(s)$$
$$CsF(s) + BF_5(g) \rightarrow CsBrF_6(s)$$
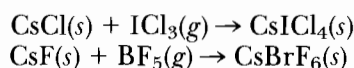
Table 9-10 Some of the known interhalogen compounds

ClF	ClF_3	ClF_5	
BrF	BrF_3	BrF_5	
IF	IF_3	IF_5	IF_7
BrCl			
ICl			
IBr			

The structures of the polyhalide ions are predicted correctly from VSEPR theory (Figure 9-6).

Diiodine chloride
(linear)

Chlorine trifluoride
(T-shaped)

Iodine tetrachloride ion
(square planar)

Chlorine pentafluoride
(square pyramidal)

Bromine hexafluoride ion
(octahedral)

Iodine heptafluoride
(pentagonal bipyramidal)

Figure 9-6 Structures of representative interhalogen species.

TERMS YOU SHOULD KNOW

halogen	bifluoride ion	interhalogen compound
tincture of iodine	disproportionation reaction	
hydrohalic acid	hypohalous acid	

QUESTIONS

9-1. Explain briefly why fluorine is capable of stabilizing unusually high oxidation states in many elements.

9-2. Describe how each of the halogens is prepared on a commercial scale.

9-3. Complete and balance the following equations.

(a) $Ca(s) + Br_2(l) \rightarrow$

(b) $Ti(s) + Cl_2(g) \rightarrow$

(c) $As(s) + Cl_2(g) \rightarrow$
    excess

(d) $Na(s) + I_2(s) \rightarrow$

9-4. Complete and balance the following equations.

(a) $F_2(g) + H_2O(l) \rightarrow$

(b) $F_2(g) + Si(s) \rightarrow$

(c) $F_2(g) + Ag(s) \rightarrow$

(d) $F_2(g) + Mg(s) \rightarrow$

9-5. Balance the following equations.

(a) $NaCl(aq) + H_2SO_4(aq) + MnO_2(s) \rightarrow$
    $Na_2SO_4(aq) + MnCl_2(aq) + H_2O(l) + Cl_2(g)$

(b) $NaIO_3(aq) + NaHSO_3(aq) \rightarrow$
    $I_2(s) + Na_2SO_4(aq) + H_2SO_4(aq) + H_2O(l)$

(c) $Br_2(l) + NaOH(aq) \rightarrow$
$$NaBr(aq) + NaBrO_3(aq) + H_2O(l)$$

9-6. Chlorine oxidizes iodine to iodic acid in water. Balance the following equation:

$$Cl_2(g) + I_2(s) + H_2O(l) \rightarrow HCl(aq) + HIO_3(aq)$$
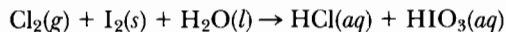
9-7. Iodine is oxidized to iodic acid by concentrated nitric acid. Balance the following equation:

$$I_2(s) + HNO_3(aq) \rightarrow HIO_3 + NO(g) + H_2O(l)$$

9-8. Give the chemical formulas and names of the oxyacids of chlorine.

9-9. Name the following oxyacids.

(a) $HBrO_2$ (b) HIO (c) $HBrO_4$ (d) HIO_3

9-10. Name the following oxyacids:

(a) HNO_2 (c) H_3PO_2 (e) $H_2N_2O_2$

(b) H_2SO_3 (d) H_3PO_3

and the following salts:

(a) K_2SO_3 (c) KIO_2

(b) $Ca(NO_2)_2$ (d) $Mg(BrO)_2$
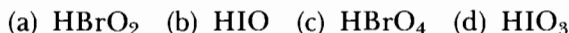
9-11. Describe by balanced chemical equations how you would prepare $KIO_3(s)$ starting with $I_2(s)$.

9-12. Why is the heat evolved per mole in the neutralization reaction of $HCl(aq)$ by $KOH(aq)$ the same as that for $HBr(aq)$ by $KOH(aq)$? Why is the heat evolved per mole much less for the reaction $HF(aq)$ plus $KOH(aq)$?

9-13. In addition to the (meta)periodate ion, IO_4^-, there are the ions $H_2IO_5^-(aq)$ and $H_4IO_6^-(aq)$ that can be viewed as mono- and dihydrates, respectively, of IO_4^-. These species are formed in acidic solutions. In strongly acidic solutions, the principal I(VII) species is paraperiodic acid, $H_5IO_6(aq)$.

(a) Write a balanced chemical equation for the formation of $H_5IO_6(aq)$ from $IO_4^-(aq)$.

(b) Paraperiodic acid is a powerful oxidizing agent that can oxidize $Mn^{2+}(aq)$ to $MnO_4^-(aq)$. Write a balanced chemical equation for this reaction. Assume that the iodine product is $IO_3^-(aq)$.

9-14. The rate of disproportionation of $I_2(aq)$ is fast at all temperatures, and the following reaction occurs rapidly and quantitatively:

$I_2(aq) + OH^-(aq) \rightarrow$
$$I^-(aq) + IO_3^-(aq) + H_2O(l) \text{ (unbalanced)}$$
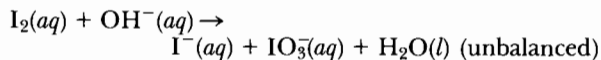
Balance this equation.

9-15. Electrolysis of $NaI(aq)$, $NaBr(aq)$, and $NaCl(aq)$ solutions yields $H_2(g)$ and the diatomic halogens, I_2, Br_2, and Cl_2, respectively. However, electrolysis of $NaF(aq)$ yields $H_2(g)$ and $O_2(g)$. Explain why $F_2(g)$ is not formed in the electrolysis of $NaF(aq)$.

9-16. When $IF(g)$ is heated it disproportionates. Write a balanced chemical equation for the disproportionation reaction.

9-17. Suggest an explanation why, in contrast to NH_3, NF_3 is not at all basic.

9-18. What is the oxidation state of the oxygen atom in HOF, an unstable substance that decomposes to HF and O_2?

9-19. When perchloric acid is dehydrated by P_4O_{10}, a colorless, unstable oily liquid, Cl_2O_7, is produced. Use hybrid orbitals to describe the bonding in Cl_2O_7 (there is a Cl—O—Cl bond).

9-20. Use VSEPR theory to predict the shapes of the following interhalogen cations.

(a) ClF_2^+ (b) ClF_4^+ (c) ClF_6^+

9-21. Name the oxidation state of each halogen in the following compounds.

(a) IF_5 (d) ClF

(b) $NaClO$ (e) $NaIO_3$

(c) $KBrO_3$

9-22. The acid $HF(aq)$ differs from the other hydrohalic acids in that it is a weak acid (25°C data):

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad pK_a = 3.17$$
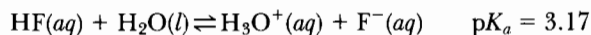
and in that the ion $HF_2^-(aq)$ forms readily:

$$HF(aq) + F^-(aq) \rightleftharpoons HF_2^-(aq) \qquad K = 5.1 \text{ M}^{-1}$$
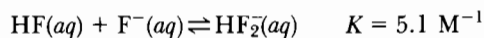
Suppose we have a solution with a stoichiometric concentration of $HF(aq)$ of 0.10 M that is buffered at pH = 3.00. Compute the concentrations of $F^-(aq)$, $HF(aq)$, and $HF_2^-(aq)$ in the solution.

9-23. Given that $\Delta \overline{G}_f^\circ[I_2(aq)] = 16.40 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta \overline{G}_f^\circ[I^-(aq)] = -51.57 \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta \overline{G}_f^\circ[I_3^-(aq)] =$

-51.40 kJ $\cdot$ mol^{-1} at 25°C, calculate the equilibrium constant for the reaction

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
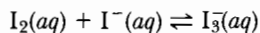
9-24. Given that $\Delta \overline{G}_f^\circ[ICl(aq)] = -17.1$ kJ $\cdot$ mol^{-1}, $\Delta \overline{G}_f^\circ[Cl^-(aq)] = -131.23$ kJ $\cdot$ mol^{-1}, and $\Delta \overline{G}_f^\circ[ICl_2^-(aq)] = -161.0$ kJ $\cdot$ mol^{-1} at 25°C, calculate the equilibrium constant for the reaction

$$ICl(aq) + Cl^-(aq) \rightleftharpoons ICl_2^-(aq)$$
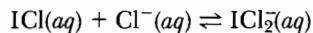
9-25. Iodine pentoxide is a reagent for the quantitative determination of carbon monoxide. The reaction is

$$5CO(g) + I_2O_5(s) \rightarrow I_2(s) + 5CO_2(g)$$
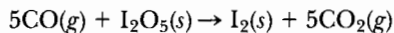
The iodine produced is dissolved in KI(aq) and then determined by reaction with $Na_2S_2O_3$:

$$2S_2O_3^{2-}(aq) + I_3^-(aq) \rightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$$
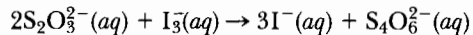
Compute the moles of CO required to produce sufficient $I_3^-(aq)$ to react completely with the $S_2O_3^{2-}(aq)$ in 10.0 mL of 0.0350 M $Na_2S_2O_3(aq)$.

9-26. The solubility of $I_2(s)$ in water at 25°C is 0.0013 M and

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K = 700 \text{ M}^{-1}$$
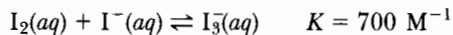
at 25°C. Compute the solubility of $I_2(s)$ in a solution that is initially 0.10 M in KI(aq).

9-27. Using the standard reduction potentials

$$H^+(aq) + HOCl(aq) + e^- \rightleftharpoons \tfrac{1}{2}Cl_2(g) + H_2O(l)$$
$$E^0 = 1.63 \text{ V}$$

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$$
$$E^0 = 1.36 \text{ V}$$

calculate the value of the equilibrium constant at 25°C for the reaction

$$Cl_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$
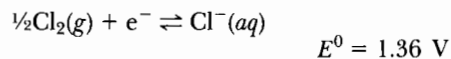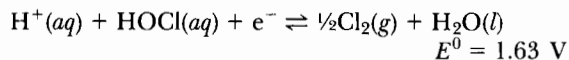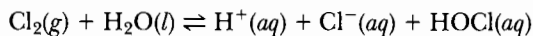
9-28. Using the result of Question 9-27, and given that

$$Cl_2(g) \rightleftharpoons Cl_2(aq) \qquad K = 0.062 \text{ M} \cdot \text{atm}^{-1}$$

calculate the value of the equilibrium constant for

$$Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$
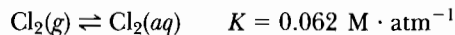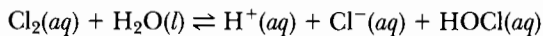
THE NOBLE GASES
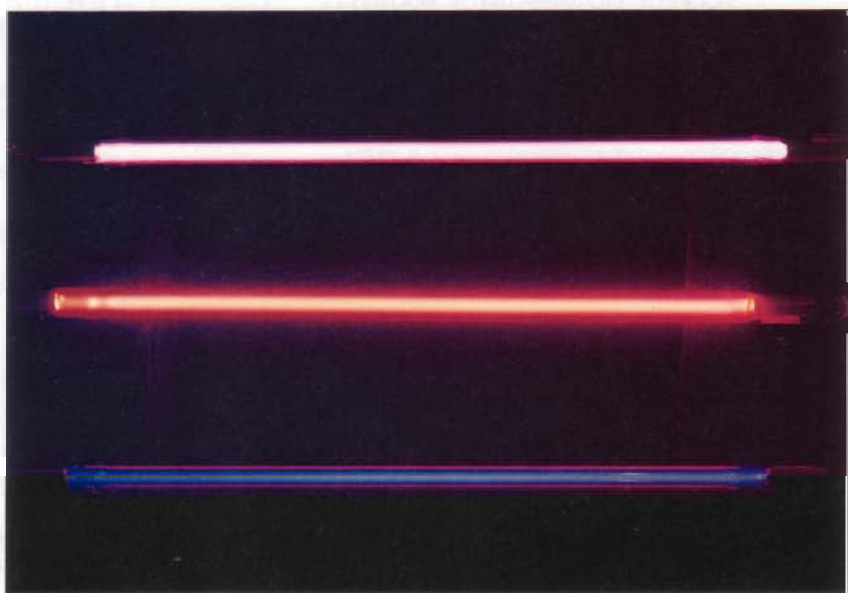
When an electric discharge is passed through a noble gas, light is emitted as electronically excited noble-gas atoms decay to lower energy levels. The tubes contain helium (top), neon (center), and argon (bottom).

The Group 8 elements, helium, neon, argon, krypton, and xenon, are called the noble gases and are noteworthy for their relative lack of chemical reactivity. Only xenon and krypton are known to enter into chemical compounds, and even then only with the two most electronegative compounds, fluorine and oxygen. As Table 10-1 indicates, the principal source of the noble gases, except for helium, is the atmosphere. The atomic and physical properties of the noble gases are given in Tables 10-2 and 10-3, respectively.

The data in Table 10-3 nicely illustrate trends in physical properties with increasing atomic size. Note that the boiling points

Table 10-1 Sources and uses of the noble gases.

Element	Principal sources	Uses
helium	natural gas wells	provide an inert atmosphere for welding, inflation of meteorlogical balloons, cryogenic, coolant, nitrogen substitute for SCBA (self-contained breathing apparatus), pressurize liquid fuel rockets
neon	fractional distillation of liquid air	fluorescent tubes, lasers, high-voltage indicators, cryogenic research
argon	fractional distillation of liquid air	provide an inert atmosphere for welding, fluorescent tubes, blanketing material for the production of titanium and other metals, lasers, deaeration of solutions
krypton	fractional distillation of liquid air	fluorescent tubes, high-speed photographic lamps, lasers
xenon	fractional distillation of liquid air	fluorescent tubes, lasers, stroboscopic lamps

and the enthalpies of vaporization increase with increasing atomic number, due to the larger London attractive forces (see Section 13-4 of the text). This same tendency can be seen in the increase of the van der Waals constants for helium through xenon (see Table 5-5 of the text). Recall that the van der Waals constants a and b are a measure of the attraction and the size, respectively, of the molecules in a gas.

10-1 THE NOBLE GASES WERE NOT DISCOVERED UNTIL 1893

In 1893, the English physicist Lord Rayleigh noticed a small discrepancy between the density of nitrogen obtained by the removal of oxygen, water vapor, and carbon dioxide from air and

Table 10-2 Atomic properties of the Group 8 elements

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
atomic number	2	10	18	36	54	86
atomic mass/amu	4.00260	20.179	39.948	83.80	131.30	(222)
number of naturally occurring isotopes	2	3	3	6	9	0
outer shell electron configuration	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$	$4s^2 4p^6$	$5s^2 5p^6$	$6s^2 6p^6$
atomic radius/pm	50	70	95	110	130	—
ionization energy/MJ $\cdot$ mol^{-1}	2.37	2.08	1.52	1.35	1.17	1.04

Table 10-3 Some physical properties of the Group 8 elements

property	Helium	Neon	Argon	Krypton	Xenon
melting point/°C	—	−248.6	−189.4	−157.2	−111.8
melting point/K	—	24.6	83.8	115.9	161.3
boiling point/°C	−268.9	−246.1	−185.9	−153.4	−108.1
boiling point/K	4.2	27.1	87.3	119.7	165.0
$\Delta \overline{H}_{fus}$/kJ · mol^{-1}	—	0.335	1.17	1.63	2.30
$\Delta \overline{H}_{vap}$/kJ · mol^{-1}	0.08	1.76	6.52	9.03	12.63
density at 20°C/g · cm^{-3}	1.66×10^{-4}	8.37×10^{-4}	1.66×10^{-3}	3.48×10^{-3}	5.46×10^{-3}
ppm in air	5.2	18.2	9340	1.1	0.08

the density of nitrogen prepared by chemical reaction, such as the thermal decomposition of ammonium nitrite:

$$NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(g)$$

One liter of nitrogen at 0°C and 1 atm obtained by the removal of all the other known gases from air (Figure 10-1) has a mass of 1.2572 g, whereas one liter of dry nitrogen obtained from ammonium nitrite has a mass of 1.2505 g under the same conditions. This slight difference led Lord Rayleigh to suspect that some other gas was present in the sample of nitrogen obtained from air.

The English chemist William Ramsay found that if hot calcium metal is placed in a sample of nitrogen obtained from air, about 1 percent of the gas fails to react. Pure nitrogen would
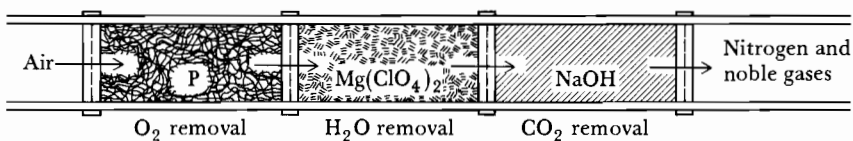
Figure 10-1 A schematic illustration of the removal of O_2, H_2O, and CO_2 from air. First the oxygen is removed by allowing the air to pass over phosphorus:

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$
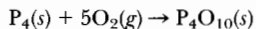
The residual air is passed through anhydrous magnesium perchlorate to remove the water vapor:

$Mg(ClO_4)_2(s) + 6H_2O(g) \rightarrow Mg(ClO_4)_2 \cdot 6H_2O(s)$
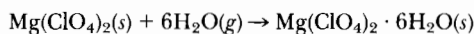
and then through sodium hydroxide to remove the CO_2:

$NaOH(s) + CO_2(g) \rightarrow NaHCO_3(s)$
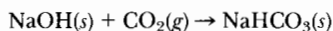
The gas that remains is primarily nitrogen with about 1 percent noble gases.

react completely. Because of the inertness of the residual gas, Ramsay gave it the name argon (Greek, idle). Ramsay then lique-fied the residual gas and, upon measuring its boiling point, dis-covered that it consisted of five components, each with its own characteristic boiling point (Table 10-3). The component present in the greatest amount retained the name argon. The others were named helium (sun), neon (new), krypton (hidden), and xenon (stranger). Helium was named after the Greek word for sun (helios) because its presence in the sun had been determined earlier by spectroscopic methods.

The noble gases in the atmosphere are thought to have arisen as by-products of the decay of radioactive elements in the earth's crust (Chapter 24). For their work in discovering and character-izing an entire new family of elements, Rayleigh received the 1904 Nobel Price in physics and Ramsay received the 1904 Nobel Prize in chemistry.

All the noble gases are colorless, odorless, and relatively inert. Helium is used in lighter-than-air craft, despite the fact that it is denser and hence has less lifting power than hydrogen, because it is nonflammable. Helium is also used in welding to provide an inert atmosphere around the welding flame and thus reduce corrosion of the heated metal. Neon is used in neon signs, which are essentially discharge tubes (see Frontispiece) filled with a noble gas or a noble-gas mixture. When placed in a discharge tube, neon emits an orange-yellow glow that penetrates fog very well. Argon, the most plentiful and least expensive noble gas, often is used in fluorescent and incandescent light bulbs because it does not react with the discharge electrodes or the hot fila-ment. Krypton and xenon are scarce and costly, which limits their application, although they are used in lasers, flashtubes for high-speed photography, and automobile-engine timing lights.

■ Helium has 93 percent of the lifting power of hydrogen.

10-2 XENON FORMS COMPOUNDS WITH FLUORINE AND OXYGEN

Prior to 1962 most chemists believed, and essentially all general chemistry textbooks proclaimed, that the noble gases did not form any chemical compounds. In fact, the gases helium through xenon were called the inert gases, indicating that they did not undergo any chemical reactions.

In 1962, Neil Bartlett, then of the University of British Col-umbia, was working with the extremely strong oxidizing agent platinum hexafluoride, PtF_6, which oxidizes $O_2(g)$ to produce the ionic compound $O_2^+PtF_6^-$:

$$O_2(g) + PtF_6(s) \rightarrow O_2^+PtF_6^-$$
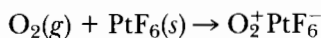
Bartlett observed that the ionization energy of $O_2(g)$ (1171 kJ · mol^{-1}) is about the same as the ionization energy of $Xe(g)$ (1176 kJ · mol^{-1}), and so reasoned that xenon might react with PtF_6

■ Linus Pauling predicted xenon compounds in the 1930's on the basis of the similarity of the ionization energies of O_2 and Xe.

in an analogous manner. When he mixed xenon and PtF_6 in a reaction chamber, he obtained a definite chemical reaction that at the time was thought to be the formation of $Xe^+PtF_6^-$. It has since been found that the product of the reaction is more complex than $Xe^+PtF_6^-$, but nevertheless Bartlett showed that xenon will react with a strong oxidizing agent under the right conditions of temperature and pressure. Bartlett's discovery prompted other research groups to investigate reactions of xenon, and within a year or so several other compounds of xenon were synthesized. Three xenon fluorides can be prepared by the direct combination of xenon and fluorine in a nickel vessel:

$$Xe(g) + F_2(g) \rightleftharpoons XeF_2(s)$$
$$XeF_2(s) + F_2(g) \rightleftharpoons XeF_4(s)$$
$$XeF_4(s) + F_2(g) \rightleftharpoons XeF_6(s)$$
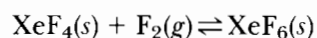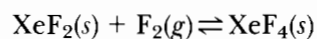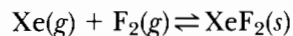
As these three equilibria indicate, the reaction of a mixture of xenon and fluorine yields a mixture of XeF_2, XeF_4, and XeF_6. The chief difficulty is the separation of the products. A favorable yield of XeF_2 can be obtained by using a large excess of xenon. Xenon difluoride forms large, colorless crystals that melt at 130°C. It is a linear molecule, as predicted by VSEPR theory (AX_2E_3). Xenon difluoride is soluble in water and evidently exists as XeF_2 molecules in solution. Xenon tetrafluoride can be obtained in quantitative yield by reacting a 1:5 mixture of Xe and F_2 at 400°C and 6 atm in a nickel vessel. Xenon tetrafluoride forms colorless crystals (see Figure 10-2) that melt at 177°C. The molecule is square planar, as predicted by VSEPR theory (AX_4E_2). Unlike XeF_2, XeF_4 hydrolyzes according to

$$6XeF_4(s) + 12H_2O(l) \rightleftharpoons 2XeO_3(s) + 4Xe(g) + 3O_2(g) + 24HF(aq)$$
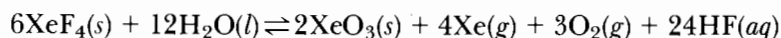
An aqueous solution of XeO_3 is stable, colorless, and odorless, and a powerful oxidizing agent. Upon evaporation to dryness $XeO_3(s)$ results. Xenon trioxide is extremely explosive, which is why work with XeF_4 (and also XeF_6) must be done under carefully dry conditions.

Some other known compounds of xenon are given in Table 10-4. Note that xenon forms chemical bonds with the most electronegative elements, fluorine and oxygen, and exhibits oxidation states of +2, +4, +6, and +8. Xenon, having the greatest atomic size of any of the nonradioactive noble gases, has the smallest ionization energy. Hence, except for radon, xenon is the most "reactive" noble gas, and we expect the reactivity of the noble gases to decrease from xenon to helium. The only known molecule containing krypton is KrF_2, and no isolable compounds of argon have been reported. The molar enthalpies of formation of XeF_2 and KrF_2 are

$$Xe(g) + F_2(g) \rightleftharpoons XeF_2(s) \qquad \Delta \overline{H}_f^\circ \simeq -110 \text{ kJ} \cdot \text{mol}^{-1}$$
$$Kr(g) + F_2(g) \rightleftharpoons KrF_2(s) \qquad \Delta \overline{H}_f^\circ \simeq +60 \text{ kJ} \cdot \text{mol}^{-1}$$

Argonne Nat. Lab.

Figure 10-2 Xenon tetrafluoride crystals. Xenon tetrafluoride was first prepared in 1962 by the direct combination of Xe(g) and $F_2(g)$ at 6 atm and 400°C.

Table 10-4 The principal compounds of xenon

Compound	Oxidation state	Physical state	Molecular shape
XeF_2	+2	colorless crystals	linear
XeF_4	+4	colorless crystals	square planar
XeF_6	+6	colorless crystals	distorted octahedron
$XeOF_4$	+6	colorless liquid	square pyramidal
XeO_2F_2	+6	colorless crystals	seesaw
XeO_3	+6	colorless crystals	trigonal pyramidal
XeO_4	+8	colorless gas	tetrahedral

The difference in the values of $\Delta \overline{H}_f^\circ$ for these two reactions can be accounted for by the difference in the ionization energies of krypton and xenon (180 kJ · mol^{-1}). Although radon has the lowest ionization energy of all the noble gases and might be expected to be the most reactive, its radioactivity makes the study of radon chemistry difficult, so little is known.

QUESTIONS

10-1. What is the principal chemical property of the noble gases?

10-2. Discuss how the noble gases were discovered by Lord Rayleigh.

10-3. What is the principal source of helium?

10-4. Why did Rayleigh and Ramsey place the newly discovered noble gases in a new group in the periodic table?

10-5. What is the source of He(g) in natural gas deposits?

10-6. Sketch an experimental set up for removing O_2, H_2O, and CO_2 from air. How could you remove the remaining N_2?

10-7. Describe the important role that the noble gases played in the theories of chemical bonding and electronic structure of atoms.

10-8. Nitrogen is also a relatively inert gas. Suggest an experiment to demonstrate the difference between nitrogen and argon.

10-9. When Bartlett prepared $O_2^+PtF_6^-$ in 1962, what reasoning did he use to conjecture that it might be possible to prepare $Xe^+PtF_6^-$?

10-10. Complete and balance.

(a) $XeF_4(s) + H_2O(l) \rightarrow$

(b) $Xe(g) + F_2(g) \rightarrow$

(c) $Kr(g) + F_2(g) \rightarrow$

(d) $XeF_6(s) + H_2O(l) \rightarrow$
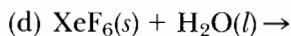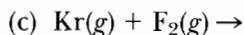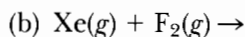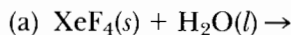
10-11. Use the data in Table 10-3 to compute the values of $\Delta \overline{S}_{vap}$ and $\Delta \overline{S}_{fus}$ for the Group 8 elements. Compare your results with the values of $\Delta \overline{S}_{vap}$ from Trouton's rule.

10-12. Why do both van der Waals constants, a and b, increase with increasing atomic number for the noble gases?

10-13. Why does $\Delta \overline{H}_{vap}$ increase with increasing atomic number for the noble gases?

10-14. Use VSEPR theory to predict the shapes of the xenon compounds given in Table 10-4.

10-15. What is the oxidation state of xenon in each of the compounds in Table 10-4?

10-16. Use VSEPR theory to predict the structures of the following compounds.
(a) RnF_2 (b) RnF_4 (c) RnO_3 (d) RnO_4
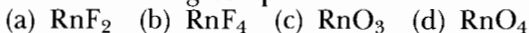
Properties of Metals:

1. conduct
2. shiny

review M.O. theory. (simple)

⇓

band theory

⇓

½ filled bands - left side of periodic table.

+ Relation of Metals + Non-Metals

Periodic Regions

M.P. vs. group#

← 3rd row
2nd row
1st row
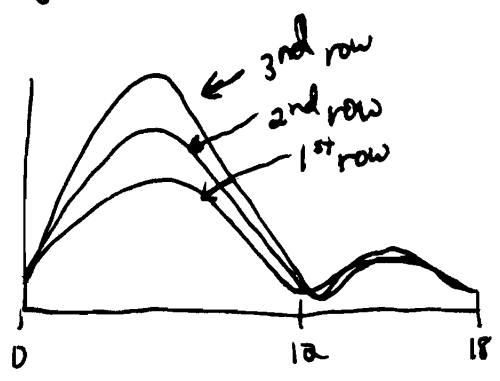
in non-metals M.P ↓ as you go down group

M.P

C
Si
Ge
Sn — Pb

period#
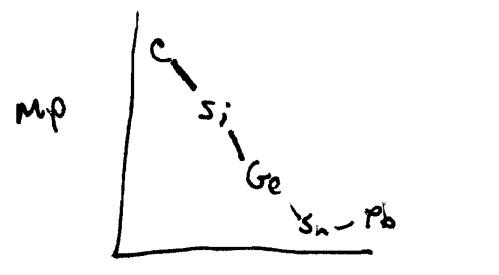
covalent bonding gets weaker as atoms get bigger

in T.M. it's reversed

Cr — Mo — W

period#
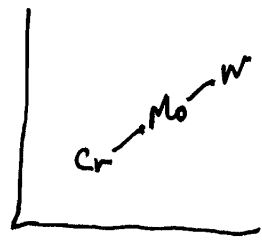
better overlap of 5d's vs. 3d's

Review

anti bonding orbital

σ*

1s   1s

σ_b

H atom   H_2 molecule   H atom   bonding orbital
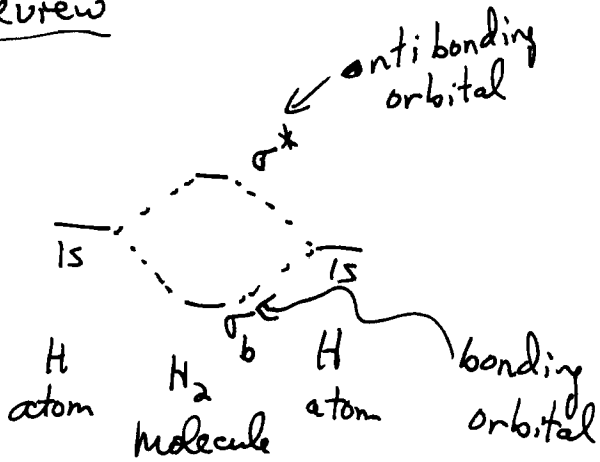
we make <u>multi</u>-atom structure

H_2 N_3 H   ⟹   H_3   H_4   H

---→   H_50   ⟹   H_alot   band of very closely spaced 1s orbitals.
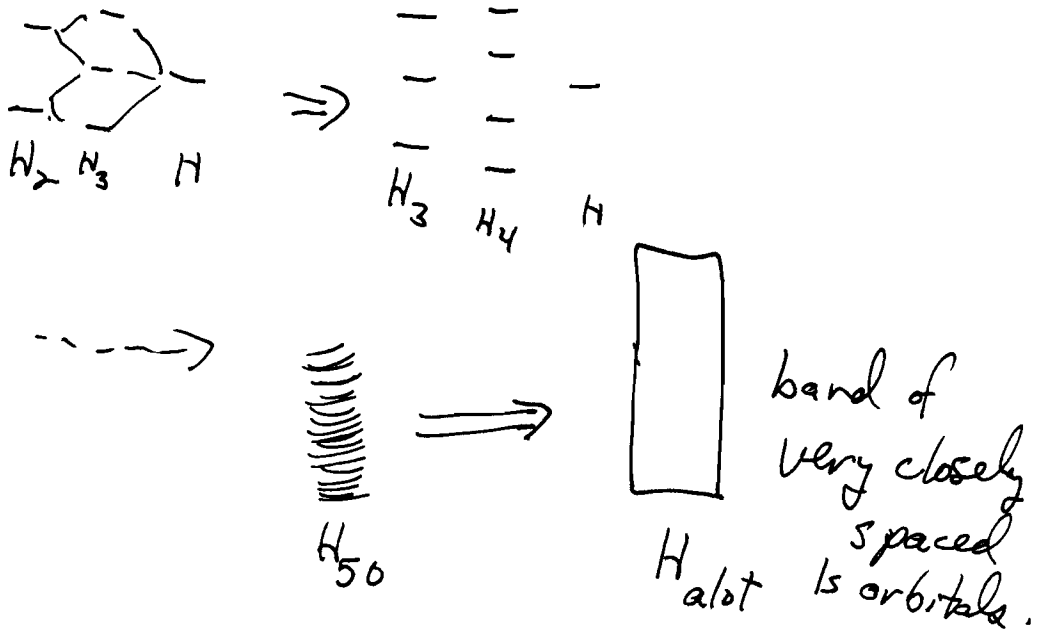
metals have these "bands"

Since valence orbitals are partially filled, band is only partially filled.
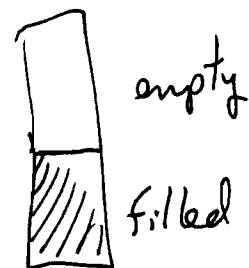
empty

filled

Visualize as e⁻'s delocalized over entire lattice
valence

conductivity of metals

to flow, electron needs to move to an empty orbital on another atom.

Since there are alot of filled orbitals near empty orbitals of very slightly higher energy, ~~because~~ it is easy for e^- to move.

∴ Since $E_{empty\ orbital} \approx E_{filled\ orbital}$

activation energy is low

Reflectivity
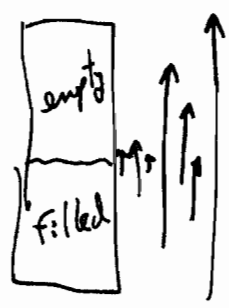
many transition for e^- to make possible.

∴ metal may absorb + emit (reflect) all visible wavelengths of light.

in physics: equation relates conductivity to reflectivity.

relation of group to strength of bonding

2nd & 3rd Period

banels overlap
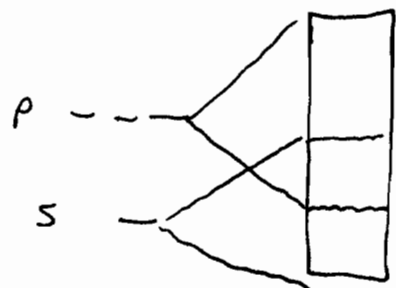
top ½ anti bonding
bottom ½ bonding } approximation

4th period: 3d orbital band also overlaps

SO: expect metal bonding to go up & then down as
crossing the periodic table.
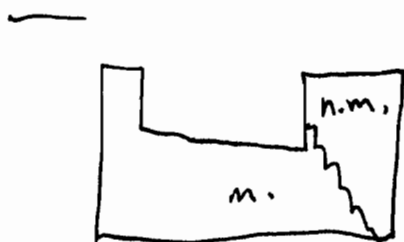
why do elements become non-metals near right
side?

why the slant down to the right

near right side it is possible to fill all valence orbitals by
covalent bonding O_2, N_2 etc.
can't do that way to the left

Slant down to the right?

   as ↓ periodic table

     covalent bonds get <u>weaker</u> → can't get <u>close</u> enough.

                              go over e^- sharing

Cl_2 243 kJ/mol

Br_2 192

I_2 151

non-metal   C–C   368

          Si–Si   340

          Ge–Ge   188

          Sn–Sn   151

metal   Pb–Pb   —

<u>Other stuff</u>: flow chart of why some reactions take place

Why $P_4 + Cl_2$ → violent (kinetically unfavored)

$Na + Cl_2$ → only coats (thermo dynamically favorable) Surface

Charge Density, Enthalpy, Entropy, and Stability

Metal Cations and Oxo Anions
in Aqueous Solution

Most of the elements are found in nature not as free elements but in the form of ions; hence we begin our study of the chemistry of the elements with some chemical properties of their ions. In this chapter we will investigate the interaction of some common ions of the elements (cations and oxo anions) with water and see how the periodic trends in these reaction tendencies can be related to the atomic properties reviewed in Chapter 1. We will then construct a physical model of what is happening during these reactions. Finally, we will apply these periodic trends and this model to a practical situation, predicting the forms that the different elements will take in unpolluted natural waters and those that are polluted with acid rain.

Your instructor may choose to have you begin your study of the chemistry of the ions of the elements with a laboratory investigation (or classroom demonstration and discussion) of the process of dissolving the cations of the elements (in the form of their chlorides) in water. This may sound trivial, but you will find some unexpected excitement in the process. You will find, upon analyzing the results, that even so simple a reaction involves some important chemistry.

You will find that the principles you derive apply to far more than just the reaction of a cation or an anion with the humble water molecule; ions react similarly with many other chemical species. The ways in which you begin looking at positively and negatively charged species in this chapter will be useful in subsequent chapters.

2.1

Hydration of Cations

When writing chemical equations for reactions of ions in solution we often write ions as if they were simple particles in solution—e.g., we may write the sodium ion as Na^+ or perhaps as $Na^+(aq)$. But there are definite reactions between ions and the solvent water that produce what we call **hydrated ions**. Hydrated ions arise as a consequence of the polar nature of the water molecule. Since the oxygen atom
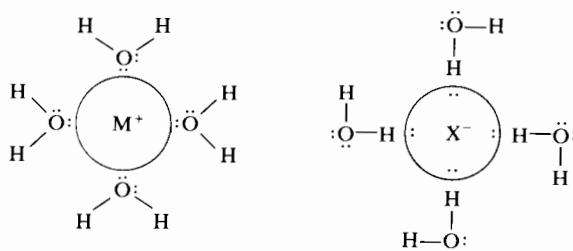
Figure 2.1 A hydrated cation and a hydrated anion.

of the water molecule is much more electronegative than the hydrogen atoms, each H—O bond is a polar covalent bond in which the bond electrons are (on the average) closer to the oxygen atom than the hydrogen atom, giving rise to a partial negative charge on oxygen and a partial positive charge on hydrogen. Since H_2O is not a linear molecule, it has a partially negatively charged end (its oxygen end) and a partially positively charged end (the hydrogen end). Since opposite charges attract, a positive ion (cation) placed in water surrounds itself with water molecules, with the oxygen ends inward toward the ion (Figure 2.1). Conversely, a negative ion surrounds itself with water molecules, hydrogen ends inward. These surrounded ions are what we call hydrated ions.

The attraction of opposite charges is really quite a strong force. If we were to plunge gaseous cations into water, they would form hydrated ions and release large amounts of energy, which we call the **hydration energy** of the cation. (This experiment is quite impossible to perform, but the energy released can be determined indirectly. Note that in the experiment that you just did, you added cations to water from the solid state and also added anions. This makes a large difference, as we will see in the next chapter, and consequently you did not usually detect a lot of energy being released.) Hydration energies of a number of cations are listed in Table 2.1; by any normal chemical standard these are large energies.

The data in Table 2.1 show that the hydration energy of a cation depends upon the charge and the radius of the cation, as expected qualitatively from Coulomb's law, and also depends upon the electronegativity of the element. Latimer [1] observed that if the electronegativity of the metal is not too great, the hydration energies of metal ions are given approximately by the equation

$$\Delta H_{hyd} = -\frac{60,900Z^2}{(r + 50)} kJ/mol \tag{2.1}$$

where Z is the charge on the cation and r is the cationic radius (in pm). (The constant added to the radius of the cation we can loosely equate with the radius of the oxygen in the water.)

No attempt is made in Latimer's equation to include the effects of electronegativity, but examination of the data for metals of Pauling electronegativities greater than 1.5 (on the right side of Table 2.1) shows that their hydration energies are substantially higher than those of ions of comparable radius and charge on the left

Table 2.1 Hydration Enthalpies of Metal Cations (kJ/mol)

Electronegativity ≤ 1.5			Electronegativity ≥ 1.5		
ION	RADIUS	ΔH_{hyd}	ION	RADIUS	ΔH_{hyd}
+1 Ions					
Cs	181	−263			
Rb	166	−296	Tl	164	−326
K	152	−321			
Na	116	−405	Ag	129	−475
Li	90	−515	Cu	91	−594
H		−1091			
+2 Ions					
Ra		−1259			
Ba	149	−1304			
Sr	132	−1445	Pb	133	−1480
No	124	−1485	Sn		−1554
Ca	114	−1592	Cd	109	−1806
			Cr	94	−1850
			Mn	97	−1845
			Fe	92	−1920
			Co	88	−2054
			Ni	83	−2106
			Cu	91	−2100
Mg	86	−1922	Zn	88	−2044
			Be	59	−2487
+3 Ions					
Pu	114	−3441			
La	117	−3283			
Lu	100	−3758	Tl	102	−4184
Y	104	−3620	In	94	−4109
Sc	88	−3960	Ga	76	−4685
			Fe	78	−4376
			Cr	75	−4402
			Al	67	−4660
+4 Ions					
Ce	101	−6489			

Ionic radii are from Table C; hydration enthalpies are taken from J. Burgess, *Metal Ions in Solution*, Ellis Horwood, Chichester, England, 1978, pp. 182–183.

side of the table. Such metals have electronegativities within about two units of that of oxygen, which suggests that for these metals there is not just an electrostatic attraction between the metal ion and the negative end of the water molecule, but that there also may be some degree of covalent bond formation, in which an unshared electron pair on water is shared with the metal ion.
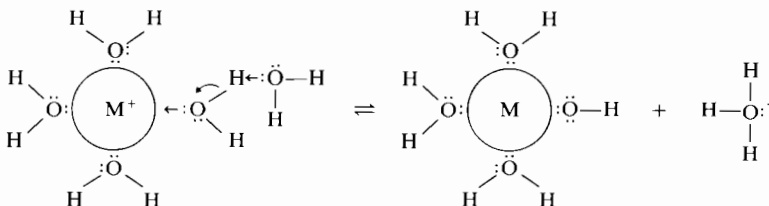
Figure 2.2 Hydrolysis of a hydrated cation.

Hydrolysis of Cations: Hydroxides, Oxides, Oxo Acids, Oxo Anions

If the attraction of the metal ion for the negative end of the water dipole is strong enough, the water molecule itself is affected (Figure 2.2). As the unshared electron pairs of the water molecule are pulled closer to (or even shared with) the metal ion, the electrons in the H—O bonds move closer to the oxygen to compensate some of its loss of electron density. Consequently the hydrogen ends up with an increased positive charge, which makes it more closely resemble a hydrogen ion. Eventually it may dissociate completely, attaching itself to solvent water molecules to make a hydronium ion and leaving a hydroxide group attached to the metal. We may represent this equilibrium by equation (2.2):

$$[M(H_2O)_6]^{z+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{(z-1)+} + H_3O^+ \qquad (2.2)$$

The aluminum ion, for example, readily undergoes this reaction:

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+ \qquad (2.3)$$
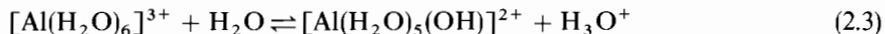
The equilibrium constant for this process may be measured, although there are many experimental difficulties. One commonly finds tabulated [2] the negative logarithm of the equilibrium constant, pK_a, for reaction (2.2); selected pK_a values are listed in Table 2.2. (An important consequence of taking negative logarithms, as in pH's, is that *lower* values of pK_a and of pH correspond to a *greater* extent of hydrolysis and a *higher* acidity of the solution.) Note the similarity of equation (2.2) to the equation for the equilibrium process of ionization of a weak acid such as acetic acid:

$$HC_2H_3O_2 + H_2O \rightleftharpoons C_2H_3O_2^- + H_3O^+ \qquad (2.4)$$
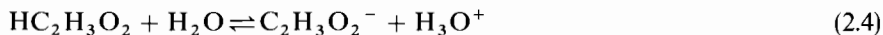
The pK_a for a hydrated ion is thus analogous to the pK_a (negative logarithm of the acid dissociation constant) of a species such as acetic acid.

Some of the pK_a values are the averages of different measurements that may differ by more than one pK_a unit, so we should not attempt to interpret small differences; but it is clear that the extent of this process, commonly called **hydrolysis** of the metal ion, increases with increasing charge and electronegativity of the metal and increases with decreasing radii of the metal ion. This process has a number of important practical consequences that we will investigate in this chapter and

Table 2.2 Hydrolysis Constants for Metal Cations

	Electronegativity < 1.5				Electronegativity > 1.5			
ION	RADIUS	(a) Z^2/r	pK$_a$	ION	RADIUS	(a) Z^2/r	(b) $Z^2/r + 0.096 (\chi - 1.50)$	pK$_a$
+1 Ions								
K	152	0.007	14.5	Tl	164	0.006	0.016	13.2
Na	116	0.009	14.2	Ag	129	0.008	0.049	12.0
Li	90	0.011	13.6					
+2 Ions								
Ba	149	0.027	13.5					
Sr	132	0.030	13.3	Pb	133	0.030	0.066	7.7
				Sn				3.4
Ca	114	0.035	12.8	Hg	116	0.034	0.082	3.4
				Cd	109	0.037	0.055	10.1
				Cr	94	0.043	0.043	10.0
				Mn	97	0.041	0.046	10.6
				Fe	92	0.043	0.075	9.5
				Co	88	0.045	0.082	9.6
				Ni	83	0.048	0.088	9.9
Mg	86	0.047	11.4	Zn	88	0.045	0.060	9.0
				Be	59	0.068	0.074	6.2
+3 Ions								
Pu	114	0.079	7.0					
La	117	0.077	8.5	Bi	117	0.077	0.127	1.1
Lu	100	0.090	7.6	Tl	102	0.088	0.140	0.6
Y	104	0.086	7.7	Au	99	0.091	0.191	−1.5
Sc	88	0.102	4.3	In	94	0.096	0.123	4.0
				Ti	81	0.111	0.115	2.2
				Ga	76	0.118	0.148	2.6
				Fe	78	0.115	0.147	2.2
				Cr	75	0.120	0.135	4.0
				Al	67	0.134	0.145	5.0
+4 Ions								
Th	108	0.148	3.2					
Pa	104	0.154	−0.8					
U	103	0.155	0.6					
Np	101	0.158	1.5					
Pu	100	0.160	0.5					
Ce	101	0.158	−1.1					
Hf	85	0.188	0.2	Sn	83	0.193	0.222	−0.6
Zr	86	0.186	−0.3	Ti	74	0.216	0.220	−4.0

SOURCES: Values of hydrolysis constants (pK$_a$) taken from C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley-Interscience, New York, 1976; and when not available there from J. Burgess, *Metal Ions in Solution*, Ellis Horwood, Chichester, England, 1978, pp. 264–267.

NOTE: (a) Z^2/r ratio for the cation; (b) $Z^2/r + 0.096 (\chi_p - 1.50)$ for the cation, as in equation (2.9).

the next, including the one suggested in part 8 of Experiment 1, and a number of environment consequences that we will see later.

Many of these consequences arise because equation (2.2) is only the first of several reactions that may occur. A second, then a third water molecule in the hydrated ion may hydrolyze, producing more hydronium ions and giving rise to cations containing more than one hydroxy group. These **hydroxy cations** undergo a bewildering variety of chemical reactions: Often they polymerize—and sometimes they lose a molecule of water from two hydroxy groups to give an **oxo cation**—but the most significant reactions are those generating usually insoluble hydroxides:

$$z[M(aq)(OH)]^{(z-1)+} \rightleftharpoons M(OH)_z(s) + (z-1)[M(aq)]^{z+} \tag{2.5}$$
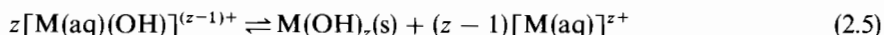
The equilibrium constant for this reaction for most metal ions is rather large (approximately $10^{5.6}$) [3], so the hydroxy cations of most metals tend not to persist over wide pH ranges but instead give rise to precipitated **metal hydroxides**, as observed for several of the metal ions in Experiment 1. Thus the partly hydrolyzed aluminum ion produced in equation (2.3) readily gives rise to a gelatinous precipitate of aluminum hydroxide:

$$3[Al(aq)(OH)]^{2+} \rightleftharpoons Al(OH)_3(s) + 2[Al(aq)]^{3+} \tag{2.6}$$

It can be shown [4] that the metal hydroxide will precipitate at a pH that is roughly equal to the pK_a value of the metal ion:

$$pH = pK_a - \left(\frac{1}{z}\right)\log[M^{z+}] - \frac{5.6}{z} \tag{2.7}$$

This equation tells us that the lower the pK_a of a given metal ion, the less basic the solution need be for the metal hydroxide to begin precipitating. Certainly the concentration of the metal ion does have some effect on this pH, but we can easily calculate that moderately acidic ions such as Al^{3+} or Fe^{3+} will form insoluble hydroxides even in solutions that have quite high hydrogen-ion concentrations (low pH's).

Often the insoluble metal hydroxides will lose molecules of water to give insoluble oxides, as represented by equation (2.8):

$$M(OH)_z(s) \rightleftharpoons MO_{z/2}(s) + \frac{z}{2}H_2O \tag{2.8}$$

Since it is difficult for us to tell when this has happened, we will not attempt to distinguish metal hydroxide and metal oxide precipitates.

Even this may not be the end of the story: If the attraction of the metal ion for the pair of electrons on oxygen is strong enough, the hydroxy groups of the metal hydroxide may start to lose their remaining hydrogens as hydronium ions:

$$M(OH)_z + zH_2O \rightleftharpoons MO_z^{z-} + zH_3O^+ \tag{2.9}$$
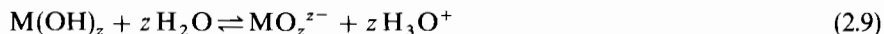
Thus the metal hydroxide may begin to act as a weak **oxo acid**, which finally may

Higher pH (more basic solutions)

or, more acidic cations (at a given pH)
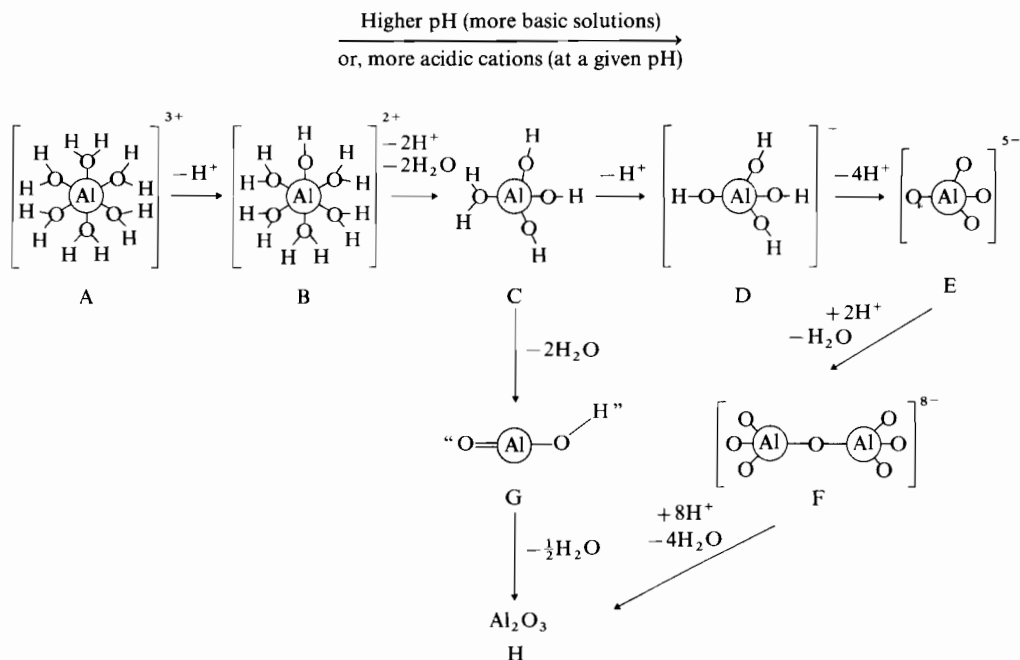
Figure 2.3 Main species arising from the hydrolysis of cations (Al^{3+} is used for purposes of illustration) in aqueous solutions and the sections in which they are discussed. (A) a hydrated ion, Sec. 2.1; (B) a hydroxy cation, Sec. 2.2; (C) a metal hydroxide, Sec. 2.2; (D) a hydroxo anion, Sec. 2.7; (E) an oxo anion, Secs. 2.6, 2.8. 2.9; (F) a polynuclear oxo anion, Secs. 4.7–4.9; (G) an oxo acid (hypothetical in the case of aluminum), Sec. 2.10; (H) an oxide, Secs. 4.1–4.6.

ionize to give an **oxo anion**, thus completely dismembering the water molecules that were originally attached in a hydrated ion. Although we will not look at oxo acids and oxo anions until later in the chapter, we can see that a remarkable variety of chemical species can arise out of the "simple" interaction of a positively charged ion and its water molecules of hydration. The main species that we will be studying in Chapters 2, 3, and 4 are summarized in Figure 2.3.

2.3

Predicting the Degree of Hydrolysis of Cations

2.3.1   Effects of Charge and Radius on Hydrolysis

There are important practical consequences of the acidic properties and hydrolysis reactions of compounds of elements with high oxidation numbers or small radii or high electronegativities. The suggested laboratory experiment hints at some of

these: A compound with an innocent-looking formula such as $TiCl_4$ may react quite violently with water. It may react with the water vapor in the air and fill the laboratory with choking fumes of the acid HCl. You may be trying to prepare a solution of a metal ion for some experiment in biology, only to find a precipitate forming. You may need to know the form a metal-ion pollutant takes in a lake, to know whether it will end up as an insoluble sludge of oxide at the bottom of the lake or whether it will remain in solution as a cation or as an oxo anion—which may be taken up or rejected by quite different mechanisms by living organisms. Thus it is important for us to be able to gauge the approximate acidity of a given cation so that we can anticipate (even in the laboratory without a calculator) how violently a given compound will react with water or atmospheric humidity and whether its hydroxide or oxide will precipitate or whether an oxo anion will be produced.

Rather accurate equations have been presented for predicting the extent of hydrolysis of metal ions [5,6], but these are not simple enough to be used for our purposes of quick estimation of approximate acidity. To obtain such a relationship, we have graphed (in Figure 2.4, using solid circles) the pK_a values of metal cations of Pauling electronegativities (χ_p) of 1.5 or below versus the Z^2/r ratios of these ions. Equation (2.10) expresses the relationship we find empirically.

$$pK_a = 15.14 - 88.16\frac{Z^2}{r} \tag{2.10}$$

Normally we will find it quicker not to solve equation (2.10) to obtain exact values of pK_a, but instead we will evaluate Z^2/r in order to place it in a certain range or category of acidity, as outlined in Table 2.3. We find experimentally that the ions in a given category of acidity share several important chemical properties. These properties include not only the degree to which the ions react with water but also (as we will see in subsequent chapters) the solubility or insolublity of salts formed by these ions and the properties of compounds formed by these ions (such as their oxides and halides) in the absence of water.

Clearly the smallest ratios of Z^2/r correspond to the least hydrolysis and belong to the cations that we can most accurately call *nonacidic cations*. We can predict that if their electronegativities are below 1.5, ions of Z^2/r *less than 0.01* should show such negligible hydrolysis reactions that their acidity does not manifest itself in any important way. Included are such ions as Cs^+ and Rb^+, whose hydrolysis constants (pK_a values) are absent from Table 2.2 because the hydrolysis of these ions is too slight to be measured. Consequently we find that the hydroxides of these elements do not precipitate from solution; on the contrary, the solid hydroxides **deliquesce** in humid air, removing water from the air to form a solution!

The hydrolysis of ions such as Li^+, Ba^{2+}, Sr^{2+}, and Ca^{2+}, which have Z^2/r values between 0.01 and 0.04, can be measured in sensitive experiments and occasionally has significant consequences. We will refer to these ions as *feebly acidic cations*. Their hydroxides also do not normally precipitate from water, but they are less soluble than the hydroxides of the nonacidic cations.

Acidity becomes an important part of the chemistry of ions of low electronegativity and Z^2/r ratios between 0.04 and 0.10, although this acidity is not apparent
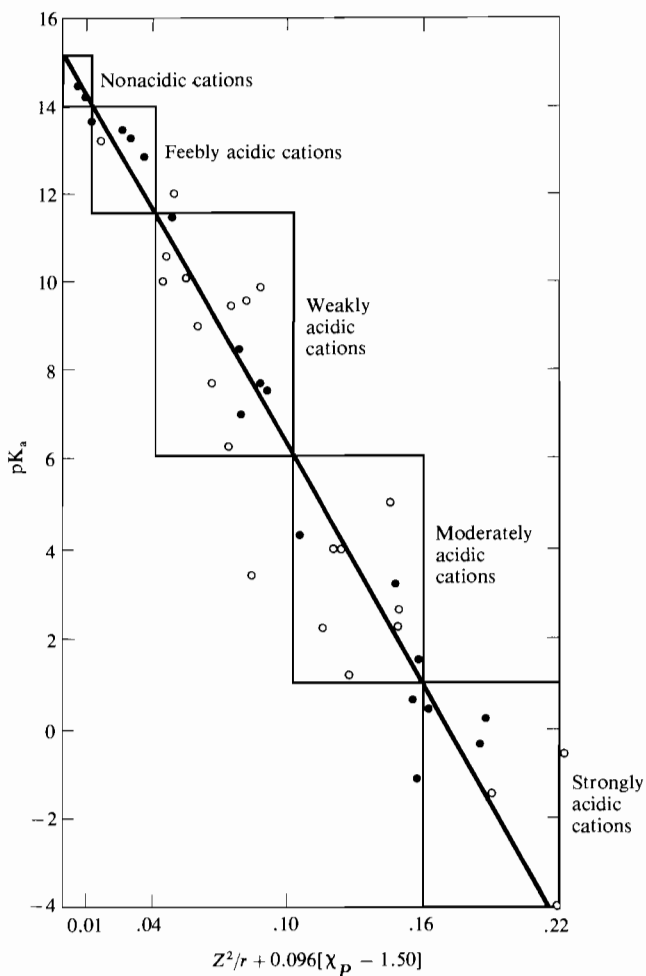
Figure 2.4 pK_a values of cations as a function of charge, size, and electronegativity. Closed circles equal metals of electronegativity(χ_P) less than 1.5, plotted as a function of Z^2/r. Open circles equal metals of electronegativity greater than 1.5, plotted as a function of $Z^2/r + 0.096(\chi_P - 1.50)$.

Table 2.3 Relationship between Z^2/r Ratios and Acidity of Metal Ions

Z^2/r Ratio	χ_P	Category	pK_a Range	Examples
0.00–0.01	<1.8	Nonacidic cations	14–15	Most +1 ions of the s-block
0.00–0.01	>1.8	Feebly acidic cations	11.5–14	Tl^+
0.01–0.04	<1.8	Feebly acidic cations	11.5–14	Most +2 ions of the s- and f-block
0.01–0.04	>1.8	Weakly acidic cations	6–11.5	Most +2 ions of the d-block
0.04–0.10	<1.8	Weakly acidic cations	6–11.5	All +3 ions of the f-block
0.04–0.10	>1.8	Moderately acidic cations	1–6	Most +3 ions of the d-block
0.10–0.16	<1.8	Moderately acidic cations	1–6	Most +4 ions of the f-block
0.10–0.16	>1.8	Strongly acidic cations	(−4)–1	Most +4 ions of the d-block
0.16–0.22	<1.8	Strongly acidic cations	(−4)–1	
0.16 and up	>1.8	Very strongly acidic cations	<(−4)	
0.22 and up	<1.8	Very strongly acidic cations	<(−4)	

NOTE: The electronegativities of the p-block elements vary too greatly to allow their inclusion in one category of "cation."

in simple pH measurements because the solution normally also contains dissolved carbon dioxide, which is at least as strong an acid as these ions. Included in this group of *weakly acidic cations* are many important $+2$ ions such as Mg^{2+} and the $+2$-charged d-block ions whose biological functions, as we will see later, revolve around their acidity. These ions show enough acidity to react with moderate concentrations of the (strong base) hydroxide ion to precipitate insoluble metal hydroxides in neutral or just slightly basic solutions.

The solutions of cations with Z^2/r ratios between 0.10 and 0.16, such as Al^{3+} and the $+3$-charged d-block ions, are unmistakably acidic, with quite low pH's and sometimes the appearance of some cloudiness due to formation of some insoluble metal hydroxide. If the solutions of these ions are not kept highly acidic, metal hydroxides will precipitate even though the pH may still be below 7. We will call these ions *moderately acidic cations*, as their pK_a values are comparable to the pK_a values of typical organic acids such as acetic acid.

Cations with Z^2/r ratios between 0.16 and 0.22, such as Ti^{4+}, react violently and nearly completely with water, giving strongly acidic solutions and copious amounts of precipitate of insoluble metal oxide or hydroxide. It is appropriate to call these *strongly acidic cations*. But we may also note that their reaction with water is usually reversible—the precipitate will often redissolve in quite concentrated hydrochloric acid, at least if it has not aged too much.

Cations with Z^2/r values over 0.22 may be expected to react irreversibly with water, generating an oxide or hydroxide. The higher the Z^2/r ratio, the more likely that this hydroxide will act as a weak acid, or even a strong acid, ionizing to give an oxo ion. We will call this group of "cations," which really cannot remain as cations in water, the *very strongly acidic cations*. Later in this chapter we will find methods for distinguishing which hydroxides from this group will act as weak acids, which as strong acids, and which will be neutral—the use of Z^2/r is not the best approach to this question. It is worth noting now, however, that the "cations" of the purely nonmetallic elements of the periodic table have Z^2/r ratios in this range, which is to say that they cannot exist in water as cations. (This is one of the characteristics by which we differentiate metals and nonmetals.) Hence the practical use of these calculations lies with the metal ions.

2.3.2   Effects of Electronegativity on Hydrolysis

So far we have not attempted to take into account the effects of high electronegativity of the cation. From Table 2.2 we can see that the cations of metals with Pauling electronegativities (χ_p) over 1.5 are more acidic than other metal ions of similar charge and size. We have derived a rough relationship between the "excess" Pauling electronegativity of a cation and its "excess" acidity, which allows us to modify equation (2.10) to include the effect of electronegativity:

$$pK_a = 15.14 - 88.16\left[\frac{Z^2}{r} + 0.096(\chi_p - 1.50)\right] \tag{2.11}$$

Note that this equation should be used *if and only if* the Pauling electronegativity of the metal exceeds 1.50.

In Figure 2.4 we have used open circles to show the relationship of the pK_a of cations to their "modified" Z^2/r ratio, $Z^2/r + 0.096\ (\chi_p - 1.50)$. There is more scatter in the data for these more electronegative cations than there was for the "simple," less electronegative cations, which suggests that we have oversimplified the relationship to electronegativity. But our main purpose is to quickly categorize the relative acidity of these cations; the scatter is not so serious as to prevent us from suggesting an even simpler rule of thumb: *If the electronegativity of the metal ion is 1.8 or greater, move it up one category in acidity.* The suggested categories of acidity, their corresponding pK_a values, and their relationships to Z^2/r and χ_p are summarized in Table 2.3.

EXAMPLE   Classify each of the following cations and describe their reactions with water: Eu^{2+}, B^{3+}, W^{6+}.

Solution   We begin by finding ionic radii in Table C; then we compute Z^2/r. For Eu^{2+}, this ratio works out to be $2^2/131 = 0.031$; for B^{3+}, $3^2/41 = 0.220$; for W^{6+}, $6^2/74 = 0.487$. Checking the table of electronegativities, we find that the latter two elements have electronegativities in excess of 1.8. Hence, using Table 2.3, we can classify Eu^{2+} as a feebly acidic cation, which should be present largely unchanged (as a hydrated ion) in water. The latter two "cations" must be classified as very strongly acidic and will not actually be present at all in water. Halides of these two cations will react violently with water to generate hydrohalic acid and the oxides, oxo acids, or oxo anions of these elements.   □

Ionic Solids and Precipitation Reactions of Hydrated Ions

Solubility Rules for Ionic Solids

In Chapter 2 we examined the acid-base properties of cations in aqueous solution as well as the acid-base properties of oxo anions. We did not consider possible interactions between cations and anions present in the same solution (except for the reaction of cations with hydroxide ions to give insoluble metal hydroxides or oxides). But if a solution contains cations it must also contain anions to preserve its electroneutrality. In Experiment 1 the solutions contained an anion, Cl^-, that did not generally perturb the chemistry of the cations being studied; in Experiment 2, the cation present, Na^+, did not appreciably alter the reactions of the anions. But, as you may see in Experiment 3, many combinations of cations and anions react with each other to give insoluble precipitates. (In Chapter 5 we will examine combinations that give rise to oxidation-reduction reactions.)

It is important to be able to anticipate when a precipitation reaction will occur in a solution containing several cations and anions. This happens, for example, in the body when the products of the concentrations of certain cations and anions come to exceed the solubility products of their salts, as when calcium ions and oxalate ions precipitate as calcium oxalate, one form of kidney stone. A laboratory worker preparing a buffered solution of a certain metal ion for biological or medical studies may be upset to find the metal ion giving a precipitate with the anion of the buffering agent. Conversely, a worker preparing a solution of a metal ion or of an oxo anion nearly always does this by dissolving an ionic salt in water. In preparing a standard solution of the barium ion for use in analytical chemistry, he or she may go to the stockroom to find a barium salt, and find not one but many different salts; he or she certainly does not want to select a salt that is insoluble in water! If a table containing the relevant solubility products (K_{sp}'s) is at hand, there is no problem; but often this is not the case. Qualitative knowledge of the solubility (precipitation) properties of inorganic salts is then quite useful.

Unfortunately, the solubility properties of ionic salts in water present certain

complexities not found in the solubilities of other classes of materials. There is a general saying, "Like dissolves like," which is often encountered in general chemistry. Nonpolar covalent materials quite generally dissolve in nonpolar covalent solvents; polar hydrogen-bonding molecules generally dissolve in hydrogen-bonding solvents. Ionic salts are usually not used as solvents, however, because they are not generally liquids below inconveniently high temperatures. (There are a few exceptions, and chemistry in molten ionic salts as solvents is an important area of current research.) Unless some specific bonding interaction is present, ionic salts will not dissolve in nonpolar covalent solvents. But with respect to the most important polar covalent solvent, water, no simple blanket statement can be made—many ionic salts are soluble in water, and many are not.

The need to be able to anticipate the solubility properties of salts leads many general chemistry textbooks to present a series of solubility rules, arranged by anion: "All sulfates are soluble except those of Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, and Ag^+," and so on. Due to the limited appeal of memorizing rules such as these, the rules do not cover all the cations, and cover only a few anions, so even if the student remembers these rules after the exam, they may not cover the situation at hand. A more reliable source of information is a chemical handbook such as the *Handbook of Chemistry and Physics* [1], which has an extensive tabulation of "Physical Constants of Inorganic Compounds." Even this tabulation can cover only a fraction of all the possible or known inorganic salts, however. Thus there is a need for generalized solubility rules that can easily be applied to predict the solubility of a wide variety of inorganic salts.

At this point your instructor may want you to carry out (or observe and discuss) Experiment 3, which gives observations from which you may be able to devise generalized solubility rules.

3.2

Thermodynamics and Generalized Solubility Rules for Salts

Several approaches to the problem of solubilities of inorganic salts have been taken by various authors. All are based on the thermodynamics of the precipitation reaction (3.1) (or of its reverse, the process of dissolution of an ionic salt):

$$y M^{m+}(aq) + m X^{y-}(aq) = M_y X_m(s) + p H_2O \tag{3.1}$$
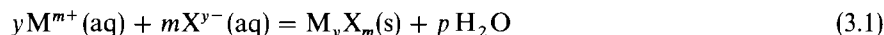
Thermodynamically, whether reaction (3.1) gives rise to a precipitate (with unit concentrations or activities of the ions) depends on the Gibbs free energy change, $\Delta G°$, for the reaction, which of course equals $\Delta H° - T\Delta S°$. For many reactions at room temperature the entropy term $-T\Delta S°$ is small compared with the enthalpy term $\Delta H°$ and can be neglected. But it is usually found (as in Experiment 3) that there is little heat evolution or absorption involved in the precipitation (or dissolution) of an ionic salt; hence in analyzing the thermodynamics of this reaction, it is necessary to consider both the enthalpy change and the entropy change. Thermodynamic data for the precipitation of some salts are shown in Table 3.1.

Table 3.1   Thermodynamic Data on Precipitation

Salt	ΔG°	ΔH°	$-T\Delta S^\circ$, 298 K	Solubility (mol/kg H_2O)
I. Acidic Cations + Basic Anions				
$Be(OH)_2$	-121	-31	-90	0.000008
$Mg(OH)_2$	-63	-3	-61	0.0002
$Ca(OH)_2$	-28	16	-44	0.025
Li_2CO_3	-17	18	-34	0.18
$MgCO_3$	-45	28	-74	0.0093
$CaCO_3$	-48	10	-57	0.0002
$SrCO_3$	-52	3	-56	0.00007
$BaCO_3$	-47	-4	-43	0.00011
$FePO_4$	-102	78	-180	slight
II. Nonacidic Cations + Nonbasic Anions				
$KClO_4$	-12	-51	39	0.054
$RbClO_4$	-14	-57	43	0.027
$CsClO_4$	-12	-55	44	0.034
$NaNO_3$	6	-21	27	8.59
IIIa. Acidic Cations + Nonbasic Anions				
$Mg(NO_3)_2$	89	85	4	1.65
$Ca(NO_3)_2$	32	20	13	2.08
$Sr(NO_3)_2$	-3	-18	14	1.89
$Ba(NO_3)_2$	-13	-40	27	0.33
$Mg(ClO_4)_2$	144	141	4	2.24
$Ba(ClO_4)_2$	46	12	34	5.91
IIIb. Nonacidic Cations + Basic Anions				
KOH	62	55	7	19.1
$RbOH$	74	63	11	17.6
$CsOH$	83	71	12	26.4
K_2CO_3	36	35	1	8.12
Rb_2CO_3	50	41	9	19.5
Cs_2CO_3	73	62	10	8.0
IV. Sulfates (Feebly Basic Anions)				
$Al_2(SO_4)_3$	96	338	-241	0.92
$BeSO_4$	59	123	-64	2.40
$MgSO_4$	30	91	-61	2.88
$CaSO_4$	-27	18	-45	0.014
$SrSO_4$	-34	9	-43	0.0006
$BaSO_4$	-50	-19	-31	0.00001

SOURCES: C. S. G. Phillips and R. J. P. Williams, *Inorganic Chemistry*, Oxford University Press, Oxford, 1965, p. 254; D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge University Press, Cambridge, 1968, p. 107; B. G. Cox and A. J. Parker, *J. Amer. Chem. Soc.*, 95, 6879 (1973); *Handbook of Chemistry and Physics*, 36th ed., Chemical Rubber Publishing Co., Cleveland, 1954, p. 1682.

NOTES: Numbers given in the table are the standard free energies, enthalpies, and entropies of precipitation i.e., for reaction (3.1) of the salts listed, in kJ/mol. Solubilities listed are often for the hydrated salts, for temperatures between 0 °C and 30 °C, and are calculated from data in the *Handbook of Chemistry and Physics*.

The data in Table 3.1 suggest the variety of causes that must exist for the solubility or insolubility of given salts. Solubilities of less than about 1 mol/L (neglecting activity effects), which show up in the table as negative free energies of precipitation, may be due to negative entropy terms ($-T\Delta S°$, i.e., positive entropies) for precipitation (as in part I of the table) or to negative enthalpies of precipitation (as in part II). Solubilities of greater than 1 mol/L seem generally to be due to positive enthalpies of precipitation (part III). To develop generalized solubility rules, however, one must go beyond such a tabulation and determine which cations and which anions will give combinations falling in parts I, II, and III of the table. This has been done mathematically by Johnson [2] in terms of the radii and of the charges of the cations and anions involved, and by Rich [3] in terms of the basicity of the anions involved. (Obviously, the approaches are related since acidity and basicity of cations and anions are functions of their charges and radii.) For ease of use and compatibility with the concepts of the previous chapter, we present the following generalized solubility rules based on acidity and basicity as related to Table 3.1. In the following sections we will return to thermodynamics to seek the physical justification for these rules.

I. ACIDIC CATIONS + BASIC ANIONS   Since most metal cations found in aqueous solution are at least weakly acidic, and most oxo anions are at least moderately basic, the reaction of an acidic cation and a basic anion is especially important. Part I of Table 3.1 shows that these ions do indeed generally react to give precipitates: $\Delta G°$ for the precipitation reaction (3.1) is negative. Hence, in general, *acidic cations and basic anions give insoluble salts.* By *acidic cations* we mean any weakly, moderately, strongly, or very strongly acidic cations. The term *basic anions* refers to any anions that are weakly, moderately, strongly, or very strongly basic. (Although not all these categories are found among simple oxo anions, they will be found later among other types of anions.)

This generalized solubility rule approximately sums up two commonly given "solubility rules": (*a*) All carbonates are insoluble except those of the Group 1 elements and NH_4^+ (which acts like K^+ in many respects); and (*b*) all hydroxides are insoluble except those of the Group 1 elements, Sr^{2+}, and Ba^{2+}. The generalized solubility rule gives up some exactness in terms of the slightly different behavior of hydroxides and carbonates, but it is clearly applicable to the salts of a number of other oxo anions, such as phosphate, arsenate, silicate, and borate, and it also suggests the behavior of some cations not considered in rules (a) and (b): Thus $TlOH$, $Eu(OH)_2$, and Tl_2CO_3 are also all soluble.

II. NONACIDIC CATIONS + NONBASIC ANIONS   Although there are relatively few nonacidic cations and nonbasic anions, this combination usually also gives rise to moderately insoluble salts, as shown by the small negative free energies in part II of Table 3.1. Hence, the generalized solubility rule here is that *nonacidic cations and nonbasic anions give insoluble salts.*

IIIA. ACIDIC CATIONS + NONBASIC ANIONS/IIIB. NONACIDIC CATIONS + BASIC ANIONS The positive free energy changes shown for the precipitation of combinations of acidic cations plus nonbasic anions (part IIIa of the table) and for combinations of nonacidic cations and basic anions (part IIIb) suggest the generalized solubility rule: *Cross-combinations give soluble salts.* By *cross-combinations* we mean nonacidic cations plus basic anions and acidic cations plus nonbasic anions. The most common solubility rule related to this rule of thumb is that for nitrate, "All nitrates are soluble." Since most cations are acidic, their soluble oxo salts will be of nonbasic anions such as nitrate and perchlorate. (The nitrates of some of the most nonacidic cations such as Ba^{2+} and Cs^+ are not highly soluble, however.)

IV. SULFATES (FEEBLY BASIC ANIONS)   Some anions cannot clearly be called basic or nonbasic in terms of these trends; there are *feebly basic* anions such as SO_4^{2-}, SeO_4^{2-}, and MoO_4^{2-}. The solubility of salts of these ions is particularly complex and difficult to predict; as can be seen from Table 3.1, their tendency to precipitate or not to precipitate varies with the relative magnitude of the opposing entropy and enthalpy terms. We will need to carry out a more detailed thermodynamic analysis before we come up with a satisfactory rule for predicting the solubilities of salts of feebly basic anions. For now we may note that *many feebly acidic cations and feebly basic anions give insoluble salts.*

V. It is perhaps useful to point out here that *the "solubilities" of insoluble salts of basic anions are enhanced in solutions of strong acids.* This is not a true case of solubility, perhaps, but of reaction: A basic anion tends to react more completely with the strong acid H_3O^+ than with a less acidic metal ion, thus generating a new salt of that metal ion and a weak acid in solution. (Of course this may not occur appreciably if the metal ion is also strongly acidic.) The equilibrium that results from the competition between H_3O^+ and the metal ion will be especially enhanced if the weak oxo acid decomposes; thus carbonates and sulfites readily "dissolve" in strong acids, since the carbonic and sulfurous acids produced decompose to carbon dioxide and sulfur dioxide, gases that escape from the solution and allow the equilibrium to shift further toward dissolution.

EXAMPLE   Without reference to a table of solubility products, classify each of the following salts as soluble or insoluble in water and in strongly acidic solutions: Ag_2SeO_4, K_3PO_4, $ZnSO_4$, and $Th_3(PO_4)_4$.

Solution   ■ The charges of the cations and anions in each salt must be identified so that their acidity and basicity can be classified. The cations are Ag^+, K^+, Zn^{2+}, and Th^{4+}. Referring to Table C, we see that Z^2/r ratios for these four cations are computed as 0.008, 0.007, 0.046, and 0.145, respectively, which allows the first two to be categorized as nonacidic, the third as weakly acidic, and the fourth as moderately acidic. The table of electronegativities, however, shows that Ag has an electronegativity exceeding 1.8, so it should be reclassified as feebly acidic.

■ The anions are SeO_4^{2-}, PO_4^{3-}, and SO_4^{2-}. Any oxo anion with a -3 or higher charge (such as phosphate) is automatically at least moderately basic. A calculation using equation (2.14) (or reference to Table 2.6) classifies sulfate and selenate as feebly basic; hence the salt Ag_2SeO_4 is a combination of a feebly acidic cation and a feebly basic anion and should be insoluble; K_3PO_4 is a combination of a nonacidic cation and a basic anion and should be soluble; $ZnSO_4$ is a combination of an (weakly) acidic cation and a feebly basic anion and should be soluble; $Th_3(PO_4)_4$ is a combination of an (moderately) acidic cation and a (moderately) basic anion and should be insoluble. A check of the *Handbook of Chemistry and Physics* confirms all these predictions.

■ Solubility in acid is of interest for compounds that are insoluble in water; we may then want to dissolve them in a strong acid such as HCl. If the anion of the insoluble salt is basic, and the cation is less strongly acidic than the (very strongly acidic) hydrogen ion, we would anticipate a chemical reaction to give the metal ion in solution and the oxo acid. The feebly basic SeO_4^{2-} ion will react somewhat with H^+, so we expect (and find) somewhat improved solubility in strong acids. The moderately basic anion PO_4^{3-} will react more with the very strong acid H^+ than with the moderately acidic Th^{4+} ion, so we also find it to be soluble in 30% HCl.

□

3.3

Entropy and Precipitation: The Structures of Hydrated Ions and Liquid Water

It may seem surprising at first that precipitation reactions of acidic cations and basic anions should be due to a negative entropy term, $-T\Delta S$, since this term corresponds to increasing randomness or disorder in the system, which is not what we expect in a reaction that produces a crystalline solid precipitate. But the reacting cations and anions exist as hydrated ions, and upon formation of the precipitate, water molecules are released. If enough water molecules are released (and if these molecules are sufficiently disordered as part of the water solvent), then the resulting positive entropy change (negative $-T\Delta S$) may exceed the ordering effect of producing a crystalline precipitate.

From Table 3.1 we can see that large negative $-T\Delta S$ terms occur characteristically only upon the reaction of acidic cations with basic anions. It has been suggested by Latimer [4] that the entropy change in precipitation reactions is independent of the type of crystalline product formed; this has made it possible, with some further assumptions, to assign separate entropies of precipitation for the hydrated cations and for the hydrated anions. (The actual practice has been to consider the reverse of equation (3.1)—the dissolution of an ionic solid—and to tabulate entropies of solution for the cations and anions [5].) Theoretically, these entropies of solution of cations or anions should also be related to the familiar ratio Z^2/r [6], as suggested by Figure 3.1.
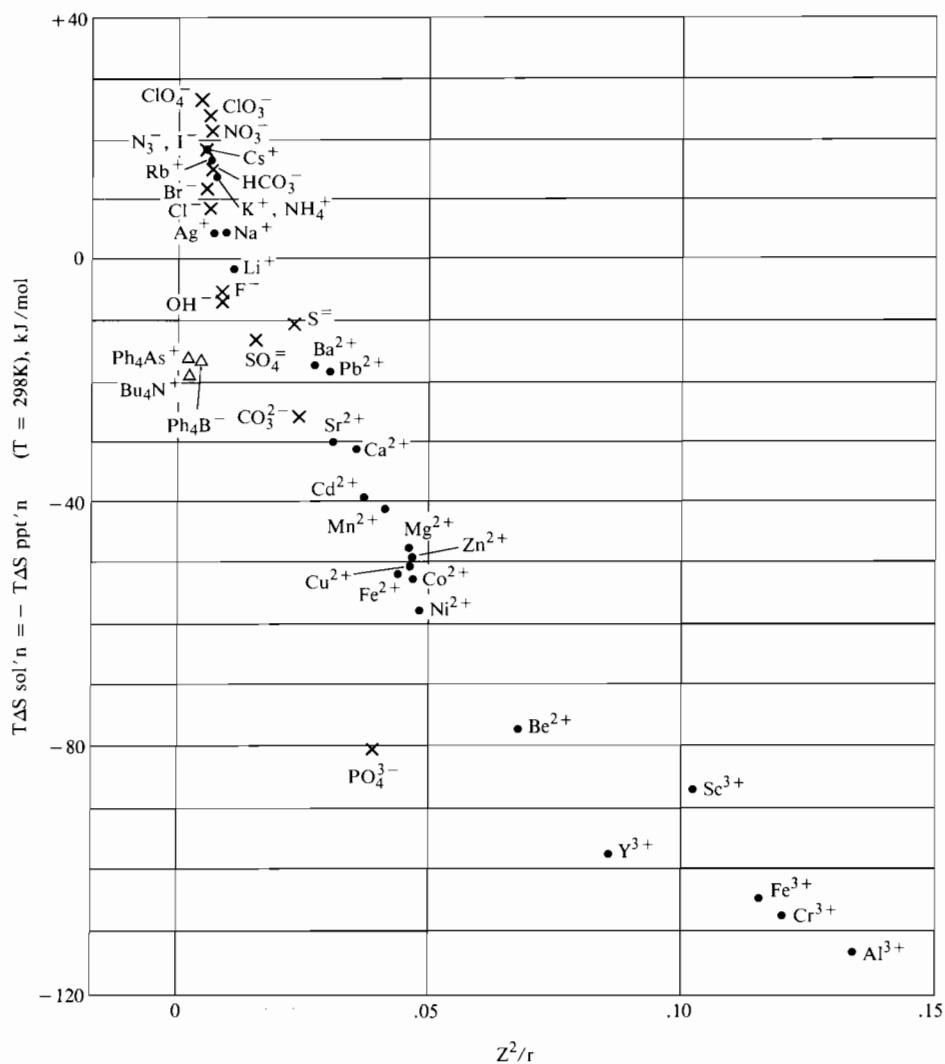
Figure 3.1 298 °K entropy terms ($T\Delta S_{\text{solution}} = -T\Delta S_{\text{precipitation}}$) for cations and anions as a function of Z^2/r. Crosses equal anions; dots equal metal cations; triangles equal organic ions. Thermodynamic data from [5]; thermochemical radii of oxo anions from J. E. Huheey, *Inorganic Chemistry*, 3d ed., Harper and Row, New York, 1983, p. 78. Points in parentheses are based on estimated radii.

It is readily apparent from Figure 3.1 that *all but the nonacidic cations* and *all but the nonbasic anions* make negative contributions to the entropy term for reaction (3.1): Most ions release enough water molecules to give a net disordering effect upon precipitation or a net ordering effect upon dissolution of a salt. Such ions are referred to as **electrostatic structure makers**.

We also note that the more acidic or basic the ion (the higher its charge or
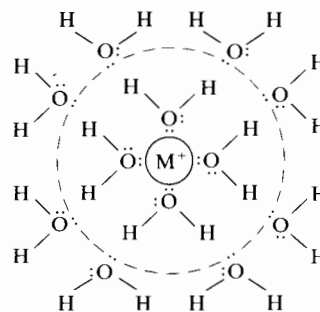
Figure 3.2 Primary and secondary hydration spheres of a hydrated cation.

the smaller its radius), the greater is the magnitude of the ion's structure-making property. The inverse relationship to size may seem surprising: Since larger cations have greater maximum coordination numbers, we might expect them to attach more water molecules. But evidently the smaller ion attaches more water molecules or at least orders them more effectively. Similarly, although increasing the charge of a cation does not increase its maximum coordination number, it does increase the ordering of water molecules in the hydrated ion.

These seeming contradictions can be explained by postulating that hydrated cations and anions have more complex structures than we have assumed up to now. Certainly all hydrated metal ions and oxo anions have a layer of water molecules surrounding the ion, as shown in Figure 2.1. This layer is referred to as the **primary hydration sphere** of the hydrated ion, and the larger the "bare" cation or anion, the more water molecules that can be accommodated in this primary hydration sphere. But ions that are at all acidic or basic exert such a strong attraction for the water molecules in their primary hydration sphere, pulling electron pairs toward a cation or hydrogens toward an anion, that these water molecules exert an enhanced hydrogen-bonding attraction for other water molecules and organize them into a **secondary hydration sphere** around the first layer (Figure 3.2). Note that this phenomenon has the same cause as does the phenomenon of hydrolysis that we discussed in Chapter 2. (In this case, however, the attraction does not have to be strong enough to pull the water molecule of the second layer apart—it only needs to attach it by strengthened hydrogen bonds.) Thus we can see why this phenomenon should be directly related to the acidity or basicity of the cation or anion.

This secondary hydration sphere may consist of more than one layer of water molecules—the stronger the attraction of the bare ion for water molecules (i.e., the greater its acidity or basicity), the more water molecules that may be attached in additional layers. Each subsequent layer would be expected to involve weaker attractions, however, so water molecules would stay immobilized by hydrogen bonds for shorter and shorter periods of time. Many methods have been used to study this phenomenon of multiple hydration layers, but these diverse methods of measuring the number of waters attached or the radius of the hydrated ion give

**Table 3.2** Hydration Numbers and Hydrated Radii of Some Hydrated Ions

Ion	Z^2/r	Hydration Number	Hydrated Radius (pm)
Cs^+	0.0055	6	228
K^+	0.0066	7	232
Na^+	0.0088	13	276
Li^+	0.0111	22	340
Ba^{2+}	0.0268	28	
Sr^{2+}	0.0303	29	
Ca^{2+}	0.0351	29	
Mg^{2+}	0.0465	36	
Cd^{2+}	0.0549	39	
Zn^{2+}	0.0599	44	

SOURCES: Hydration numbers from A. T. Rutgers and Y. Hendrikx, *Trans. Faraday Soc.*, 58, 2184 (1962). Hydrated radii from R. P. Hanzlik, *Inorganic Aspects of Biological and Organic Chemistry*, Academic Press, New York, 1976, p. 31.

NOTE: Z^2/r ratios corrected for electronegativity using equation (2.11).

inconsistent answers, since each method requires a different amount of time for the water molecules to remain attached in order to be counted. But nearly all measurements give consistent *trends* in hydration numbers among series of ions, such as the results for the ions in Table 3.2, obtained from transference measurements by way of the *Stokes radii* or *hydrated radii* of the hydrated ions, also in Table 3.2.

In summary, the reason that most acidic cations and basic anions react to give precipitates is due to the disorder resulting from the release of numerous water molecules from the multiple hydration spheres of the cations and of the anions. This is apparent when we write the seemingly simple precipitation reaction of, say, magnesium and carbonate ions in full, including a reasonable number of water molecules:

$$Mg(H_2O)_{36}^{2+} + CO_3(H_2O)_{28}^{2-} \rightleftharpoons MgCO_3(s) + 64\,H_2O \tag{3.2}$$
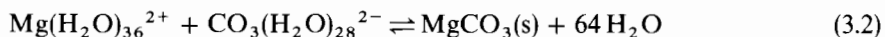
Since the *hydrated* ions of smaller bare ions may be larger than those of larger bare ions, we sometimes see unexpected chemical results. For example, an important question in biochemistry has to do with how metal ions can migrate across cell membranes, which consist largely of lipids in which metal ions are quite insoluble. One model of this process, called the *pore model* [7], envisions the cell membrane as containing pores through which hydrated ions can pass without having to dissolve in the lipids. The antibiotic gramicidin A in fact contains a hollow center of about 400-pm diameter that, when in biological membranes, causes cells to pass ions readily. The relative rate of passage of ions through this pore is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, which makes sense if the hydrated cesium ion is indeed the smallest hydrated ion in this series.

Oxides and Polynuclear Oxo Anions of the Elements: Their Physical, Chemical, and Environmental Properties

In this chapter we will examine some of the chemical and physical properties of two classes of compounds, the oxides of the elements and the salts of polynuclear oxo anions of the elements. The chemical properties we will focus on are the acid-base properties of these compounds, applying the theories developed in the last chapter. Physical properties (such as the ease of melting and boiling and thus whether given compounds are solids, liquids, or gases at room temperature and atmospheric pressure) are of great practical importance: Before preparing and handling a new compound, a scientist needs to know whether that compound is a solid, liquid, or gas so that he or she will know how to handle and measure it out. Many of the oxides and the salts of the polynuclear oxo anions are very important in industry, geology, and soil science, as well as in pollution chemistry. We will see how the applied properties of these substances relate to their physical and chemical properties. Since some of the oxides are ionic and some are covalent (and polynuclear oxo anions include both types of bonds), we will see how these physical and chemical properties relate to the type of bonding.

4.1

Periodic Trends in Acid-Base and Solubility Properties of Oxides

Due to its very small size and high charge, the oxide ion (O^{2-}) is a very strongly basic anion that cannot exist in water but instead reacts completely to generate the hydroxide ion (still a very strong base):

$$O^{2-} + H_2O \rightarrow 2\,OH^- \tag{4.1}$$

This reaction is an illustration of the **leveling** property of very strong bases: Any base that is stronger than the characteristic base of the solvent will react with the solvent (in this case, water) to generate its characteristic base (i.e., hydroxide

ion). We have already seen this happen to the very strong oxo anions such as SbO_6^{7-}. Similarly, the very strongly acidic hypothetical cations such as S^{6+} are leveled by reaction with water to generate the characteristic acid of water solutions, H_3O^+. Thus no acid stronger than H_3O^+ and no base stronger than OH^- can persist in water.

Since the oxide ion is a very strong base, we expect and find that the solubility principles of the previous chapter apply to it. Among metal oxides, only the oxides of the nonacidic and feebly acidic cations dissolve in water, in which they react very exothermically to give the hydroxides of these cations. (By extension, only the hydroxides of the nonacidic and feebly acidic cations dissolve in water.) The solutions of these oxides or hydroxides, of course, have high pH's and are very basic; thus these oxides are logically called **basic oxides** even though they do not contain hydroxide ions.

The oxides of the nonacidic cations react so strongly with water that they are seldom seen; they cannot be prepared by heating the hydroxides to drive off water. Even the hydroxides are deliquescent and release heat on dissolving. By far the most important strongly basic compound of the nonacidic cations is NaOH, which is manufactured on a very large scale by electrolysis of NaCl solutions (an oxidation-reduction process that will be discussed later).

The oxides of the feebly acidic cations are more commonly seen than those of the nonacidic cations. CaO, commonly called lime, is the cheapest basic oxide and is easily manufactured by heating the abundant $CaCO_3$ (limestone):

$$CaCO_3(s) + heat \rightarrow CaO(s) + CO_2(g) \tag{4.2}$$
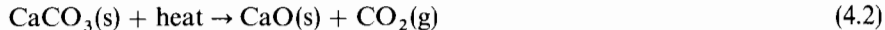
Oxides of the feebly acidic cations react exothermically with water to give the hydroxide (with CaO this reaction is called *slaking*):

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \tag{4.3}$$

This reaction can be reversed by heating the hydroxide to a high temperature (853 K) to drive off the water. The hydroxides of these feebly acidic cations are not notably deliquescent.

The oxides and hydroxides of the weakly and moderately acidic cations are insoluble in water, and so alter its pH little or not at all. Nonetheless, both show a characteristic of other bases: They react with (i.e., neutralize) strong acids:

$$FeO + 2H_3O^+(aq) \rightleftharpoons Fe^{2+}(aq) + 3H_2O \tag{4.4}$$
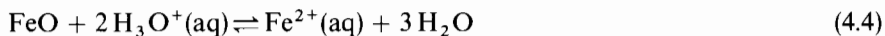
This large body of metal oxides is also called "basic oxides."

Correspondingly, acidic properties persist in many of the covalent oxides of the very acidic (hypothetical) cations. Many of these oxides dissolve in water to give solutions of the oxo acid in which the element has the same oxidation number:

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 \tag{4.5}$$

These oxo acids ionize (to a greater or lesser extent, depending on their strength) to give hydronium (hydrogen) ions and a pH below 7, so it seems logical to call

Table 4.1 Major Acidic and Amphoteric Oxides of the *p*- and *d*-Block Elements

B_2O_3	CO_2	N_2O_5			
		N_2O_3			
Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7	
		P_4O_6	SO_2	Cl_2O	
Ga_2O_3	GeO_2	As_2O_5	SeO_3		
		As_4O_6	SeO_2	Br_2O	
In_2O_3	SnO_2	Sb_2O_5	TeO_3		XeO_4
	SnO	Sb_2O_3	TeO_2	I_2O_5	XeO_3
	PbO_2				
	PbO				
		V_2O_5	CrO_3	Mn_2O_7	
		Nb_2O_5	MoO_3	Tc_2O_7	RuO_4
		Ta_2O_5	WO_3	Re_2O_7	OsO_4

NOTE: Oxides above and to the right of the dashed line dissolve in water (at least to some extent) and act as acids. Oxides between the dashed and solid lines are not soluble in water but do dissolve in (react with) strong bases. Oxides below and to the left of the solid line are amphoteric. (These are not included for the *d*-block elements.) The oxides of Tl and Bi_2O_3 are exclusively basic oxides.

these oxides **acidic oxides** or **acidic anhydrides**. (The latter term suggests that they are acids that are missing the elements of water).

Soluble acidic oxides of the *p*- and *d*-block elements are shown in Table 4.1. The oxide will be soluble if its reaction product with water is a *strong* or *very strong* acid. These acids are completely ionized into highly hydrated hydrogen ions and oxo anions, which helps shift the solubility equilibrium toward high solubility. If the oxo acid produced is *moderately acidic*, the oxide may or may not be soluble. (Some ions are produced, and the un-ionized acid may hydrogen-bond to the water, which may or may not suffice to ensure solubility.) If the oxo acid produced is *weakly acidic*, the oxide is usually (but not always) insoluble in water. Some of these acidic oxides (especially those of sulfur and nitrogen) are air pollutants; these oxides react with the moisture of the air and produce "acid rain."

The oxides between the dashed and solid lines in Table 4.1, although not soluble enough in water to alter its pH appreciably, do react with solutions of strong bases to generate oxo or hydroxo anions and thus also can be justifiably termed "acidic oxides."

As mentioned in Section 2.7, hydroxo anions can be formed in strongly basic solution even by many metal ions that are only moderately acidic; hence there are oxides of metals that are insoluble in water but that dissolve in both strong acids and strong bases; such oxides are termed **amphoteric oxides**. In Table 4.1 these are shown (for *p*-block elements only) to the left of and below the solid line.

In addition, there are a few oxides, such as NO_2 and ClO_2, that do not correspond in oxidation state to a stable or known oxo acid; these can give rise to a mixture of oxo acids or anions by **disproportionation**:

$$2\,NO_2 + 2\,OH^- \rightarrow NO_2^- + NO_3^- + H_2O \tag{4.6}$$
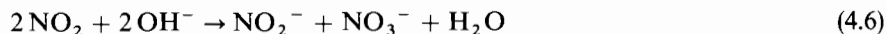
Only three nonmetal oxides from the upper-right portion of the *p*-block have such low oxidation numbers for the nonmetal atom that their aqueous solutions are neutral, namely, CO, N_2O, and NO.

Because the acidity of a cation rises rapidly with its charge, there are several *d*-block elements possessing several oxidation numbers (such as chromium) that have one or more oxides that show only basic properties (e.g., chromium(II) oxide, CrO), one or more oxides that are amphoteric (e.g., chromium(III) oxide, Cr_2O_3), and one or more oxides that possess only acidic properties (chromium(VI) oxide, CrO_3). Clearly, the higher the oxidation number of a given element, the more acidic the corresponding oxide will be.

Since basic oxides can react with the hydronium ion, a strong aqueous acid, and acidic oxides can react with the hydroxide ion, a strong aqueous base, it is not too surprising that basic oxides and acidic oxides can react with each other:

$$2\,MgO \text{ (basic oxide)} + SiO_2 \text{ (acidic oxide)} \rightarrow Mg_2SiO_4 \tag{4.7}$$
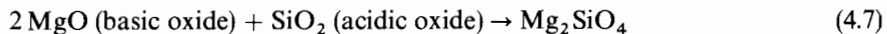
The products of these reactions are salts of oxo acids and, since water is not involved in the reaction, can be salts of oxo anions such as SiO_4^{4-} that are too basic to persist in aqueous solution. As we will discuss later in this chapter, direct reactions of acidic and basic oxides are of enormous practical importance in such areas as control of pollution by gaseous acidic oxides and in the production of materials such as concrete, glass, and ceramics.

EXAMPLE   Complete and balance the following chemical equations for reactions of oxides:

(a) $N_2O_3 + H_2O \rightarrow ?$
(b) $BaO + OsO_4 \rightarrow ?$

Solution   ■ a. N_2O_3 is the oxide of a very acidic nonmetal "cation," N^{3+}, from the upper right of the periodic table; hence it is expected to be an acidic oxide and will likely dissolve in water to give the oxo acid containing nitrogen in the $+3$ oxidation state, HNO_2. The complete balanced equation is

$$N_2O_3 + H_2O \rightarrow 2\,HNO_2$$
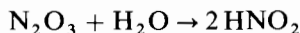
■ b. BaO is the oxide of a feebly acidic cation, Ba^{2+}, so the strong basicity of the oxide ion will be virtually undiminished: This is a basic oxide. The hypothetical Os^{8+} cation in OsO_4 will be so acidic that the oxide itself might also be expected to be acidic. The product of the reaction of a basic oxide with an acidic oxide will be the salt of an oxo anion. For the relatively large Os, an oxo anion with six oxygens is expected: OsO_6^{4-} (Table 2.7). Balancing the -4 charge of this anion with two Ba^{2+} cations, we complete and balance the equation:

$$2\,BaO + OsO_4 \rightarrow Ba_2OsO_6 \qquad \square$$

See:
www.climate.org
www.noaa.gov/climate.html

Composition of Atmosphere:

Gas	Mole Percent
N2	78.08
O2	20.95
Ar	0.934
CO2	0.03
O3	1.0x10-7

The amounts of these gases are pretty much consistent except for carbon dioxide (it's increasing) and ozone (it's hopefully decreasing in the upper atmosphere).
Carbon dioxide is important for global warming and ozone is important for absorbing UV.
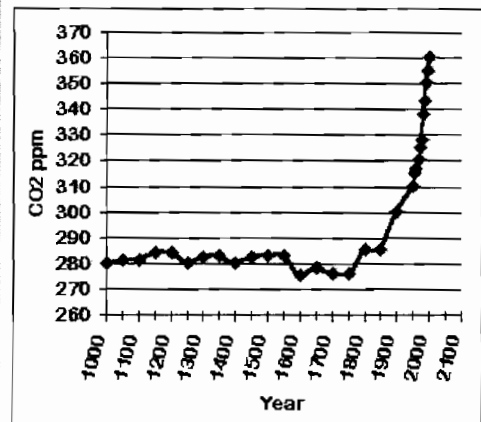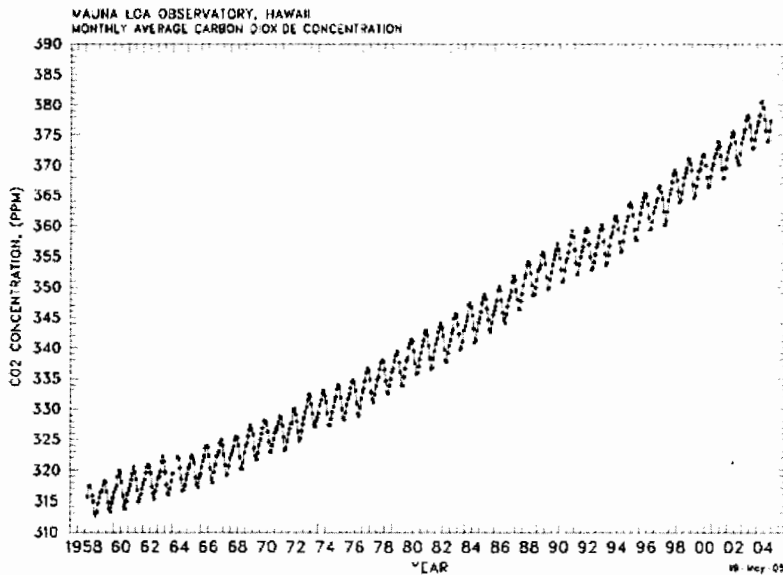
Global Warming and CO$_2$

Carbon dioxide is important in the greenhouse effect. When the sun's light shines on the earth, the radiation is either reflected by clouds, etc. When radiation hits the surface of the earth, it is emitted as IR radiations. Carbon dioxide is an absorber in the IR region; it absorbs in 3 regions of the IR.

Blackbody radiation: all matter gives off radiation and the wavelength of the radiation is temperature dependent.

Nitrogen and oxygen will not absorb IR because they cannot form a dipole.

IR absorption has the following requirements:
1. Molecules need to vibrate (atoms move with respect to each other)
2. Vibration must change the dipole moment of the molecule.

All nitrogen vibrations are nonpolar regardless of the bond length. Nitrogen doesn't absorb in the IR, and is therefore not a greenhouse gas.

Importance of Carbon dioxide:
It has an absorption that coincides with emission of earth and it's reasonably abundant. CO for example, is not a greenhouse gas because it absorbs IR radiation where the earth doesn't give off IR radiation.

Planetary temperature is based on an energy balance.

Es=solar intensity (related to the distance from the sun), Es=1380 W/m^2 for the earth.

α= albedo (light reflected), $\alpha = 0.28$ for earth

$E_{in} = (Es/4)(1-\alpha)$ and $E_{out} = \sigma T^4$, where $\sigma = 5.67 \times 10^{-8}$ W/m^{2}K^4

To find the equilibrium temperature of a planet, set $E_{in} = E_{out}$. After a little math, you get the following expression:
$$T_{calc} = (Es(1-\alpha)/4\sigma)^{1/4}$$

This equation doesn't account for the greenhouse effect. $T_{calc} = 257$ K for earth. The actual temperature of earth is 291K. To account for the greenhouse affect, another constant, f is added to the expression. f=IR transmission factor (the fraction of IR light that escapes the atmosphere):

$E_{out} = f\sigma T^4$
You can calculate f by using $f = Es(1-\alpha)/(4\sigma T^4)$.

For the earth, f = 0.61. This means that 39% of the IR radiation is trapped by the green house gases in the atmosphere.

For practice, calculate f for Venus given that Es = 2600, $\alpha = 0.71$, and Tactual = 750K.

Elemental cycles can be used to figure out how much of an element is in a particular form. The carbon cycle was handed out in class as an example. Looking at the handout, you can see that most of the carbon on the earth is in the form of inorganic sediments. The lines between different forms of an element give paths for conversion of one form to another and how much is converted.

Carbon in the atmosphere as CO2

Photosynthesis   Respiration   Respiration

Stored in oceans, etc.
by dissolving

Plants ————→ Animals
Food

Combustion

Dead, stored in soil as fossil fuels
as Carbon or Hydrocarbons
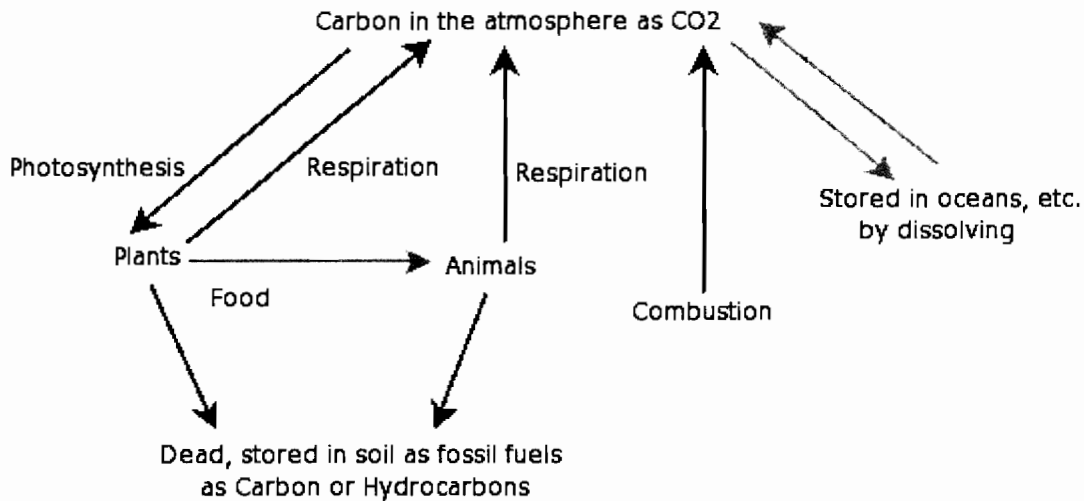
Processes transforming Carbon and Oxygen into Carbon Dioxide and Water

Carbon is stored as energy

Hydrocarbons are formed

Processes using Carbon/it's compounds

Prediction of the temperature increase of the earth is difficult to predict based on the increase in carbon dioxide. One must consider how much carbon dioxide is converted by plants and how much goes into the land. Scientists test models by using data from 50 years ago, and seeing what their models predict for present day conditions.

Ozone:

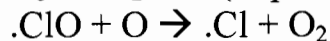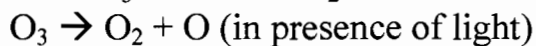O3 in the upper atmosphere is good; it blocks UV radiation. O3 in the lower atmosphere is bad; it is toxic.

Ozone generation: $O2 \rightarrow 2O$ (in presence of light); $O + O2 \rightarrow O3$

Ozone is measured in units called the Dobson. 1 DU= a 10mm thick layer of ozone @ 1 atm and 0oC

The ozone hole is over the South Pole. In Antarctica, the amount of ozone is lowest in October.

A 25% decrease in ozone leads to a 50% drop in crop yields.

Chlorine radicals decrease the ozone levels in the upper atmosphere. CFC's (Chlorofluorocarbons), once used as refrigerants and propellants, have high heats of vaporization at low pressure and at room temperature. CFC's are very stable and have long lifetimes in the atmosphere. CFC's are invert, but can be broken down by UV light in the atmosphere.

$CCl_3F \rightarrow CCl_2F + .Cl$

$2O_3 \rightarrow 3O_2$ (reaction is slow)

$.Cl + O_3 \rightarrow .ClO + O_2$

$O_3 \rightarrow O_2 + O$ (in presence of light)

$.ClO + O \rightarrow .Cl + O_2$
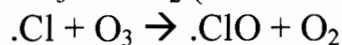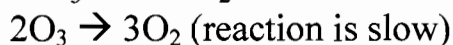
.Cl is a catalyst in the destruction of O_3 and .ClO is an intermediate in the overall reaction.

Intermediates are species that are produced in one step on a reaction and are used in a following step of the reaction.

Catalysts help to speed up a reaction. They are involved in the reaction, but are not consumed.

Why is the ozone hole over Antarctica and in October?
In Antarctic winter, there is no light from the sun hitting the pole and, because of weather patterns, there is a vortex around the South Pole that prevents the atmosphere from mixing.

$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$ (rxn is slow and is catalyzed by ice crystals)

$Cl_2 \rightarrow$ .Cl (done in presence of light, but during the Artic winter, no light is present. As the winter progresses. the concentration of chlorine, Cl_2, increases.)

The high concentration of chlorine in the atmosphere over the Antarctic breaks down a lot of ozone in the other seasons because light leads to chlorine radicals.
CFC's are no longer manufactured. HCFC's were tried as alternatives by taking advantage of the weaker H-C bonds compared to C-Cl bonds. HCFC's still deplete the ozone and are being phased out from use.

Acid Rain
$SO_2 + O_2 \rightarrow SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4$
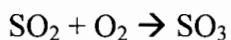
Sulfuric acid dissolves in the rain.

Nitrogen Oxides, Smog, and Catalytic Converters
Catalytic Converters:

$O_2 + N_2 \rightarrow 2\ NO$ $\Delta H > 0$ & $\Delta S > 0$

@ STP, $\Delta G >> 0$
at high temperatures, $\Delta G < 0$ and rxn becomes favorable.

This reaction is favored in car engines because of the high temperatures. In the exhaust stream, the temperature is lower and the reverse reaction,

$2\ NO \rightarrow N_2 + O_2$
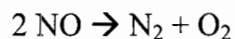
is favored. But, at those lower temperatures, it is also very slow. Catalytic converts speed up that reaction and take NO and convert it to O_2 and N_2 at lower temperatures.

Information Page

Global Temperatures and Planetary Thermal Balance

There exists for any planet an energy balance, illustrated by the figure below.
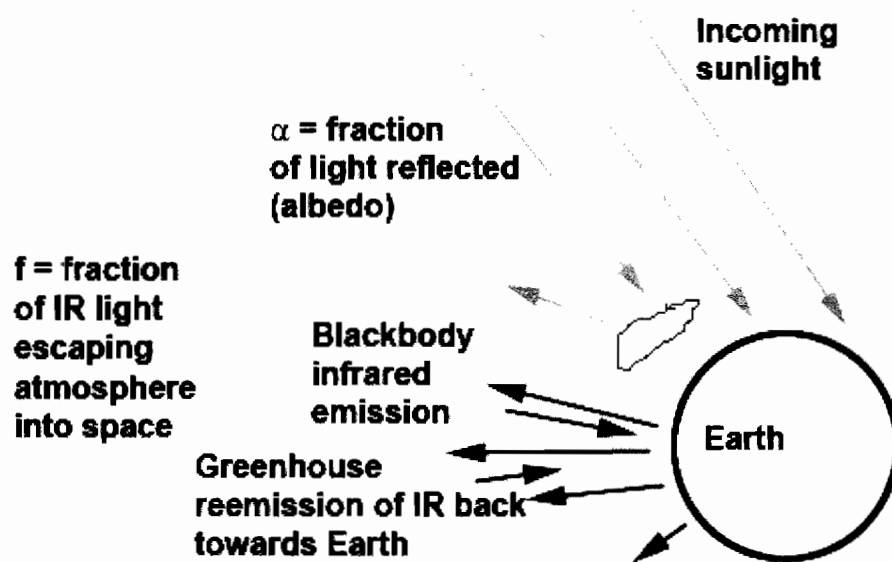
Energy In:
Energy comes in in the form of sunlight. Some is reflected, some is absorbed by the planet.

$$E_{in} = \frac{Es}{4}(1-\alpha)$$

The value of Es, the solar constant, depends only on the distance of the planet from the sun.

Planet	Es, W/m^2
Venus	2600
Earth	1380
Mars	600
Jupiter	49
Saturn	15
Uranus	3.7
Neptune	1.5

The albedo, α, is the reflectivity of the planet. Therefore, the fraction of sunlight reaching and being absorbed at the surface is 1- α .

Albedo values for some planets are:

Planet	α,
Venus	0.71
Earth	0.28
Mars	0.17
Jupiter	0.73
Saturn	0.76
Uranus	0.93
Neptune	0.84

Energy Out:

Energy is radiated away from the planet in the form of blackbody radiation, which is heavily dependent on the temperature of the planet.

$$E_{out} = \sigma T_E^4$$

The Stefan-Boltzmann constant, σ, is 5.67×10^{-8} W/m$^2\cdot$K^4. T_E is the equilibrium planetary temperature, in Kelvins.

Equilibrium Temperature, in the absence of greenhouse gases:

The equilibrium temperature for the planet can be obtained by setting $E_{in} = E_{out}$, and solving for T_E.

$$T_E = \sqrt[4]{\frac{Es(1-\alpha)}{4\sigma}}$$

Equilibrium Temperature, in the presence of greenhouse gases:

The temperature of most planets is higher than would be calculated using the equation above because it does not account for re-radiation of blackbody infrared light back to the planet from greenhouse gases.

The value of Eout needs to be adjusted, showing the fraction of energy that actually escapes the planet's atmosphere.

$$E_{out} = f\sigma T_E^4$$

Where f is the IR transmission factor, indicating the fraction of IR radiation that escapes the atmosphere.

The equilibrium between Ein and Eout therefore becomes,

$$\frac{Es}{4}(1-\alpha) = f\sigma T_E^4$$

The value of f for a planet can be calculated using values for the albedo and solar constant, along with the actual surface temperature.

$$f = \frac{\dfrac{Es}{4}(1-\alpha)}{\sigma T_E^4}$$

Some measured planetary surface temperatures are:

Planet	T, K
Venus	733
Earth	291
Mars	240

$N \equiv N$

nitrogen

$C \cong O$

Carbon monoxide

$O = C = O$
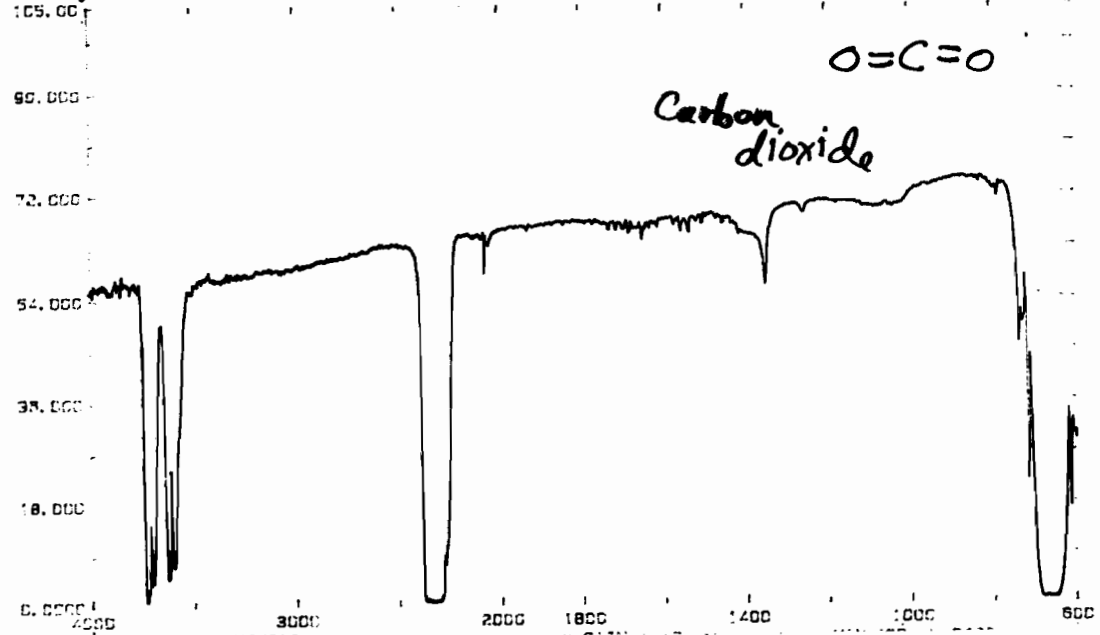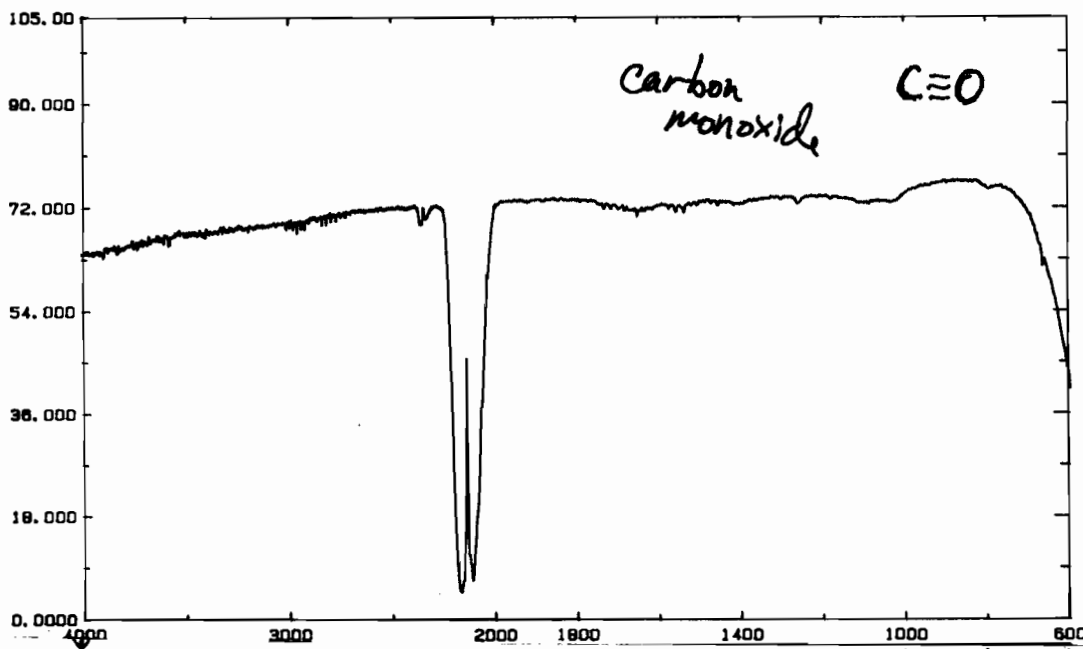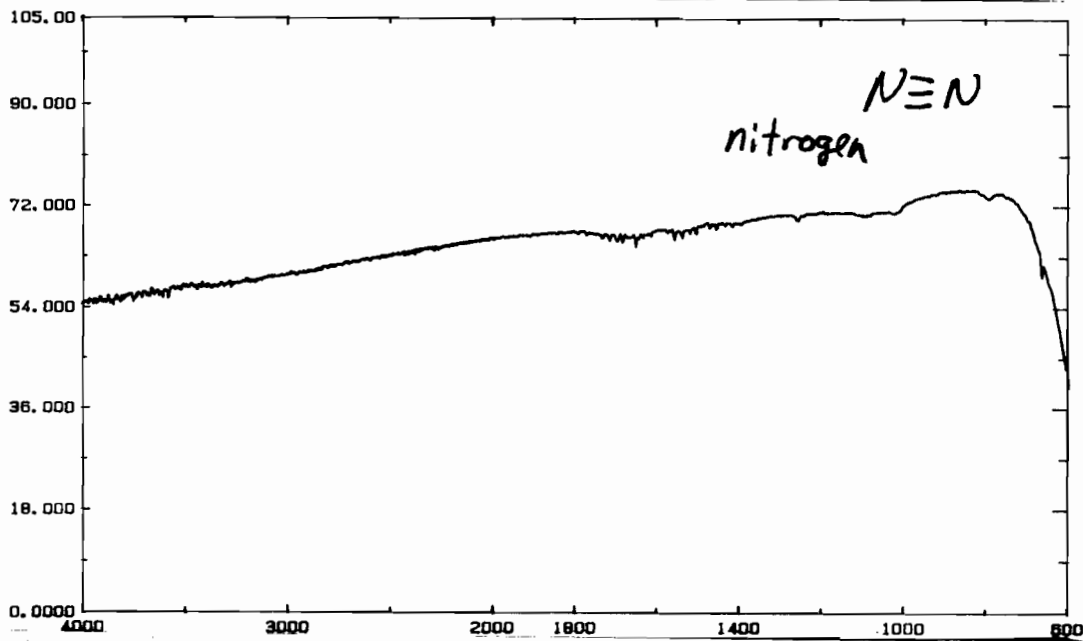
Carbon dioxide
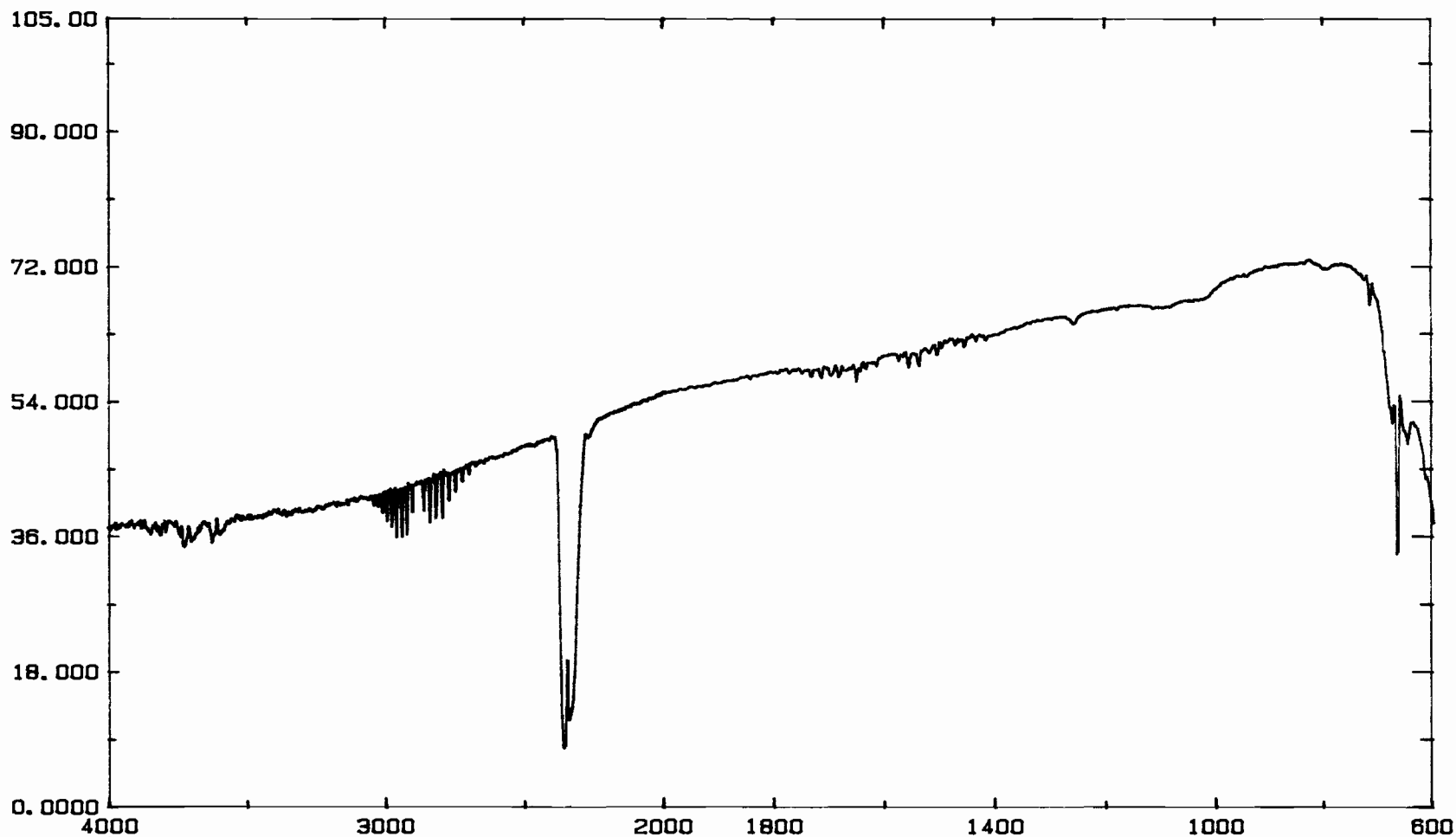
FILE NAME : DUDE0005	GAIN : 2	ANALECT FX-6260
#SCANS : 8	DET : TGS	ORD : %T
#BKG : 16	RES : 4 CM-1	ABSC: WAVENUMBER
APOD : HAPP-GENZEL	DATE : 03/18/93	TIME: 20:52:06
COMMENT : CL2		

IR spectrum of ethylene, with structure:

$$H_2C=CH_2$$ ethylene

IR spectrum of Butane, with structure:

$$H-CH_2-CH_2-CH_2-CH_3-H$$ Butane

IR spectrum of Butadiene, with structure:

$$H_2C=CH-CH=CH_2$$ Butadiene
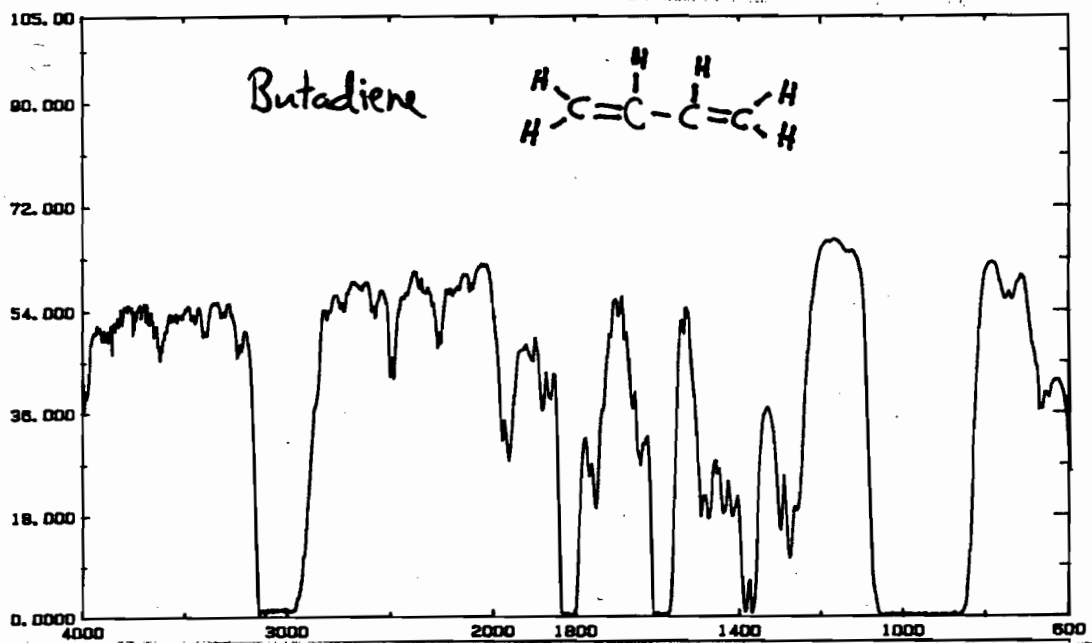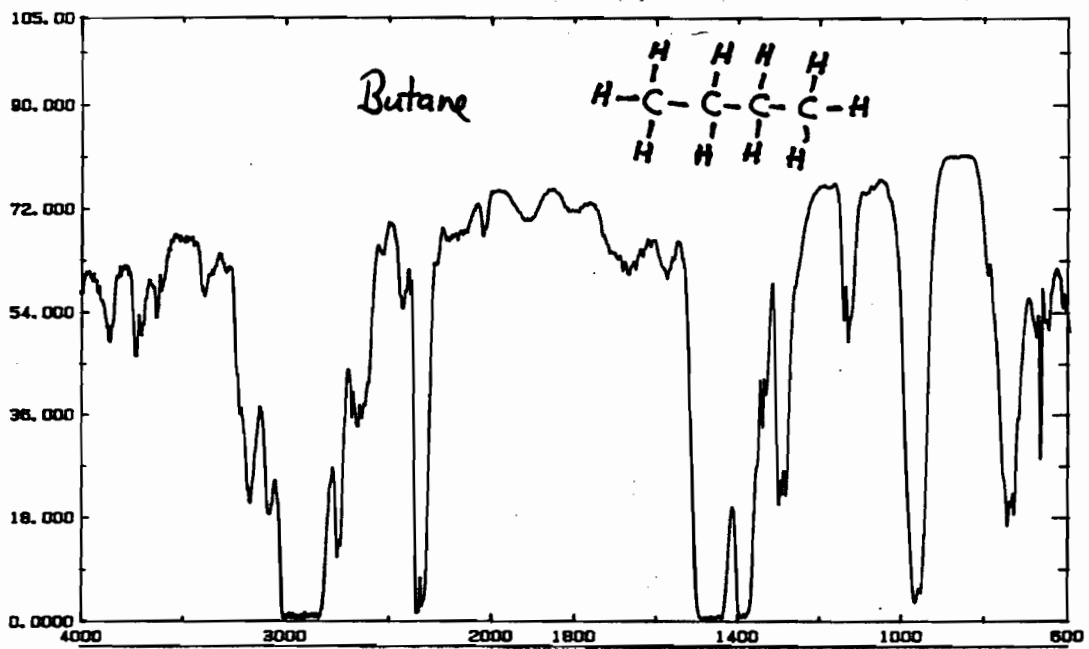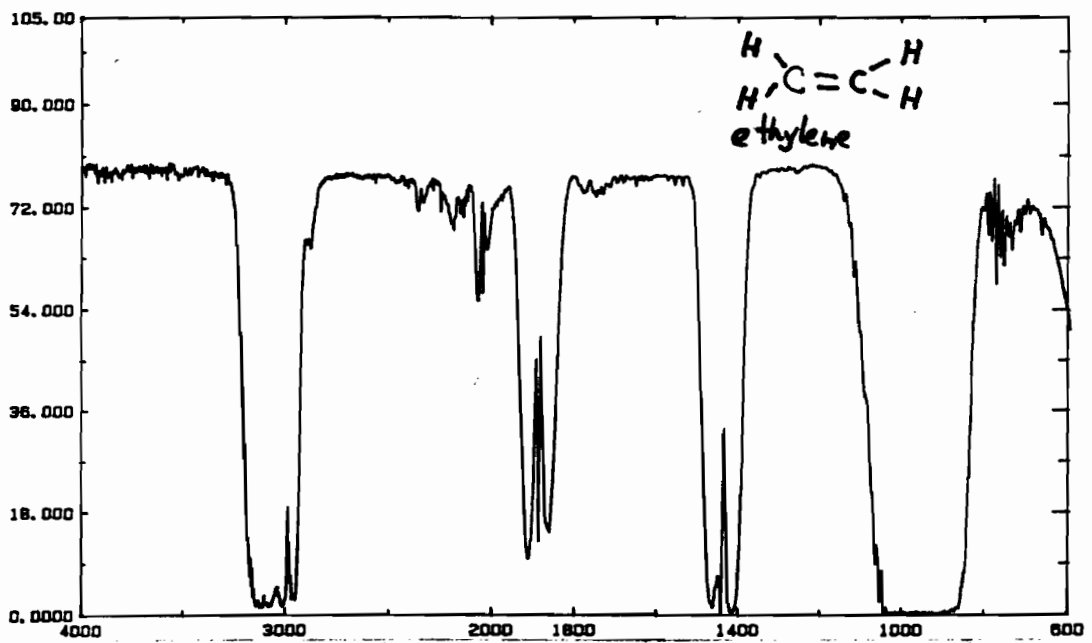
GASSES IN THE ATMOSPHERE THAT ABSORB OUTGOING RADIATION
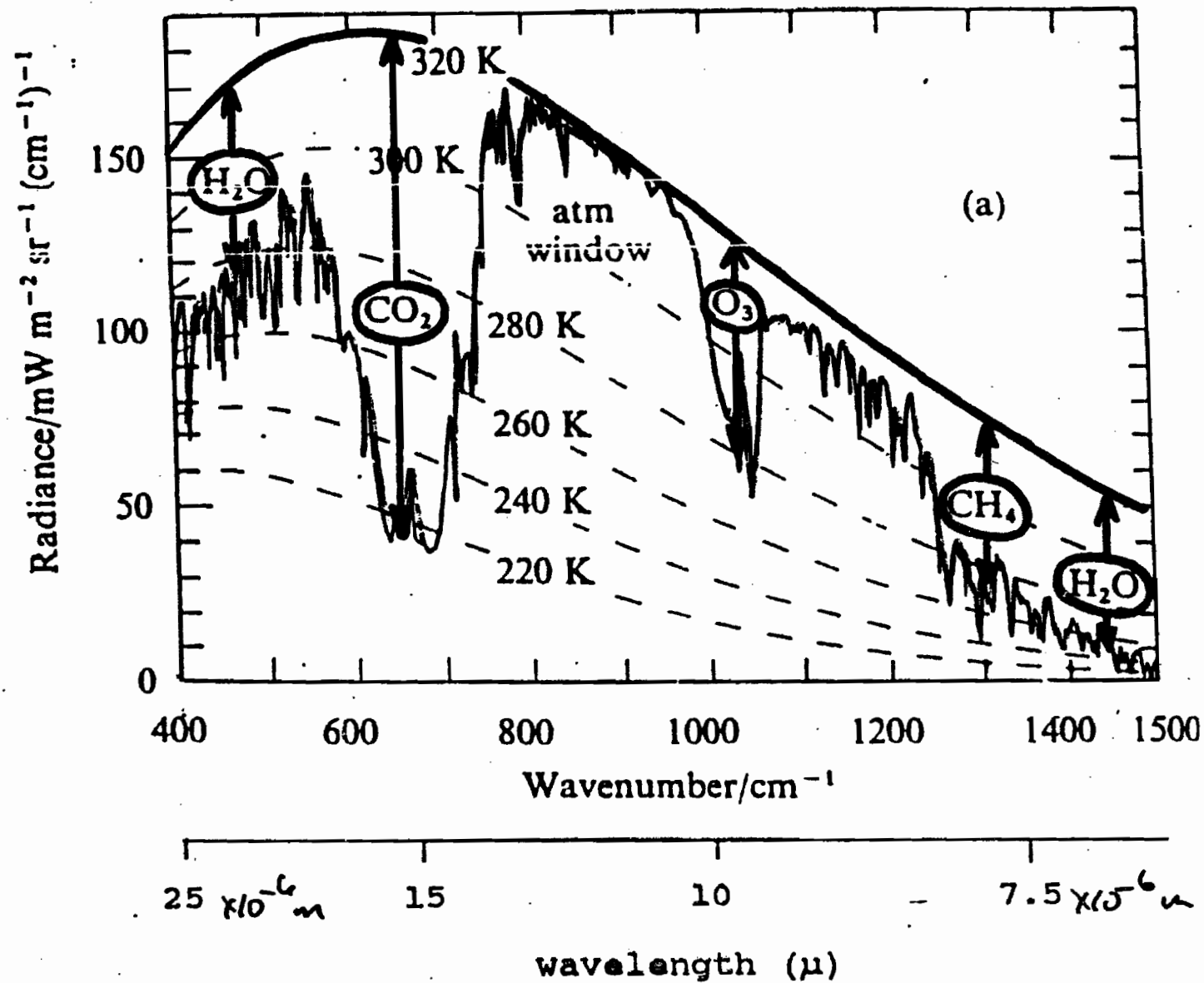
Figure 2-11: Earth's spectrum as viewed by Nimbus 4 over Sahara. Note that the wavelength scale is decreasing to the right. (source: Hanel et al., 1971)

Figure 2-9: Solar emissions as viewed from space and on the earth's surface.
(source: Valley, 1965)

A FRACTION OF THE SOLAR RADIATION IS ABSORBED BY THE ATMOSPHERE BEFORE IT REACHES THE EARTH. THE MOST IMPORTANT IS THE ABSORPTION OF U.V. AND VISIBLE BY O_3 (OZONE). THIS PREVENTS MUCH HARMFUL U.V. FROM REACHING US.

Mauna Loa Observatory, Hawaii

LIVING CARBON, ?

DEAD ORGANIC CARBON, ?

ATMOSPHERE, $CO_2 - C$, 670

CH_4, 3

CO, 0.3

Fossil fuel combustion, 3.6

Troposphere, 610
Stratosphere, 60

Hetero-trophic respiration and fire, 13

Gross photosyn-thesis, 100

Plant respiration, 50

Solution input, 100

Net flux 1.8

Solution loss, 98.2

OCEAN SURFACE LAYERS

LIVING ORGANIC CARBON (mostly plant), 833

0.2 to 1 flow to ocean

Inorganic carbon, 500

Gross photo-synthesis, 50

Plant respir-ation, 25

Decompo-sition, 35

Detritus transfer, 37

Decom-position, 37

LIVING ORGANIC, 1.5

Detritus transfer, 20

DEAD ORGANIC CARBON, 700

DEAD ORGANIC CARBON, 1000

Detritus and dissolved carbon transfer, ?

Layer mixing, 45

Layer mixing, 40

LAND

OCEAN DEEP LAYERS

FRESHWATERS, 330

Inorganic carbon, 35 000

Decompo-sition, 5

Rock weathering, ?

SEDIMENTS

FOSSIL FUEL, 10 000

Sedimentation, >1

DIFFUSE CARBON AND INORGANIC CARBON SEDIMENTS, 20 000 000

Solution, ?

FIG. 8.1 Diagrammatic model of the global carbon cycle. Questions marks indicate that no estimates are available. Figures are in uni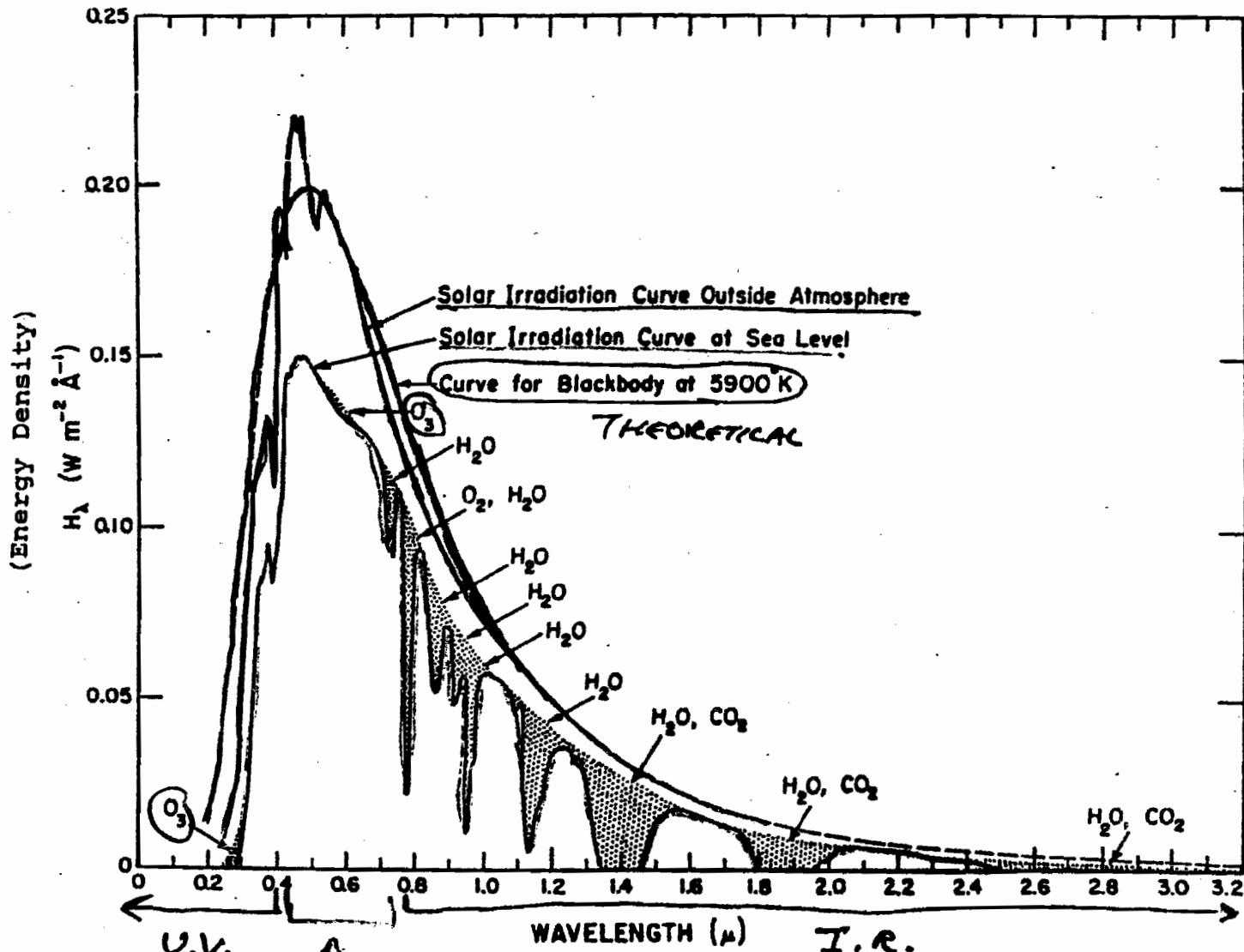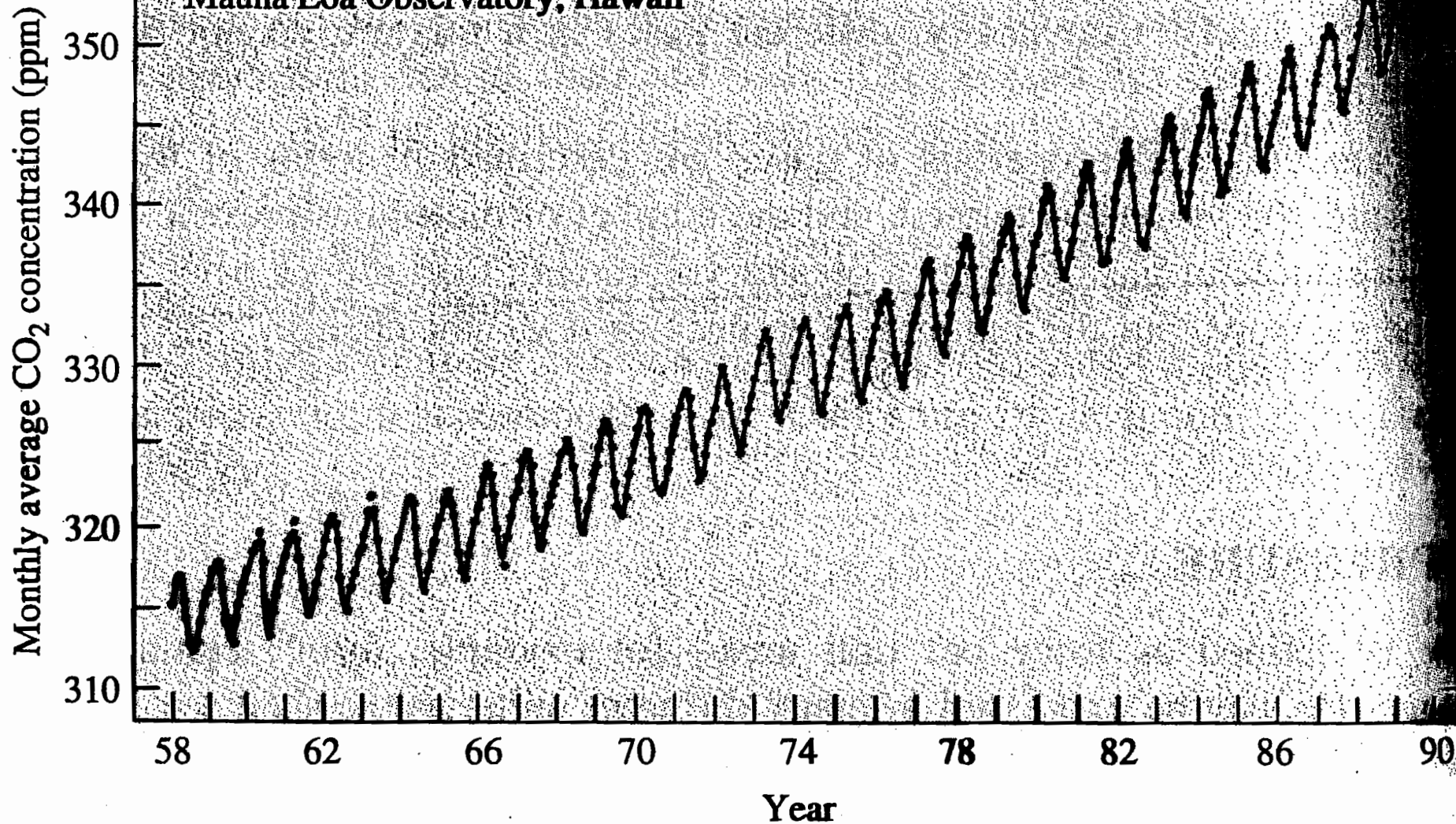ts of 10^9 tonnes of contained carbon but estimates from various sources sometimes differ by factors of 3 or more. The diagram is based on one by B. Bolin[5] modified to include more recent data.[6]

Allotropic Forms

Million tonnes CO_2

18 000
16 000
14 000
12 000
10 000
8000
6000
4000
2000
0

1860 1870 1880 1890 1900 1910 1920 1930 1940 1950 1960 1970 1980

Year

FIG. 8.2 Annual production of CO_2 from combustion of fossil fuels and calcination of limestone for cement.[6]

CHAPTER
4

Symmetry and Group Theory

Symmetry is a phenomenon of the natural world, as well as the world of human invention (Figure 4-1). In nature, many types of flowers and plants, snowflakes, insects, certain fruits and vegetables, and a wide variety of microscopic plants and animals exhibit characteristic symmetry. Many engineering achievements have a degree of symmetry that contributes to their esthetic appeal. Examples include cloverleaf intersections, the pyramids of ancient Egypt, and the Eiffel Tower.
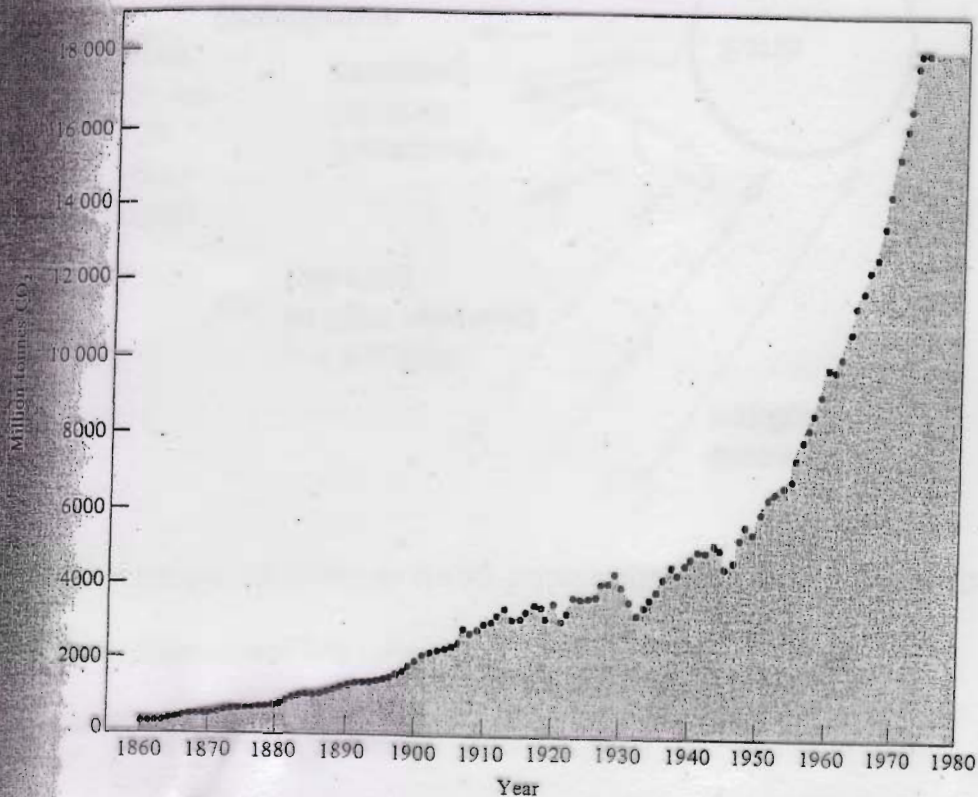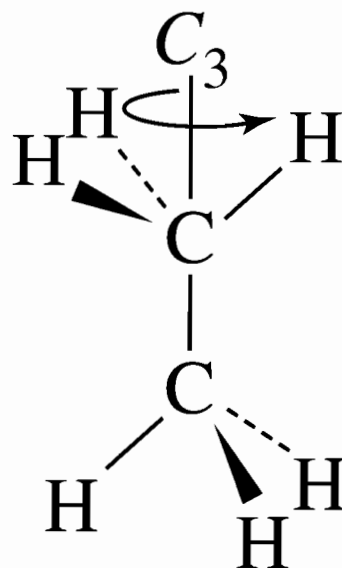
Symmetry concepts can be extremely useful in chemistry. By analyzing the symmetry of molecules, we can predict infrared spectra, describe the types of orbitals used in bonding, predict optical activity, interpret electronic spectra, and study a number of additional molecular properties. In this chapter, we first define symmetry very specifically in terms of five fundamental symmetry operations. We then describe how molecules can be classified on the basis of the types of symmetry they possess. We conclude with examples of how symmetry can be used to predict optical activity of molecules and to determine the number and types of infrared-active stretching vibrations.

In later chapters, symmetry will be a valuable tool in the construction of molecular orbitals (Chapters 5 and 10) and in the interpretation of electronic spectra of coordination compounds (Chapter 11) and vibrational spectra of organometallic compounds (Chapter 13).

A molecular model kit is a very useful study aid for this chapter, even for those who can visualize three-dimensional objects easily. We strongly encourage the use of such a kit.

4-1
SYMMETRY ELEMENTS AND OPERATIONS

All molecules can be described in terms of their symmetry, even if it is only to say they have none. Molecules or any other objects may contain **symmetry elements** such as mirror planes, axes of rotation, and inversion centers. The actual reflection, rotation, or inversion is called the **symmetry operation**. To contain a given symmetry element, a molecule must have exactly the same appearance after the operation as before. In other words, photographs of the molecule (if such photographs were possible!) taken from the same location before and after the symmetry operation would be indistinguishable. If a symmetry operation yields a molecule that can be distinguished from the original in
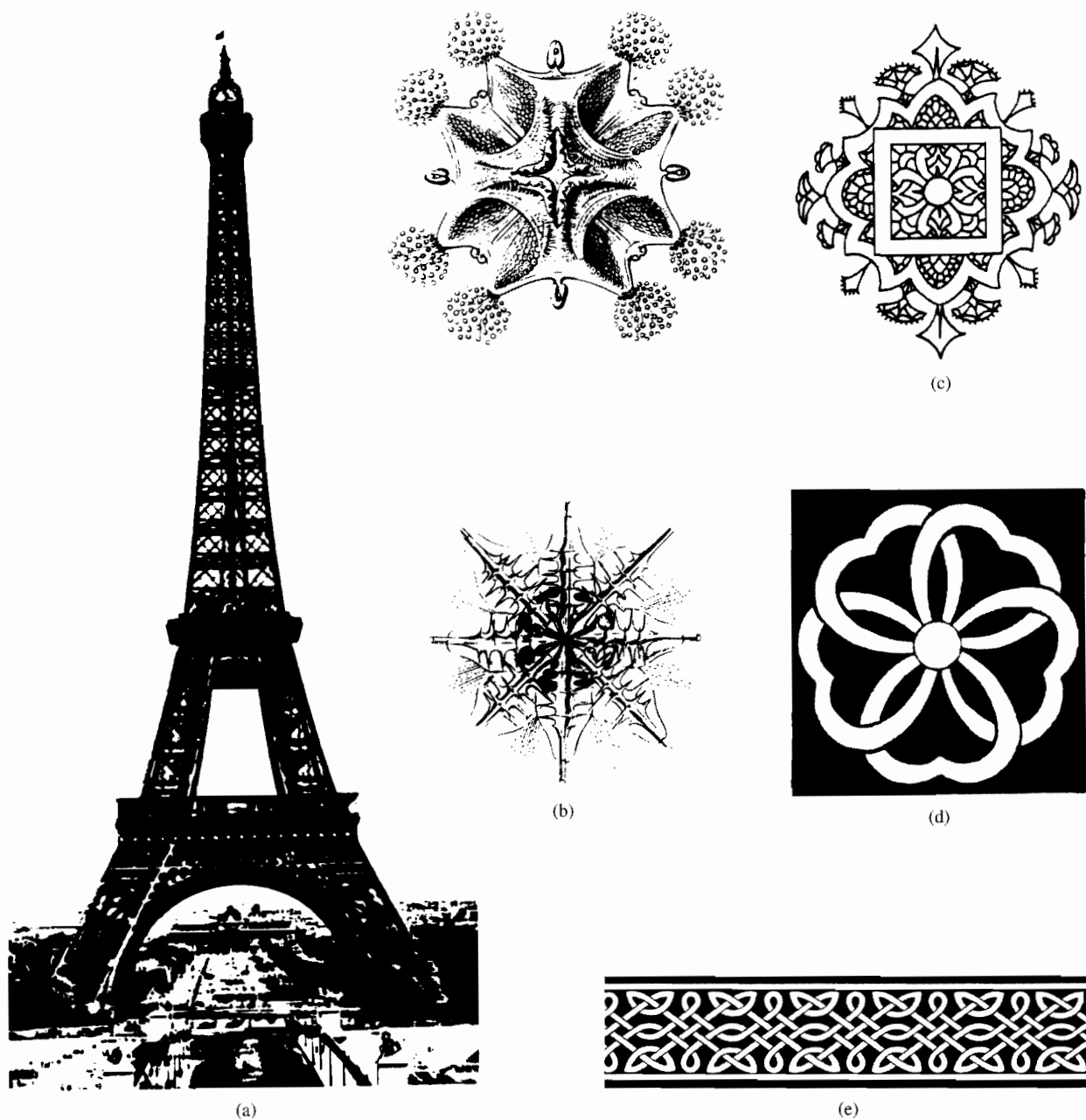
FIGURE 4-1 Symmetry in Nature, Art, and Architecture.

any way, then that operation is *not* a symmetry operation of the molecule. The examples in Figures 4-2 through 4-6 illustrate the possible types of molecular symmetry operations and elements.

The **identity operation (E)** causes no change in the molecule. It is included for mathematical completeness. An identity operation is characteristic of every molecule, even if it has no other symmetry.

The **rotation operation (C_n)** (also called **proper rotation**) is rotation through $360°/n$ about a rotation axis. We use counterclockwise rotation as a positive rotation. An example of a molecule having a threefold (C_3) axis is $CHCl_3$. The rotation axis is coincident with the C—H bond axis, and the rotation angle is $360°/3 = 120°$. Two C_3 operations may be performed consecutively to give a new rotation of $240°$. The resulting

C_3 rotations of $CHCl_3$

Cross section of protein disk
of tobacco mosaic virus

C_2, C_3 and C_6 rotations
of a snowflake design
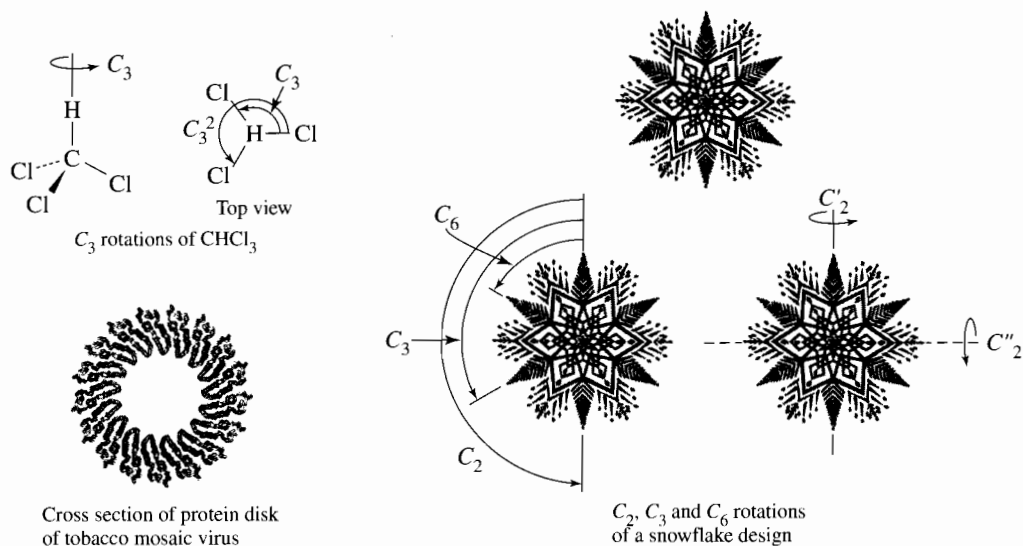
FIGURE 4-2 Rotations. The cross section of the tobacco mosaic virus is a cover diagram from *Nature*, 1976, *259*. © **1976**, Macmillan Journals Ltd. Reproduced with permission of Aaron Klug.

operation is designated C_3^2 and is also a symmetry operation of the molecule. Three successive C_3 operations are the same as the identity operation $(C_3^3 \equiv E)$. The identity operation is included in all molecules. Many molecules and other objects have multiple rotation axes. Snowflakes are a case in point, with complex shapes that are nearly always hexagonal and nearly planar. The line through the center of the flake perpendicular to the plane of the flake contains a twofold (C_2) axis, a threefold (C_3) axis, and a sixfold (C_6) axis. Rotations by 240° (C_3^2) and 300° (C_6^5) are also symmetry operations of the snowflake.

Rotation Angle	Symmetry Operation
60°	C_6
120°	C_3 $(\equiv C_6^2)$
180°	C_2 $(\equiv C_6^3)$
240°	C_3^2 $(\equiv C_6^4)$
300°	C_6^5
360°	E $(\equiv C_6^6)$

There are also two sets of three C_2 axes in the plane of the snowflake, one set through opposite points and one through the cut-in regions between the points. One of each of these axes is shown in Figure 4-2. In molecules with more than one rotation axis, the C_n axis having the largest value of n is the **highest order rotation axis** or **principal axis**. The highest order rotation axis for a snowflake is the C_6 axis. (In assigning Cartesian coordinates, the highest order C_n axis is usually chosen as the z axis.) When necessary, the C_2 axes perpendicular to the principal axis are designated with primes; a single prime (C_2') indicates that the axis passes through several atoms of the molecule, whereas a double prime (C_2'') indicates that it passes between the outer atoms.

Finding rotation axes for some three-dimensional figures is more difficult, but the same in principle. Remember that nature is not always simple when it comes to symmetry—the protein disk of the tobacco mosaic virus has a 17-fold rotation axis!

In the **reflection operation** (σ) the molecule contains a mirror plane. If details such as hair style and location of internal organs are ignored, the human body has a left-right mirror plane, as in Figure 4-3. Many molecules have mirror planes, although they may not be immediately obvious. The reflection operation exchanges left and right, as if each point had moved perpendicularly through the plane to a position exactly as far from the plane as when it started. Linear objects such as a round wood pencil or molecules
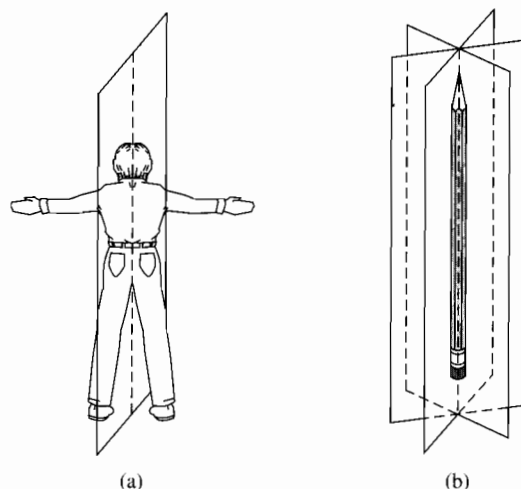
FIGURE 4-3 Reflections.   (a)   (b)

such as acetylene or carbon dioxide have an infinite number of mirror planes that include the center line of the object.

When the plane is perpendicular to the principal axis of rotation, it is called σ_h (horizontal). Other planes, which contain the principal axis of rotation, are labeled σ_v or σ_d.

Inversion (i) is a more complex operation. Each point moves through the center of the molecule to a position opposite the original position and as far from the central point as when it started.[1] An example of a molecule having a center of inversion is ethane in the staggered conformation, for which the inversion operation is shown in Figure 4-4.

Many molecules that seem at first glance to have an inversion center do not; for example, methane and other tetrahedral molecules lack inversion symmetry. To see this, hold a methane model with two hydrogen atoms in the vertical plane on the right and two hydrogen atoms in the horizontal plane on the left, as in Figure 4-4. Inversion results in two hydrogen atoms in the horizontal plane on the right and two hydrogen atoms in the vertical plane on the left. Inversion is therefore *not* a symmetry operation of methane, because the orientation of the molecule following the i operation differs from the original orientation.

Squares, rectangles, parallelograms, rectangular solids, octahedra, and snowflakes have inversion centers; tetrahedra, triangles, and pentagons do not (Figure 4-5).

A **rotation-reflection operation** (S_n) (sometimes called **improper rotation**) requires rotation of $360°/n$, followed by reflection through a plane perpendicular to the axis of rotation. In methane, for example, a line through the carbon and bisecting the

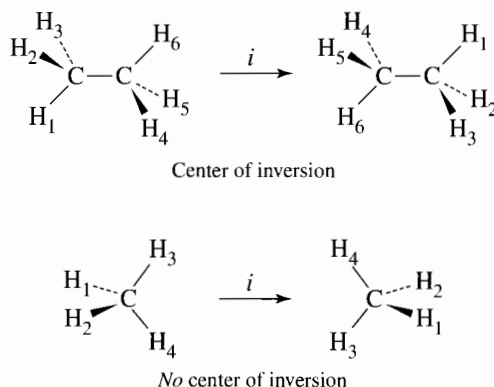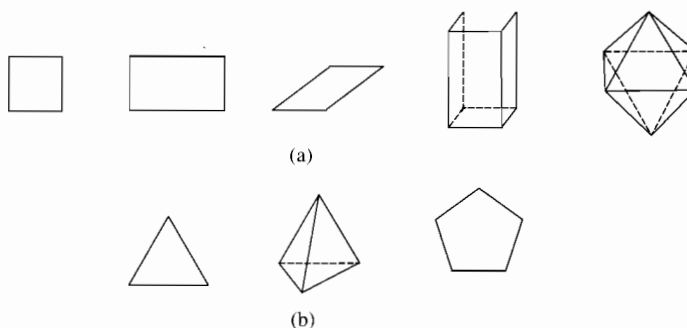

Center of inversion

No center of inversion

FIGURE 4-4 Inversion.

[1]This operation must be distinguished from the inversion of a tetrahedral carbon in a bimolecular reaction, which is more like that of an umbrella in a high wind.

**FIGURE 4-5** Figures (a) With and (b) Without Inversion Centers.

angle between two hydrogen atoms on each side is an S_4 axis. There are three such lines, for a total of three S_4 axes. The operation requires a 90° rotation of the molecule followed by reflection through the plane perpendicular to the axis of rotation. Two S. operations in succession generate a $C_{n/2}$ operation. In methane, two S_4 operations generate a C_2. These operations are shown in Figure 4-6, along with a table of C and S equivalences for methane.

Molecules sometimes have an S_n axis that is coincident with a C_n axis. For example. in addition to the rotation axes described previously, snowflakes have $S_2 (\equiv i)$, S_3, and S. axes coincident with the C_6 axis. Molecules may also have S_{2n} axes coincident with C_r. methane is an example, with S_4 axes coincident with C_2 axes, as shown in Figure 4-6.

Note that an S_2 operation is the same as inversion; an S_1 operation is the same as a reflection plane. The i and σ notations are preferred in these cases. Symmetry elements and operations are summarized in Table 4-1.

Rotation Angle	Symmetry Operation
90°	S_4
180°	$C_2 \quad (\equiv S_4{}^2)$
270°	$S_4{}^3$
360°	$E \quad (\equiv S_4{}^4)$

First S_4:
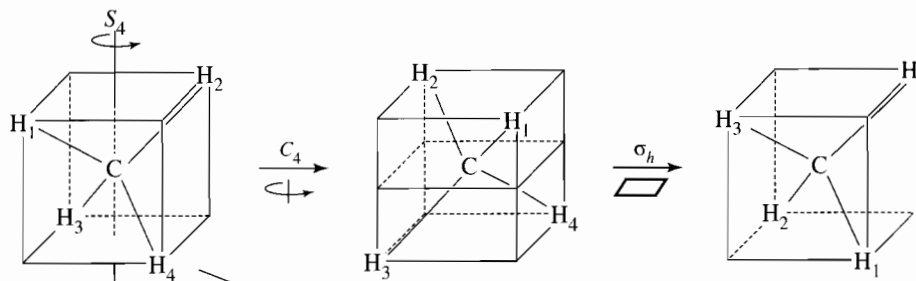
Second S_4:
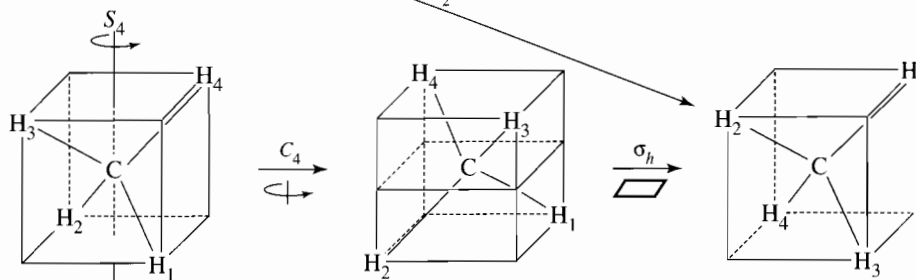
FIGURE 4-6 Improper Rotation or Rotation-Reflection.

TABLE 4-1
Summary Table of Symmetry Elements and Operations

| Symmetry Operation	Symmetry Element	Operation	Examples
Identity, E	None	All atoms unshifted	CHFClBr
Rotation, C_2	Rotation axis	Rotation by $360°/n$	p-dichlorobenzene
C_3			NH_3
C_4			$[PtCl_4]^{2-}$
C_5			Cyclopentadienyl group
C_6			Benzene
Reflection, σ	Mirror plane	Reflection through a mirror plane	H_2O
Inversion, i	Inversion center (point)	Inversion through the center	Ferrocene (staggered)
Rotation-reflection, S_4	Rotation-reflection axis (improper axis)	Rotation by $360°/n$, followed by reflection in the plane perpendicular to the rotation axis	CH_4
S_6			Ethane (staggered)
S_{10}			Ferrocene (staggered)

EXAMPLES

Find all the symmetry elements in the following molecules; consider only the atoms when as signing symmetry. Lone pairs influence shapes, but molecular symmetry is based on the geometry of the atoms.

H₂O

H_2O has two planes of symmetry, one in the plane of the molecule and one perpendicular to the molecular plane, as shown in Table 4-1. It also has a C_2 axis collinear with the intersection of the mirror planes. H_2O has no inversion center.

p-**Dichlorobenzene**   This molecule has three mirror planes: the molecular plane; a plane perpendicular to the molecule, passing through both chlorines; and a plane perpendicular to the first two, bisecting the molecule between the chlorines. It also has three C_2 axes, one perpendicular to the molecular plane (see Table 4-1) and two within the plane: one passing through both chlorines and one perpendicular to the axis passing through the chlorines. Finally, *p*-dichlorobenzene has an inversion center.
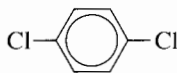
Ethane (staggered conformation)   Ethane has three mirror planes, each containing the $C-C$ bond axis and passing through two hydrogens on opposite ends of the molecule. It has a C_3 axis collinear with the carbon-carbon bond and three C_2 axes bisecting the angles between the mirror planes. (Use of a model is especially helpful for viewing the C_2 axes). Ethane also has a center of inversion and an S_6 axis collinear with the C_3 axis (see Table 4-1).
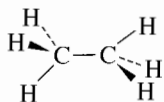
EXERCISE 4-1

Using diagrams as necessary, show that $S_2 \equiv i$ and $S_1 \equiv \sigma$.

EXERCISE 4-2

Find all the symmetry elements in the following molecules:

NH_3 Cyclohexane (boat conformation)   Cyclohexane (chair conformation) XeF_2

**4-2
POINT GROUPS**

Each molecule has a set of symmetry operations that describes the molecule's overall symmetry. This set of symmetry operations is called the **point group** of the molecule. **Group theory**, the mathematical treatment of the properties of groups, can be used to determine the molecular orbitals, vibrations, and other properties of the molecule. With only a few exceptions, the rules for assigning a molecule to a point group are simple and straightforward. We need only to follow these steps in sequence until a final classification of the molecule is made. A diagram of these steps is shown in Figure 4-7.

1. Determine whether the molecule belongs to one of the cases of very low symmetry (C_1, C_s, C_i) or high symmetry ($T_d, O_h, C_{\infty v}, D_{\infty h}$, or I_h) described in Tables 4-2 and 4-3.

2. For all remaining molecules, find the rotation axis with the highest n, the highest order C_n axis for the molecule.

3. Does the molecule have any C_2 axes perpendicular to the C_n axis? If it does, there will be n of such C_2 axes, and the molecule is in the D set of groups. If not, it is in the C or S set.

4. Does the molecule have a mirror plane (σ_h) perpendicular to the C_n axis? If so, it is classified as C_{nh} or D_{nh}. If not, continue with Step 5.

5. Does the molecule have any mirror planes that contain the C_n axis (σ_v or σ_d)? If so, it is classified as C_{nv} or D_{nd}. If not, but it is in the D set, it is classified as D_n. If the molecule is in the C or S set, continue with Step 6.
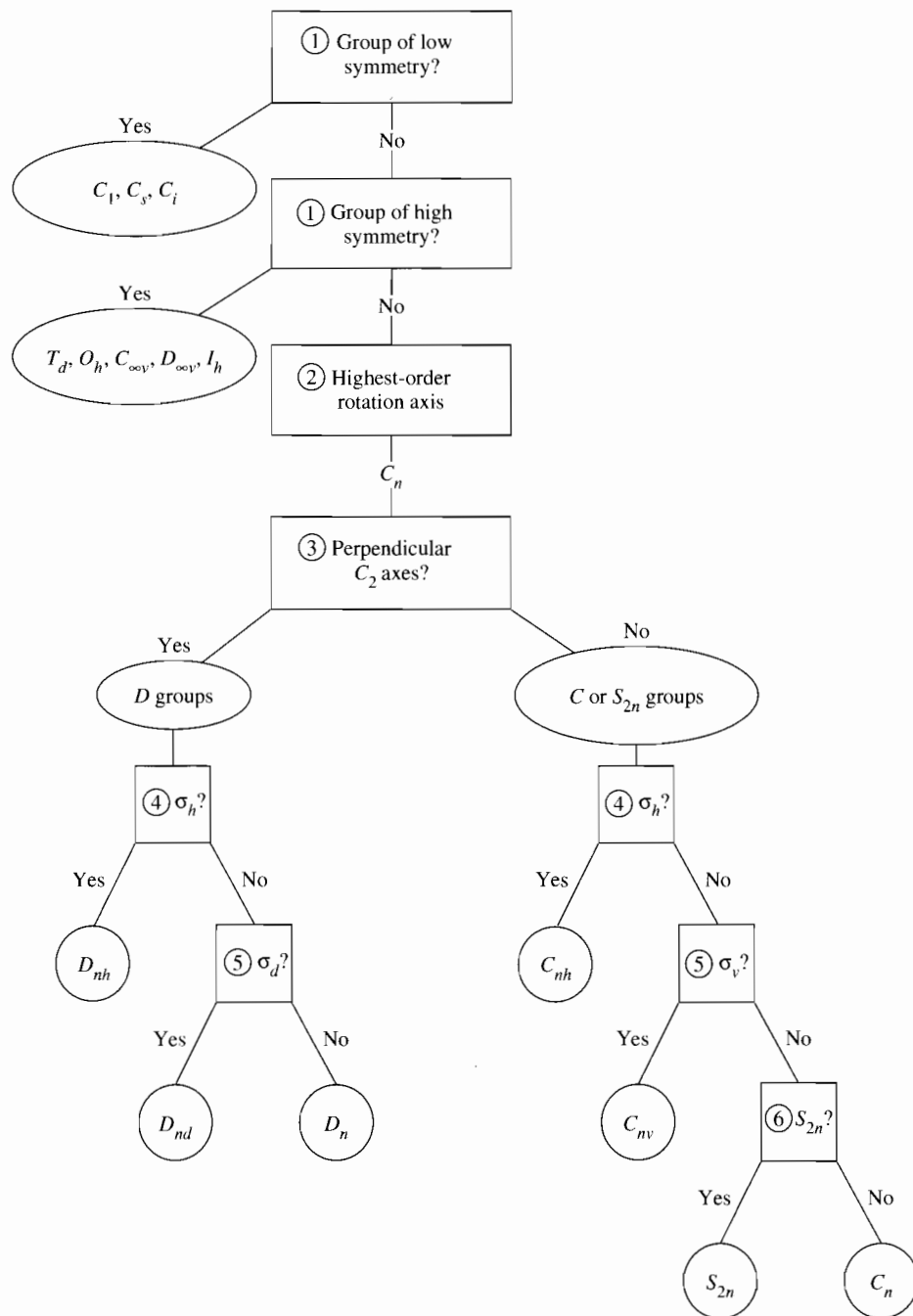
FIGURE 4-7 Diagram of the Point Group Assignment Method.

6. Is there an S_{2n} axis collinear with the C_n axis? If so, it is classified as S_{2n}. If not, the molecule is classified as C_n.

Each step is illustrated in the following text by assigning the molecules in Figure 4-8 to their point groups. The low- and high-symmetry cases are treated differently because of their special nature. Molecules that are not in one of these low- or high-symmetry point groups can be assigned to a point group by following Steps 2 through 6.

H—Cl
HCl

O=C=O
CO_2

PF_5

H_3CCH_3

$[Co(en)_3]^{3+}$ [a]

NH_3

CH_4

CHFClBr

$H_2C=CClBr$

$HClBrC—CHClBr$

SF_6

H_2O_2

1,5-dibromonaphthalene

1,3,5,7-tetrafluoro-cyclooctatetraene

dodecahydro-*closo*-dodecaborate (2−) ion, $B_{12}H_{12}^{2-}$ (each corner has a BH unit)
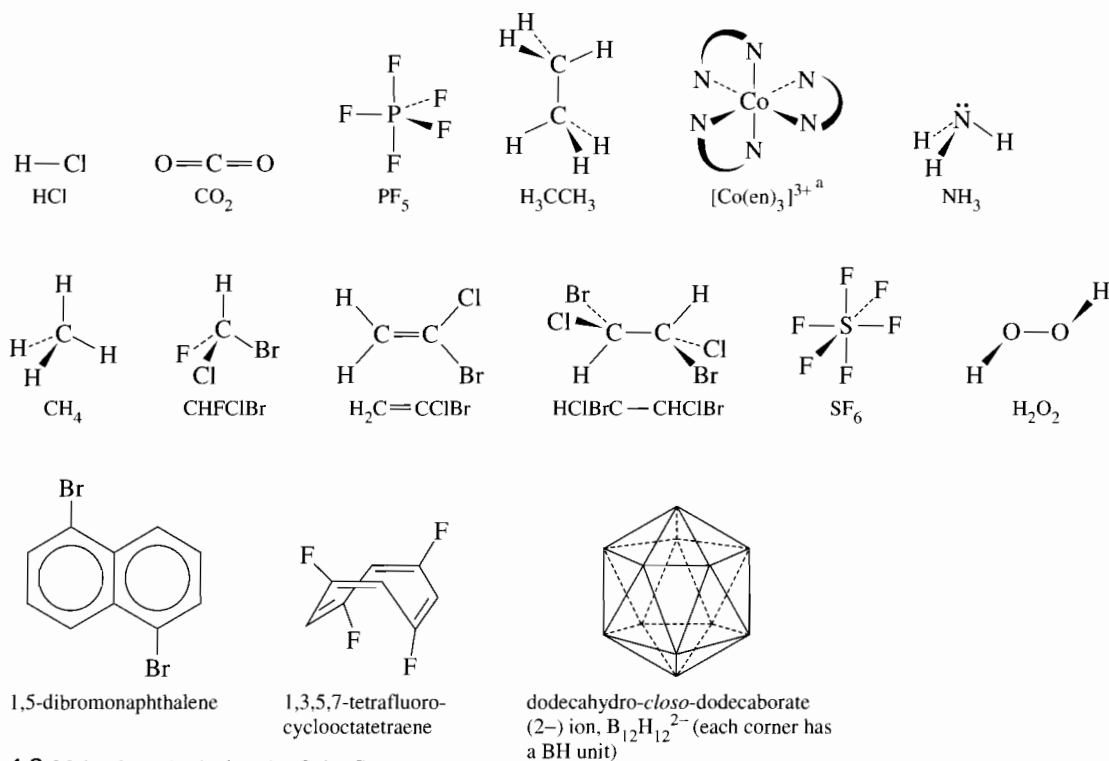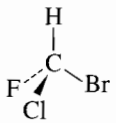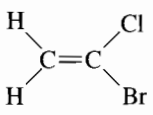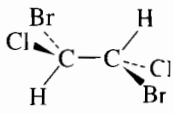
FIGURE 4-8 Molecules to be Assigned to Point Groups.
[a]en = ethylenediamine = $NH_2CH_2CH_2NH_2$, represented by N⌒N.

4-2-1 GROUPS OF LOW AND HIGH SYMMETRY

1. Determine whether the molecule belongs to one of the special cases of low or high symmetry.

First, inspection of the molecule will determine if it fits one of the low-symmetry cases. These groups have few or no symmetry operations and are described in Table 4-2

TABLE 4-2
Groups of Low Symmetry

Group	Symmetry	Examples	
C_1	No symmetry other than the identity operation	CHFClBr	
C_s	Only one mirror plane	$H_2C=CClBr$	
C_i	Only an inversion center; few molecular examples	$HClBrC—CHClBr$ (staggered conformation)	

Low symmetry

CHFClBr has no symmetry other than the identity operation and has C_1 symmetry, $H_2C=CClBr$ has only one mirror plane and C_s symmetry, and $HClBrC-CHClBr$ in the conformation shown has only a center of inversion and C_i symmetry.

High symmetry

Molecules with many symmetry operations may fit one of the high-symmetry cases of linear, tetrahedral, octahedral, or icosahedral symmetry with the characteristics described in Table 4-3. Molecules with very high symmetry are of two types, linear and polyhedral. Linear molecules having a center of inversion have $D_{\infty h}$ symmetry; those lacking an inversion center have $C_{\infty v}$ symmetry. The highly symmetric point groups T_d, O_h, and I_h are described in Table 4-3. It is helpful to note the C_n axes of these molecules. Molecules with T_d symmetry have only C_3 and C_2 axes; those with O_h symmetry have C_4 axes in addition to C_3 and C_2; and I_h molecules have C_5, C_3, and C_2 axes.

TABLE 4-3
Groups of High Symmetry

Group	Description	Examples
$C_{\infty v}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.	$C_\infty \updownarrow H-Cl$
$D_{\infty h}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular C_2 axes, a perpendicular reflection plane, and an inversion center.	$C_\infty \updownarrow O=C=O$ $\;C_2$
T_d	Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d planes. They have no C_4 axes.	H—C—H (H, H)
O_h	These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four C_3 rotations, three C_4 rotations, and an inversion.	F—S—F (octahedral SF_6)
I_h	Icosahedral structures are best recognized by their six C_5 axes (as well as many other symmetry operations—120 total).	$B_{12}H_{12}^{2-}$ with BH at each vertex of an icosahedron

In addition, there are four other groups, T, T_h, O, and I, which are rarely seen in nature. These groups are discussed at the end of this section.

HCl has $C_{\infty v}$ symmetry, CO_2 has $D_{\infty h}$ symmetry, CH_4 has tetrahedral $(T_d$ symmetry, SF_6 has octahedral (O_h) symmetry, and $B_{12}H_{12}{}^{2-}$ has icosahedral $(I_h$ symmetry

There are now seven molecules left to be assigned to point groups out of the original 15.

4-2-2 OTHER GROUPS

> 2. Find the rotation axis with the highest n, the highest order C_n axis for the molecule. This is the principal axis of the molecule.

The rotation axes for the examples are shown in Figure 4-9. If they are all equivalent, any one can be chosen as the principal axis.

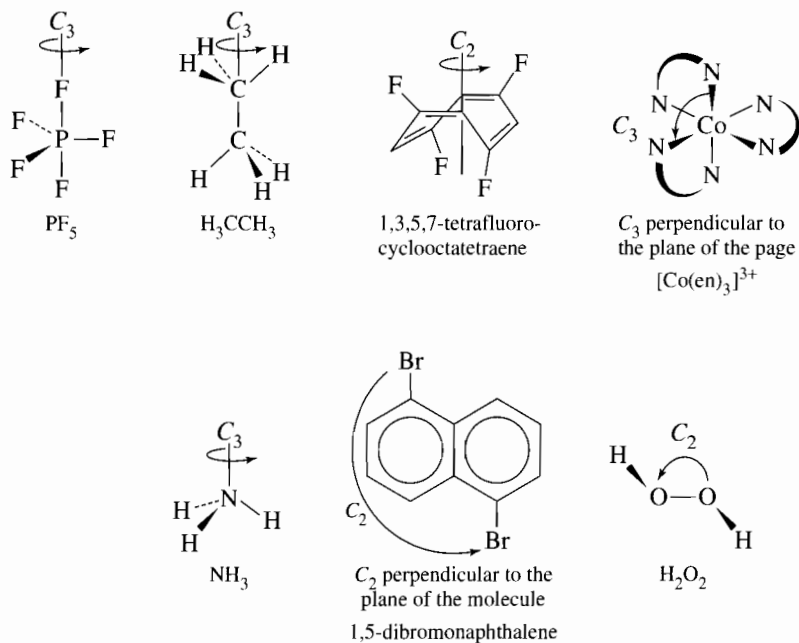FIGURE 4-9 Rotation Axes.

> 3. Does the molecule have any C_2 axes perpendicular to the C_n axis?

The C_2 axes are shown in Figure 4-10.

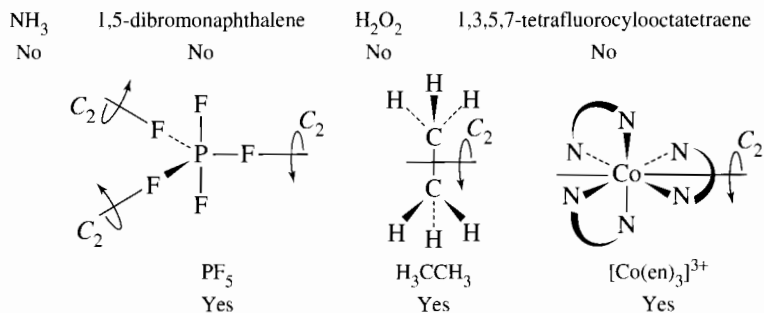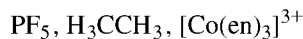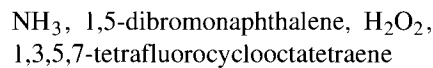| NH_3	1,5-dibromonaphthalene	H_2O_2	1,3,5,7-tetrafluorocylooctatetraene
No	No	No	No

	PF_5	H_3CCH_3	$[Co(en)_3]^{3+}$
	Yes	Yes	Yes

FIGURE 4-10 Perpendicular C_2 Axes.

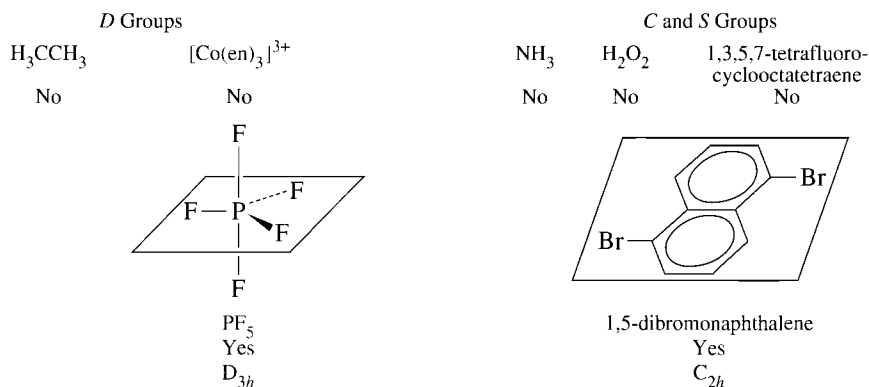| **Yes** *D Groups*	**No** *C or S Groups*
PF_5, H_3CCH_3, $[Co(en)_3]^{3+}$	NH_3, 1,5-dibromonaphthalene, H_2O_2, 1,3,5,7-tetrafluorocyclooctatetraene
Molecules with C_2 axes perpendicular to the principal axis are in one of the groups designated by the letter *D*; there are *n* C_2 axes.	Molecules with no perpendicular C_2 axes are in one of the groups designated by the letters *C* or *S*.

No final assignments of point groups have been made, but the molecules have now been divided into two major categories, the *D* set and the *C* or *S* set.

---

4. Does the molecule have a mirror plane (σ_h horizontal plane) perpendicular to the C_n axis?

The horizontal mirror planes are shown in Figure 4-11.

FIGURE 4-11 Horizontal Mirror Planes.

D Groups

H_3CCH_3 $[Co(en)_3]^{3+}$

No   No

C and S Groups

NH_3 H_2O_2 1,3,5,7-tetrafluoro-cyclooctatetraene

No   No   No

PF_5
Yes
D_{3h}

1,5-dibromonaphthalene
Yes
C_{2h}

D Groups

Yes $\boxed{D_{nh}}$

PF_5 is D_{3h}

C and S Groups

Yes $\boxed{C_{nh}}$

1,5-dibromonaphthalene is C_{2h}

These molecules are now assigned to point groups and need not be considered further. Both have horizontal mirror planes.

No D_n *or* D_{nd}

H_3CCH_3, $[Co(en)_3]^{3+}$

No C_n, C_{nv}, *or* S_{2n}

NH_3, H_2O_2, 1,3,5,7-tetrafluorocyclooctatetraene
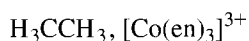
None of these have horizontal mirror planes; they must be carried further in the process.

---

5. Does the molecule have any mirror planes that contain the C_n axis?

D Groups σ_d?	C and S Groups σ_v?		S_{2n}?
$[Co(en)_3]^{3+}$	H_2O_2	1,3,5,7,-tetrafluoro-cyclooctatetraene	H_2O_2
No D_3	No	No	No C_2

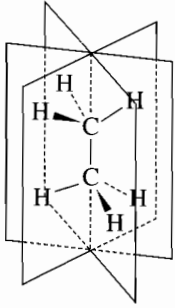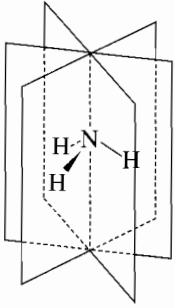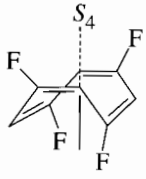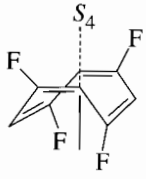| H_3CCH_3	NH_3	1,3,5,7,-tetrafluoro-cyclooctatetraene
Yes D_{3d}	Yes C_{3v}	Yes S_4

FIGURE 4-12 Vertical or Dihedral Mirror Planes or S_{2n} Axes.

These mirror planes are shown in Figure 4-12.

D Groups

Yes | D_{nd}

H_3CCH_3 (staggered) is D_{3d}

C and S Groups

Yes | C_{nv}

NH_3 is C_{3v}

These molecules have mirror planes containing the major C_n axis, but no horizontal mirror planes, and are assigned to the corresponding point groups. There will be n of these planes.

No | D_n

$[Co(en)_3]^{3+}$ is D_3

No C_n or S_{2n}

H_2O_2, 1,3,5,7-tetrafluorocyclooctatetraene

These molecules are in the simpler rotation groups D_n, C_n, and S_{2n} because they do not have any mirror planes. D_n and C_n point groups have *only* C_n axes. S_{2n} point groups have C_n and S_{2n} axes and may have an inversion center.

---

6. Is there an S_{2n} axis collinear with the C_n axis?

D Groups

Any molecules in this category that have S_{2n} axes have already been assigned to groups. There are no additional groups to be considered here.

C and S Groups

Yes | S_{2n}

1,3,5,7-tetrafluorocyclooctatetraene is S_4

No | C_n

H_2O_2 is C_2

We have only one example in our list that falls into the S_{2n} groups, as seen in Figure 4-12.
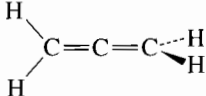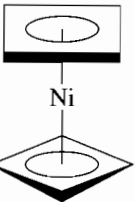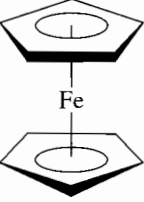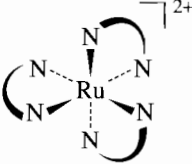
A branching diagram that summarizes this method of assigning point groups was given in Figure 4-7 and more examples are given in Table 4-4.

TABLE 4-4
Further Examples of C and D Point Groups

General Label	Point Group and Example	
C_{nh}	C_{2h}	difluorodiazene
	C_{3h}	$B(OH)_3$, planar
C_{nv}	C_{2v}	H_2O
	C_{3v}	PCl_3
	C_{4v}	BrF_5 (square pyramid)
	$C_{\infty v}$	HF, CO, HCN
C_n	C_2	N_2H_4, which has a *gauche* conformation
	C_3	$P(C_6H_5)_3$, which is like a three-bladed propeller distorted out of the planar shape by a lone pair on the P
D_{nh}	D_{3h}	BF_3
	D_{4h}	$PtCl_4{}^{2-}$
	D_{5h}	$Os(C_5H_5)_2$ (eclipsed)

TABLE 4-4—cont'd
Further Examples of C and D Point Groups

General Label	Point Group and Example'	
	D_{6h} benzene	
	$D_{\infty h}$ F_2, N_2, acetylene (C_2H_2)	F—F N≡N H—C≡C—H
D_{nd}	D_{2d} H_2C=C=CH_2, allene	
	D_{4d} Ni(cyclobutadiene)$_2$ (staggered)	
	D_{5d} Fe(C_5H_5)$_2$ (staggered)	
D_n	D_3 [Ru($NH_2CH_2CH_2NH_2$)$_3$]$^{2+}$ (treating the $NH_2CH_2CH_2NH_2$ group as a planar ring)	

EXAMPLES

Determine the point groups of the following molecules and ions from Figures 3-13 and 3-16:

XeF$_4$ 1. XeF$_4$ is not in the groups of low or high symmetry.
2. Its highest order rotation axis is C_4.
3. It has four C_2 axes perpendicular to the C_4 axis and is therefore in the D set of groups.
4. It has a horizontal plane perpendicular to the C_4 axis. Therefore its point group is D_{4h}.

SF$_4$ 1. It is not in the groups of high or low symmetry.
2. Its highest order (and only) rotation axis is a C_2 axis passing through the lone pair.
3. The ion has no other C_2 axes and is therefore in the C or S set.
4. It has no mirror plane perpendicular to the C_2.
5. It has two mirror planes containing the C_2 axis. Therefore, the point group is C_{2v}.

IOF$_3$ 1. The molecule has no symmetry (other than E). Its point group is C_1.

EXERCISE 4-3

Use the procedure described above to verify the point groups of the molecules in Table 4-4.

C versus D point group classifications

All molecules having these classifications must have a C_n axis. If more than one C_n axis is found, the highest order axis (largest value of n) is used as the reference axis. In general, it is useful to orient this axis vertically.

	D Classifications	C Classifications
General Case: Look for C_n axes perpendicular to the highest order C_n axis.	nC_2 axes $\perp$ C_n axis	No C_2 axes $\perp$ C_n axis
Subcategories:		
If a horizontal plane of symmetry exists:	D_{nh}	C_{nh}
If n vertical planes exist:	D_{nd}	C_{nv}
If no planes of symmetry exist:	D_n	C_n

Notes:

1. Vertical planes contain the highest order C_n axis. In the D_{nd} case, the planes are designated *dihedral* because they are between the C_2 axes—thus, the subscript d.

2. Simply having a C_n axis does not guarantee that a molecule will be in a D or C category; don't forget that the high-symmetry T_d, O_h, and I_h point groups and related groups have a large number of C_n axes.

3. When in doubt, you can always check the character tables (Appendix C) for a complete list of symmetry elements for any point group.

Groups related to I_h, O_h, and T_d groups

The high-symmetry point groups I_h, O_h, and T_d are well known in chemistry and are represented by such classic molecules as C_{60}, SF_6, and CH_4. For each of these point groups, there is also a purely rotational subgroup (I, O, and T, respectively) in which the only symmetry operations other than the identity operation are proper axes of rotation. The symmetry operations for these point groups are in Table 4-5.

We are not yet finished with high-symmetry point groups. One more group, T_h, remains. The T_h point group is derived by adding a center of inversion to the T point group; adding i generates the additional symmetry operations S_6, $S_6{}^5$, and σ_h.

TABLE 4-5
Symmetry Operations for High-Symmetry Point Groups and Their Rotational Subgroups

Point Group	Symmetry Operations									
I_h	E	$12C_5$	$12C_5{}^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}{}^3$	$20S_6$	15σ
I	E	$12C_5$	$12C_5{}^2$	$20C_3$	$15C_2$					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2\ (\equiv C_4{}^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2\ (\equiv C_4{}^2)$					
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$					
T	E	$\overline{4C_3\,4C_3{}^2}$	$3C_2$							
T_h	E	$4C_3 4C_3{}^2$	$3C_2$			i	$4S_6$	$4S_6{}^5$	$3\sigma_h$	
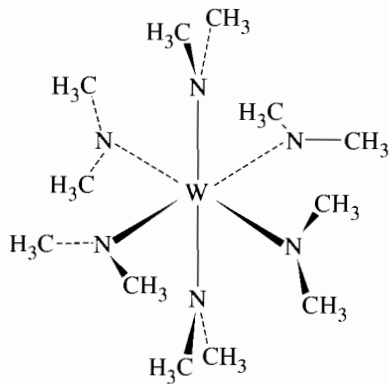
FIGURE 4-13 W[N(CH$_3$)$_2$]$_6$, a Molecule with T_h Symmetry.

T_h symmetry is rare but is known for a few molecules. The compound shown in Figure 4-13 is an example. I, O, and T symmetry are rarely if ever encountered in chemistry.

That's all there is to it! It takes a fair amount of practice, preferably using molecular models, to learn the point groups well, but once you know them, they can be extremely useful. Several practical applications of point groups appear later in this chapter, and additional applications are included in later chapters.

H
|
H—C—H   109⁰ → 109°
|
H

H   H
 \   /
  C=C 120°
 /   \
H   H

H—C≡C—H 180°

H
|
H—C—O—H   (with lone pairs on O)
| 107°
H
109°

:O:
||
C 120°
/ \
H   H

H
|
H—C—C≡N: 180°
|
H

120°
:F: :F:
  \ /
F—S—F
  / \
:F: :F:
90°

120°
:Ö—Ö—Ö:

:Cl:
|
B
/   \
:Cl: :Cl:
120°

H
|
H—N:
|
H
107°

90°
F   F
 \ /
F—Br
 / \
F   F

90°
F
|
:F—Cl:
|
F

120°
Cl   Cl
  \ /
Cl—P
  / \
Cl   Cl
90°

90°
F   F
 \ /
F—S—F
 / \
F   F
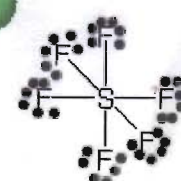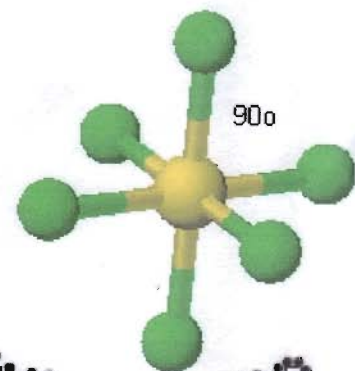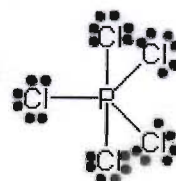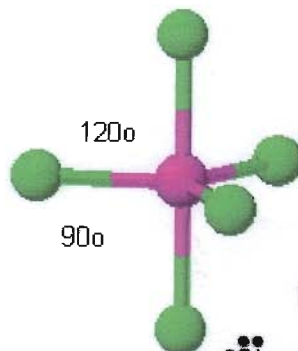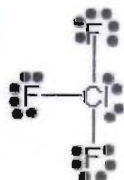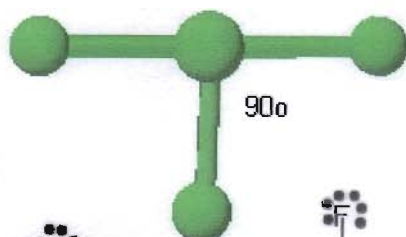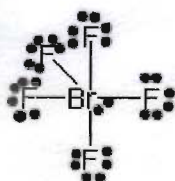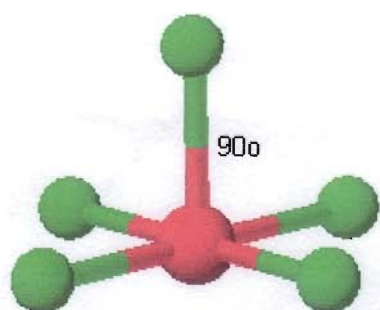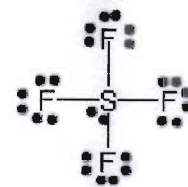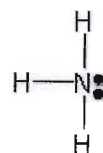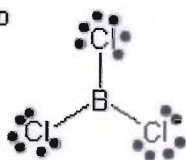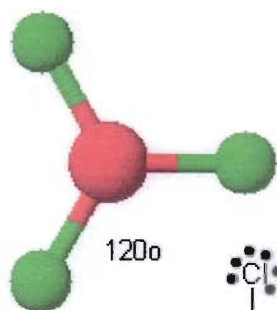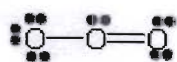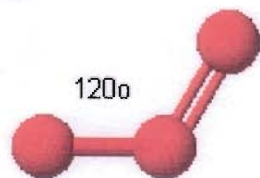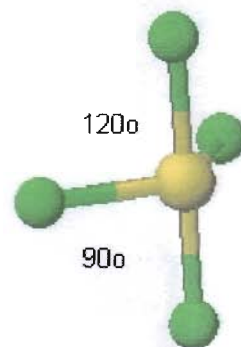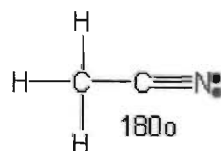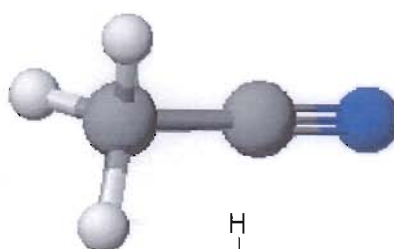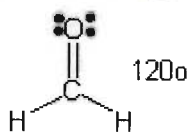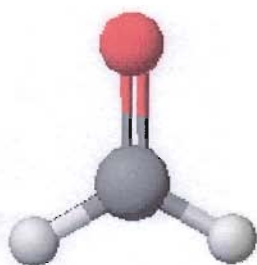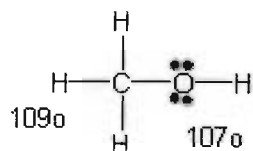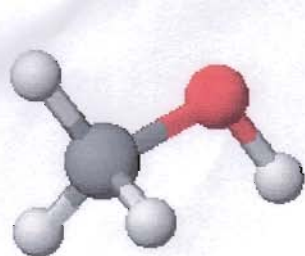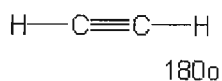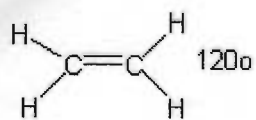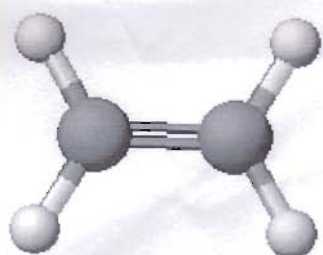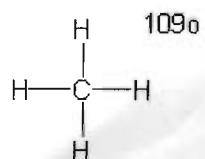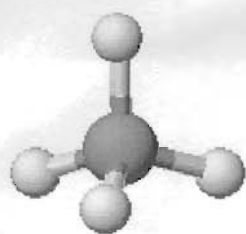
22.6 Coordinate Covalent Bonds: Complex Ions and Coordination Compounds

In Section 8.10, the formation of BF_3NH_3 was described as occurring by the sharing of a lone pair from NH_3 with BF_3. This type of covalent bond, in which one atom contributes *both* electrons for the shared pair, is called a **coordinate covalent bond.** Atoms with lone pairs of electrons, such as nitrogen, phosphorus, and sulfur, can use those lone pairs to form coordinate covalent bonds. For example,

the formation of the ammonium ion from ammonia results from formation of a coordinate covalent bond between H^+ and the lone pair of electrons of nitrogen in NH_3.

$$H—\overset{\displaystyle H}{\underset{\displaystyle H}{N}}\!: + H^+ \longrightarrow \left[H—\overset{\displaystyle H}{\underset{\displaystyle H}{N}}\!:H \right]^+ \quad \text{or} \quad \left[H—\overset{\displaystyle H}{\underset{\displaystyle H}{N}}—H \right]^+$$
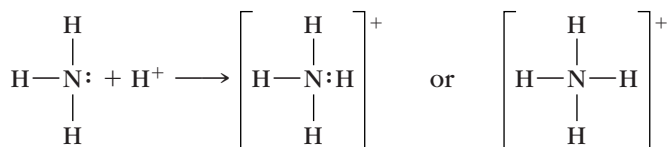
Once the coordinate covalent bond is formed, it is impossible to distinguish which of the N—H bonds it is; all four bonds are equivalent.

Metals and Coordination Compounds

Much of the chemistry of *d*-block transition metals is related to their ability to form coordinate covalent bonds with molecules or ions that have lone pair electrons. Transition metals with vacant *d* orbitals can accept the lone pairs into those orbitals.

You have seen that metal ions in aqueous solution are surrounded by water molecules; for example, the Ni^{2+} ion in aqueous solution is surrounded by six water molecules. This type of ion, in which several molecules or ions are connected to a central metal ion or atom by coordinate covalent bonds, is known as a *complex ion.* The molecules or ions bonded to the central metal ion are called **ligands,** from the Latin verb *ligare*, "to bind." Each ligand (a water molecule in this example) has one or more atoms with lone pairs that can form coordinate covalent bonds to the metal ion. To write the formula of a complex ion, the ligand formulas are placed in parentheses following the metal ion. The entire complex ion formula is enclosed by brackets, and the ionic charge, if any, is a superscript outside the brackets. For the nickel(II) complex ion with six water ligands this gives $[Ni(H_2O)_6]^{2+}$.

The charge of a complex ion is determined by the charges of the metal ion and the charges of its ligands. In $[Ni(H_2O)_6]^{2+}$ the water ligands have no net charge, so the charge of the complex ion is that of the Ni^{2+} ion. In the complex ion formed by Ni^{2+} with four chloride ions, $[NiCl_4]^{2-}$, the net $2-$ charge of this complex ion results from the $4-$ charge of four chloride ions and the $2+$ charge of the nickel ion.

Compounds that contain metal ions surrounded by ligands are called **coordination compounds.** Usually, complex ions are combined with oppositely charged ions *(counter ions)* to form neutral compounds. Coordination compounds are generally brightly colored as solids or in solution (Figure 22.8, two left flasks). The complex ion part of a coordination compound's formula is enclosed in brackets; counter ions are outside the brackets, as in the formula $[Ni(H_2O)_6]Cl_2$ of the compound consisting of chloride counter ions with the $[Ni(H_2O)_6]^{2+}$ complex ion. The two Cl^- ions compensate for the $2+$ charge of the complex ion. $[Ni(H_2O)_6]Cl_2$ is an ionic compound analogous to $CaCl_2$, which also contains a $2+$ cation and two Cl^- ions. In some cases, no compensating ions are needed outside the brackets for a coordination compound. For example, the anticancer drug $[Pt(NH_3)_2Cl_2]$ (cisplatin) is a coordination compound containing NH_3 and Cl^- ligands coordinated to a central Pt^{2+} ion. The two Cl^- ions compensate for the charge of the Pt^{2+} ion, resulting in a neutral coordination compound rather than a complex ion.

Margin notes:

Brackets in the formulas of complex ions do not mean concentration.

Ligands act as Lewis bases, electron pair donors; transition metal ions are Lewis acids (electron pair acceptors). (Section 16.9).

Ni^{2+}

$[Ni(H_2O)_6]^{2+}$
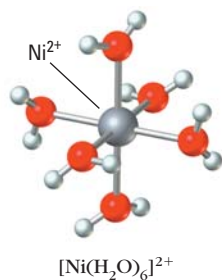
When the word *coordinated* is used in chemistry, such as in "the chloride ions in $[NiCl_4]^{2-}$ are coordinated to the nickel ion," it means that coordinate covalent bonds have been formed.

PROBLEM-SOLVING EXAMPLE **22.6**   **Coordination Compounds**

For the coordination compound $K_3[Fe(CN)_6]$, identify
(a)   The central metal ion.
(b)   The ligands.
(c)   The formula and charge of the complex ion and the charge of the central metal ion.

Answer

(a) Iron

(b) Six cyanide ions, CN^-

(c) $[Fe(CN)_6]^{3-}$, Fe^{3+}

Strategy and Explanation We apply the guidelines and concepts described previously. In a formula, a complex ion is enclosed in square brackets; within the brackets, ligands coordinated to the central metal ion are enclosed by parentheses.

(a) The iron ion is the central metal ion, as shown by its placement inside the brackets.

(b) Cyanide ions, CN^-, are coordinated to the central iron ion.

(c) The charge on three potassium ions is $(3 \times 1+) = 3+$. Therefore, the compensating charge of the complex ion must be $3-$, arising from the $6-$ charge of six cyanide ions $(6 \times 1- = 6-)$, combined with the $3+$ charge of the central iron(III) ion: $(6-) + (3+) = 3-$.

PROBLEM-SOLVING PRACTICE 22.6

For the coordination compound $[Cu(NH_3)_4]SO_4$, identify

(a) The counter ion.

(b) The central metal ion.

(c) The ligands.

(d) The formula and charge of the complex ion.

CONCEPTUAL EXERCISE **22.8** Coordination Complex Ion

In a complex ion, a central Cr^{3+} ion is bonded to two ammonia molecules, two water molecules, and two hydroxide ions. Give the formula and the net charge of this complex ion.

Naming Complex Ions and Coordination Compounds

Like other compounds, coordination compounds in early times were known by common names, for example, "roseo" salt and Zeise's salt. Since then, a systematic nomenclature has been developed for complex ions and coordination compounds. This nomenclature system indicates the central metal ion and its oxidation state, as well as the number and kinds of ligands. Table 22.4 lists the names and formulas of some common ligands. Although there are extensive rules for such nomenclature, we will consider only some basic aspects of the system by interpreting the names

---

Table 22.4 Names and Formulas of Some Common Ligands

Neutral Ligand	Ligand Name	Anionic Ligand	Ligand Name
NH_3	Ammine	Br^-	Bromo
CO	Carbonyl	CO_3^{2-}	Carbonato
$H_2NCH_2CH_2NH_2$	Ethylenediamine, en	Cl^-	Chloro
H_2O	Aqua	CN^-	Cyano
		F^-	Fluoro
		OH^-	Hydroxo
		$C_2O_4^{2-}$	Oxalato, ox
		NCS^-	Isothiocyanato
		SCN^-	Thiocyanato

of a neutral coordination compound and two other coordination compounds, one containing a complex cation and the other a complex anion.

Consider the coordination compound $[Co(NH_3)_3(OH)_3]$, which is named triamminetrihydroxocobalt(III). From Table 22.4, we see that the name and formula indicate that three ammonia molecules and three hydroxide ions are bonded to a central cobalt ion. The three hydroxide ions carry a total $3-$ charge; ammonia molecules have no net charge, and thus cobalt must be Co^{3+} because the compound has no net charge. In naming any coordination compound or complex ion, the ligands are named in alphabetical order—in this case ammine for ammonia precedes hydroxo for hydroxide (for anions *-ide* is changed to *o*). The name and oxidation state (in parentheses) of the metal ion are given last. Greek prefixes *di, tri, tetra,* and so on are used to denote the number of times each of these ligands is used. Such prefixes are ignored when determining the alphabetical order of the ligands.

$$[Co(NH_3)_3(OH)_3]$$

Co^{3+} ion	Three NH_3; triammine	Three OH^-; trihydroxo

triamminetrihydroxocobalt(III)
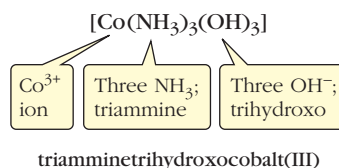
Next, consider $[Fe(H_2O)_2(NH_3)_4]Cl_3$, a coordination compound that consists of a complex *cation,* $[Fe(H_2O)_2(NH_3)_4]^{3+}$, and three chloride ions as counter ions. In such cases the complex cation is always named first, followed by the name of the anionic counter ions. The compound's name is tetraamminediaquairon(III) chloride. From Table 22.4, we see that the ligands are ammine (NH_3, four of them) and aqua (H_2O, two of them). For complex cations, the metal ion and its oxidation state follow the names of the ligands.

$$[Fe(H_2O)_2(NH_3)_4]Cl_3$$

Fe^{3+} ion	Two H_2O; diaqua	Four NH_3; tetraammine	Three Cl^- counter ions

tetraamminediaquairon(III) chloride
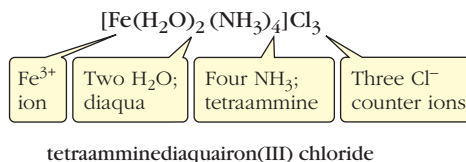
The compound $K_2[PtCl_4]$ contains a complex *anion,* $[PtCl_4]^{2-}$, and two K^+ ions as counter ions and is named potassium tetrachloroplatinate(II). As with any ionic compound, the cation is named first, followed by the anion name. For complex anions, the central metal ion's name ends in *-ate* followed by its oxidation state in parentheses.

$$K_2[PtCl_4]$$

Two K^+ counter ions	Pt^{2+} ion	Four Cl^-; tetrachloro

potassium tetrachloroplatinate(II)
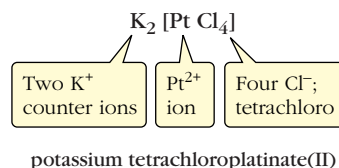
PROBLEM-SOLVING EXAMPLE 22.7 **Formulas and Names of Coordination Compounds**

(a) Write the formula of diamminetriaquahydroxochromium(III) nitrate.
(b) Name $K[Cr(NH_3)_2(C_2O_4)_2]$.

Answer

(a) $[Cr(NH_3)_2(H_2O)_3(OH)](NO_3)_2$
(b) Potassium diamminedioxalatochromate(III)

Strategy and Explanation   Use the names and formulas of the ligands in Table 22.4. Compound (a) contains a complex cation, and compound (b) contains a complex anion.

(a)   diamminetriaquahydroxochromium(III) nitrate

$[Cr(NH_3)_2(H_2O)_3(OH)](NO_3)_2$

(b) $K[Cr(NH_3)_2(C_2O_4)_2]$

potassium diamminedioxalatochromate(III)
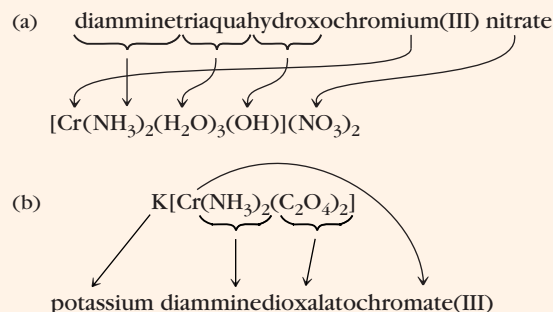
PROBLEM-SOLVING PRACTICE 22.7

(a)   Name this coordination compound: $[Ag(NH_3)_2]NO_3$.
(b)   Write the formula of pentaaquaisothiocyanatoiron(III) chloride.

CONCEPTUAL EXERCISE   **22.9** Coordination Compounds

$CaCl_2$ and $[Ni(H_2O)_6]Cl_2$ have the same formula type, MCl_2. Give the formula of a simple ionic compound (noncoordination) that has a formula analogous to $K_2[NiCl_4]$.

Types of Ligands and Coordination Number

The number of coordinate covalent bonds between the ligands and the central metal ion in a coordination compound is the **coordination number** of the metal ion, usually 2, 4, or 6.

Coordination Number	Examples
2	$[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
4	$[NiCl_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
6	$[Fe(H_2O)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$

Ligands such as H_2O, NH_3, and Cl^- that form only one coordinate covalent bond to the metal are termed **monodentate** ligands. The word *dentate* derives from the Latin word *dentis,* for tooth, so NH_3 is a "one-toothed" ligand. Common monodentate ligands are shown in Figure 22.9.

Some ligands can form two or more coordinate covalent bonds to the same metal ion because they have two or more atoms with lone pairs separated by several intervening atoms. The general term **polydentate** is used for such ligands. **Bidentate** ligands are those that form *two* coordinate covalent bonds to the central metal ion. A good example is the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, commonly called ethylenediamine and abbreviated *en.* When lone pairs of electrons from both nitrogen atoms in en coordinate to a metal ion, a stable five-membered ring forms (Figure 22.10). Notice that Co^{3+} has a coordination number of 6 in this complex ion.

Monodentate ligands

| Water | Ammonia | Chloride ion | Cyanide ion | Carbon monoxide | Hydroxide ion |

Bidentate ligands

Carbonate ion

Oxalate ion (ox²⁻)

Ethylenediamine (en)

Ortho-phenanthroline (phen)

Hexadentate ligand

EDTA⁴⁻, ethylenediaminetetraacetate ion

Figure 22.9 **Monodentate ligands; bidentate and hexadentate chelating ligands.** Ligands with two (bidentate) or more lone pairs to share with a central metal ion are chelating ligands.

Figure 22.10 **The [Co(en)₃]³⁺ complex ion.** Cobalt ion (Co³⁺) forms a coordination complex ion with three ethylenediamine ligands.

Note that Cl₂ in the complex ion's formula represents two chloride ions, not a diatomic chlorine molecule.

The word "chelating," derived from the Greek *chele*, "claw," describes the pincer-like way in which a ligand can grab a metal ion. Some common **chelating ligands,** those that are polydentate ligands and can share two or more electron pairs with the central metal ion, are also shown in Figure 22.9.

PROBLEM-SOLVING EXAMPLE 22.8 Chelating Agents

Two ethylenediamine (en) ligands and two chloride ions form a complex ion with Co³⁺.
(a) Write the formula of this complex ion.
(b) What is the coordination number of the Co³⁺ ion?
(c) Write the formula of the coordination compound formed by Cl⁻ counter ions and the Co³⁺ complex ion.

Answer
(a) [Co(en)₂Cl₂]⁺   (b) 6   (c) [Co(en)₂Cl₂]Cl
Strategy and Explanation Recall that ethylenediamine is a bidentate ligand that forms two coordinate covalent bonds per en molecule.
(a) Two en molecules and two chloride ions are bonded to the central cobalt ion, so the formula of the complex ion is [Co(en)₂Cl₂]⁺. Ethylenediamine is a neutral ligand, each chloride ion is 1−, and cobalt has a 3+ charge. The charge on the complex ion is 2(0) + 2(1−) + (3+) = 1+.
(b) The coordination number is 6 because there are six coordinate covalent bonds to the central Co³⁺ ion—two from each bidentate ethylenediamine and one from each monodentate chloride ion.
(c) The 1+ charge of the complex ion requires one chloride ion as a counter ion: [Co(en)₂Cl₂]Cl.

PROBLEM-SOLVING PRACTICE **22.8**

The dimethylglyoximate anion (abbreviated DMG^-),

$$CH_3C—CCH_3$$
$$\overset{||}{}\quad\overset{||}{}$$
$$HO—\underset{..}{N}\quad\underset{..}{N}—O^-$$

is a bidentate ligand used to test for the presence of nickel. It reacts with Ni^{2+} to form a beautiful red solid in which the Ni^{2+} has a coordination number of 4. DMG^- coordinates to Ni^{2+} by the lone pairs on the nitrogen atoms.

(a) How many DMG^- ions are needed to satisfy a coordination number of 4 on the central Ni^{2+} ion?

(b) What is the net charge after coordination occurs?

(c) How many atoms are in the ring formed by one DMG^- and one Ni^{2+}?

Check your answer to Problem-Solving Practice 22.8 by viewing Figure 22.11 at the Web site.

CONCEPTUAL EXERCISE   **22.10** Chelating and Complex Ions

Oxalate ion forms a complex ion with Mn^{2+} by coordinating at the oxygen lone pairs (see Figure 22.9).

(a) How many oxalate ions are needed to satisfy a coordination number of 6 on the central Mn^{2+} ion?

(b) What is the charge on this complex ion?

(c) How many atoms are in the ring formed between one oxalate ion and the central metal ion?

The nickel-dimethylglyoxime complex

$[Ni(H_2O)_6]^{2+}$
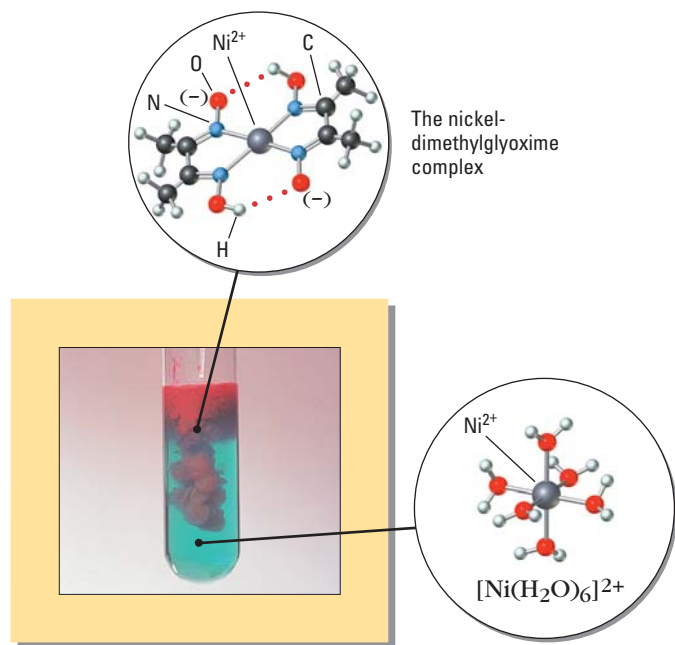
Active Figure 22.11   **The nickel-dimethylglyoxime complex.** Ni^{2+} ions react with the dimethylglyoximate anion (DMG^-) to form a beautiful red solid. **Go to the Active Figures menu at ThomsonNOW to test your understanding of the concepts in this figure.**

A Penny for Your Thoughts

You will need the following items to do the experiment:

- Two glasses or plastic cups that will each hold about 50 mL liquid
- About 30 to 40 mL household vinegar
- About 30 to 40 mL household ammonia
- A copper penny

Place the penny in one cup and add 30 to 40 mL vinegar to clean the surface of the penny. Let the penny remain in the vinegar until the surface of the penny is cleaner (reddish-coppery) than it was before (darker copper color). Pour off the vinegar and wash the penny thoroughly in running water.

Next, place the penny in the other cup and add 30 to 40 mL household ammonia. Observe the color of the solution over several hours.

1. What did you observe happening to the penny in the ammonia solution?

2. What did you observe happening to the ammonia solution?

3. Interpret what you observed happening to the solution on the nanoscale level, citing observations to support your conclusions.

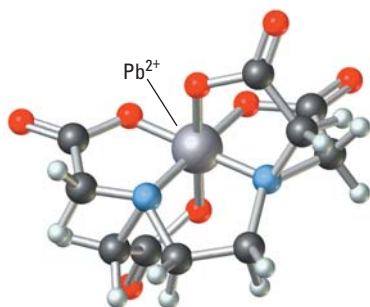4. What is necessary to form a complex ion?

5. Are all of these kinds of reactants present in the solution in this experiment? If so, identify them.

6. How do the terms "ligand," "central metal ion," and "coordination complex" apply to your experiment?

7. Try to write a formula for a complex ion that might form in this experiment.

Figure 22.12 A Pb^{2+}-EDTA complex ion. The structure of the chelate formed when the $EDTA^{4-}$ anion forms a complex with Pb^{2+}.

Some household products that contain EDTA. Check the label on your shampoo container. It will likely list disodium EDTA as an ingredient. The EDTA in this case has a 2− charge because two of the four organic acid groups have each lost an H^+, but $EDTA^{2-}$ still coordinates to metal ions in the shampoo.

For metals that display a coordination number of 6, an especially effective ligand is the **hexadentate** ethylenediaminetetraacetate ion (abbreviated EDTA; Figure 22.9) that encapsulates and firmly binds metal ions. It has six lone pair donor atoms (four O atoms and two N atoms) that can coordinate to a single metal ion, so $EDTA^{4-}$ is an excellent chelating ligand. $EDTA^{4-}$ is often added to commercial salad dressing to remove traces of metal ions from solution, because these metal ions could otherwise accelerate the oxidation of oils in the product and make them rancid.

Another use of $EDTA^{4-}$ is in bathroom cleansers, where it removes hard water deposits of insoluble $CaCO_3$ and $MgCO_3$ by chelating Ca^{2+} or Mg^{2+} ions, allowing them to be rinsed away. EDTA is also used in the treatment of lead and mercury poisoning because it has the ability to chelate these metals and aid in their removal from the body (Figure 22.12).

Coordination compounds of d-block transition metals are often colored, and the colors of the complexes of a given transition metal ion depend on both the metal ion and the ligand (Figure 22.13). Many transition metal coordination compounds are used as pigments in paints and dyes. For example, Prussian blue, $Fe_4[Fe(CN)_6]_3$, a deep-blue compound known for hundreds of years, is the "bluing agent" in engineering blueprints. The origin of colors in coordination compounds will be discussed in Section 22.7.

CONCEPTUAL EXERCISE   22.11 Complex Ions

Prussian blue contains two kinds of iron ions. What is the charge of the iron in
(a) The complex ion $[Fe(CN)_6]^{4-}$?
(b) The iron ion not in the complex ion?

Geometry of Coordination Compounds and Complex Ions

The geometry of a complex ion or coordination compound is dictated by the arrangement of the electron donor atoms of the ligands attached to the central metal ion. Although other geometries are possible, we will discuss only the four

(a) (b)
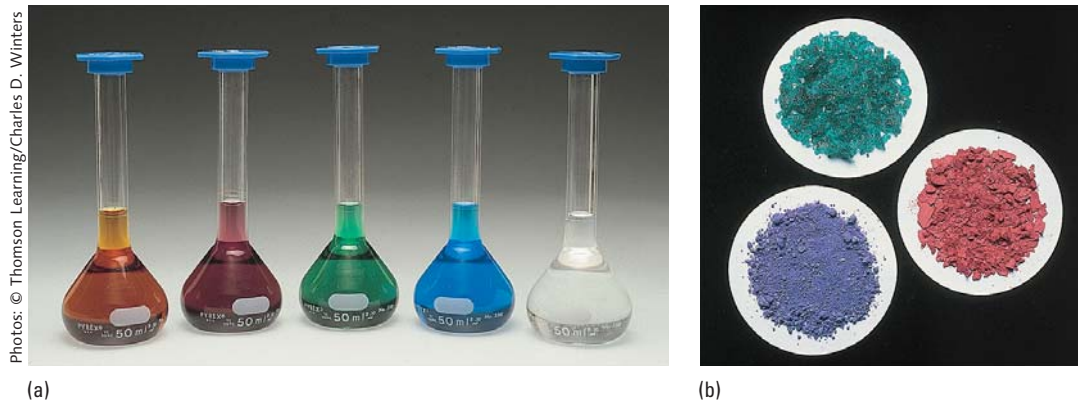
Figure 22.13 **Color of transition metal compounds.** (a) Concentrated aqueous solutions of the nitrate salts containing hydrated transition metal ions of (*left to right*) Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Aqueous Zn^{2+} compounds are colorless. (b) The colors of the complexes of a given transition metal ion depend on the ligand(s). All of the complexes pictured here contain the Ni^{2+} ion. The green solid is $[Ni(H_2O)_6](NO_3)_2$; the purple solid is $[Ni(NH_3)_6]Cl_2$; the red solid is $Ni(dimethylglyoximate)_2$.

most common ones, those associated with coordination numbers of 2, 4, and 6. To simplify matters, we will consider only monodentate ligands, L, bonded to a central metal ion, M^{n+}.

Coordination Number = 2, ML_2^{n+}

All such complex ions have a *linear* geometry with the two ligands on opposite sides of the central metal ion to give an L—M—L bond angle of 180°, such as that in $[Ag(NH_3)_2]^+$. Other examples are $[CuCl_2]^-$ and $[Au(CN)_2]^-$, the complex ion used to extract gold from ores (p. 1078).

$[Cl-Cu-Cl]^-$ $[H_3N-Ag-NH_3]^+$

Coordination Number = 4, ML_4^{n+}

Four-coordinate complex ions have either tetrahedral or square planar geometries. In the *tetrahedral* case, the four monodentate ligands are at the corners of a tetrahedron, such as in $[Zn(NH_3)_4]^{2+}$. In *square pla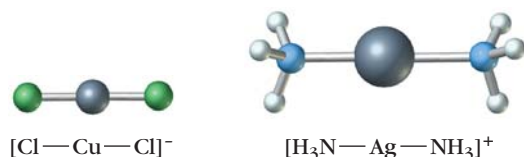nar* geometry, the ligands lie in a plane at the corners of a square as in $[Ni(CN)_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ ions.

Tetrahedral   Square planar
$[Zn(NH_3)_4]^{2+}$ $[Pt(NH_3)_4]^{2+}$
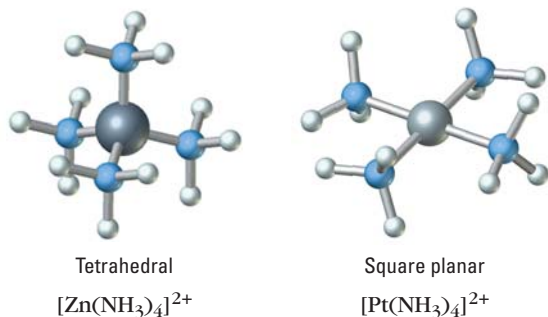
Alfred Werner
1866–1919

In 1893, while still a young professor, Alfred Werner published a revolutionary paper about transition metal compounds. He asserted that transition metal ions could exhibit a secondary valence as well as a primary one, such as in $CoCl_3 \cdot 6\ NH_3$ (now written as $[Co(NH_3)_6]Cl_3$). The primary valence was represented by the ionic bonds between Co^{3+} and the chloride ions; the secondary valence was represented by the coordinate covalent bonds between the metal ion and six NH_3 molecules, what we now called the coordination sphere around the central metal ion. Werner also made the inspired proposal that the ammonia molecules were octahedrally coordinated around the Co^{3+} ion, thereby laying the foundation for understanding the geometry of complex ions. For his groundbreaking work, Werner received the 1913 Nobel Prize in chemistry.
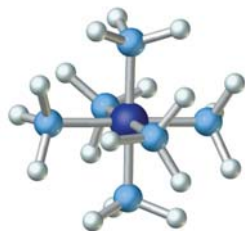
Octahedral
$[Co(NH_3)_6]^{3+}$

Coordination Number = 6, ML_6^{n+}

Octahedral geometry is characteristic of this coordination number. The six ligands are at the corners of an octahedron with the central metal ion at its center. Octahedral geometry can be regarded as derived from a square planar geometry by adding two ligands, one above and one below the square plane. Two common octahedral complex ions are $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, in which the six ligands are equidistant from the central metal ion and all six ligand sites are equivalent.

Isomerism in Coordination Compounds and Complex Ions

Various types of isomerism have been discussed previously with regard to organic compounds. *Constitutional isomerism* occurs with molecules that have the same molecular formula but differ in the way their atoms are connected together, such as occurs with butane and 2-methylpropane (⟸ *p. 88). Stereoisomerism* is a second general category of iso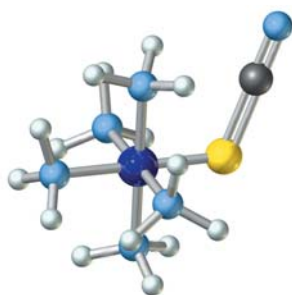merism in which the isomers have the same bond connections, but the atoms are arranged differently in space. One type of stereoisomerism is *geometric isomerism,* such as that found in *cis-* and *trans-*1,2-dichloroethene (⟸ *p. 345).* The other type of stereoisomerism is *optical isomerism,* which occurs when mirror images are nonsuperimposable (⟸ *p. 559).* Constitutional, geometric, and optical isomers also occur with coordination complex ions and coordination compounds.

Linkage Isomerism, a Type of Constitutional Isomerism

Linkage isomerism occurs when a ligand can bond to the central metal using either of two different electron-donating atoms. Thiocyanato $(SCN)^-$ and isothiocyanato $(NCS)^-$ ions are examples of such ligands with coordination to a metal ion by sulfur in the first case and by nitrogen in the second, as illustrated for the Co^{3+} complex ions shown in the margin.

Geometric Isomerism

Geometric isomerism does not exist in tetrahedral complex ions because all the corners of a tetrahedron are equivalent. Geometric isomerism, however, does occur with square planar complex ions and compounds of the type Ma_2b_2 or Ma_2bc, where M is the central metal ion and a, b, and c are different ligands. The square planar coordination compound $[Pt(NH_3)_2Cl_2]$, an Ma_2b_2 type, occurs in two geometric forms. The *cis-*$[Pt(NH_3)_2Cl_2]$ isomer has the chloride ligands as close as possible at 90° to one another. In *trans-*$[Pt(NH_3)_2Cl_2]$, the chloride ions are as far apart as possible, directly across the square plane of the molecule at 180° from each other.

pentaammine-
thiocyanatocobalt(III) ion
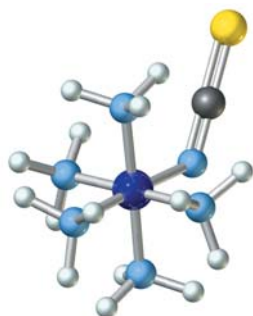
pentaammine-
isothiocyanatocobalt(III) ion
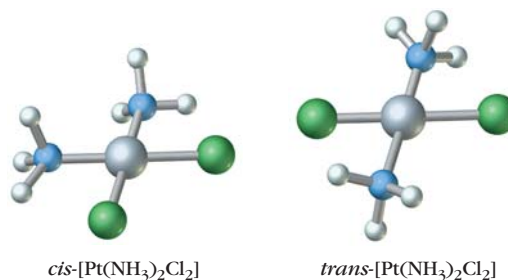
cis-$[Pt(NH_3)_2Cl_2]$ *trans-*$[Pt(NH_3)_2Cl_2]$

These two isomers differ in water solubility, color, melting point, and chemical reactivity. The *cis* isomer is used in cancer chemotherapy, whereas the *trans* form is not effective against cancer.

Cis-trans isomerism is also possible in octahedral complex ions and compounds, as illustrated with $[Co(NH_3)_4Cl_2]^+$. In this complex ion the *cis* isomer has the chloride ions adjacent to each other; the *trans* isomer has them opposite each other. The differences in properties are striking, particularly the color. The *cis* isomer is violet, whereas the *trans* form is green.

cis-$[Co(NH_3)_4Cl_2]^+$
(violet)

trans-$[Co(NH_3)_4Cl_2]^+$
(green)

PROBLEM-SOLVING EXAMPLE 22.9   Geometric Isomerism

How many geometric isomers are there for $[Co(en)_2Cl_2]^+$?

Answer   Only two geometric isomers are possible, *cis* and *trans*.

trans   *cis*

Strategy and Explanation   Start by putting the two Cl^- ions in *trans* positions, that is, one at the "top" of the octahedron and the other at the "bottom." The two ethylenediamine ligands (en), represented here as $\widehat{N\ N}$, occupy the other four sites around the cobalt ion. This is the *trans* isomer. The *cis* isomer has the Cl^- ions in adjacent *(cis)* positions.

PROBLEM-SOLVING PRACTICE 22.9

How many geometric isomers are there for the square planar compound $[Pt(NH_3)_2ClBr]$?

EXERCISE   22.12 Geometric Isomerism

How many isomers are possible for $[Co(NH_3)_3Cl_3]$? Write the structural formulas of the isomers.

Optical Isomerism

Optical isomers are mirror images that are not superimposible. Such nonsuperimposable mirror images are known as *enantiomers* (⟸ *p. 560)*. An example of a complex ion that has optical isomerism is $[Cr(en)_2Cl_2]^+$. There are two enantiomers, as shown in Figure 22.14. No matter how they are twisted and turned, the two enantiomers are nonsuperimposable.

$[Cr(en)_2Cl_2]^+$

Figure 22.14   Optical isomerism in $[Cr(en)_2Cl_2]^+$. The ion on the left cannot be superimposed on its mirror image *(right)*.

Optical isomerism is not possible for square planar complexes based on the geometry around the metal ion; the mirror images are superimposable. Although optical isomers of tetrahedral complex ions with four different ligands are theoretically possible, no such stable complexes are known.

Coordination Compounds and Life

Bioinorganic chemistry, the study that applies chemical principles to inorganic ions and compounds in biological systems, is a rapidly growing field centered mainly around coordination compounds. This is because the very existence of living systems depends on many coordination compounds in which metal ions are chelated to the nitrogen and oxygen atoms in proteins and especially in enzymes. Copper-containing proteins, for example, give the blood of crabs, lobsters, and snails its blue color, as well as transport oxygen.

In humans, molecular oxygen (O_2) is transported through the circulatory system by hemoglobin, a very large protein (molecular weight of about 68,000 amu) in red blood cells. Hemoglobin is blue but becomes red when oxygenated. This is why arterial blood is bright red (high O_2 concentration) and blood in veins is bluish (low O_2 concentration).

A hemoglobin molecule carries four O_2 molecules, each of which forms a coordinate covalent bond to one of four Fe^{2+} ions. Each Fe^{2+} ion is at the center of one heme, a nonprotein part of the hemoglobin molecule that consists of four linked nitrogen-containing rings (Figure 22.15). Bound in this way, molecular oxygen is carried to the cells, where it is released as needed by breaking the Fe—O_2 coordinate covalent bond.

Other substances that can donate an electron pair can also bond to the Fe^{2+} in heme. Carbon monoxide is such a ligand and forms an exceptionally strong Fe^{2+}—CO bond, nearly 200 times stronger than the O_2—Fe^{2+} bond. Therefore, when a person breathes in CO, it displaces O_2 from hemoglobin and prevents red blood cells from carrying oxygen. The initial effect is drowsiness. But if CO inhalation continues, cells deprived of oxygen can no longer function and the person suffocates.

Structures similar to the oxygen-carrying unit in hemoglobin are also found in other biologically important compounds, including such diverse ones as myoglobin and vitamin B-12. Myoglobin, like hemoglobin, contains Fe^{2+} and carries and stores

The blue blood of horseshoe crabs is used to test for bacterial contamination of drugs.

It is interesting (and fortunate) that $N \equiv N$ does not behave chemically like $C \equiv O$, even though each contains 14 electrons.
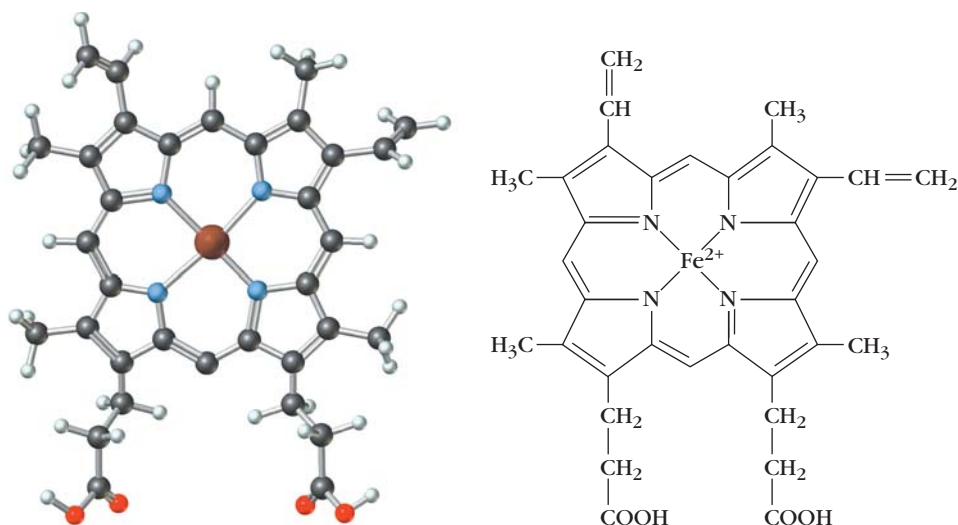
Figure 22.15   Heme, the carrier of Fe^{2+} in hemoglobin. Fe^{2+} is coordinated to four nitrogen atoms in heme. There are four hemes in each hemoglobin molecule.

molecular oxygen, principally in muscles. At the center of a vitamin B-12 molecule is a Co^{3+} ion bonded to the same type of group that Fe^{2+} bonds to in hemoglobin. Vitamin B-12 is the only known dietary use of cobalt, but it makes cobalt an essential mineral *(⟸ p. 111).*

The dietary necessity of zinc for humans has become established only since the 1980s. Zinc, in the form of Zn^{2+} ions, is essential to the functioning of several hundred enzymes, including those that catalyze the breaking of P—O—P bonds in adenosine triphosphate (ATP), an important energy-releasing compound in cells *(⟸ p. 895).*

Copper ranks third among biologically important transition metal ions in humans, trailing only iron and zinc. Although we generally excrete any dietary excess of copper, a genetic defect causes Wilson's disease, a condition in which Cu^{2+} accumulates in the liver and brain. Fortunately, Wilson's disease can be treated by administering chelating agents that coordinate excess Cu^{2+} ions, allowing them to be excreted harmlessly.

10-4
ANGULAR OVERLAP

Although the formation of bonding orbitals is included in the description of the ligand field model, there is no explicit use of the energy change that results. In addition, the ligand field approach to energy levels in coordination complexes is more difficult to use when considering an assortment of ligands or structures with symmetry other than octahedral, square planar, or tetrahedral. A variation with the flexibility to deal with a variety of possible geometries and with a mixture of ligands is called the **angular overlap** model.[17,18] This approach estimates the strength of interaction between individual ligand orbitals and metal d orbitals based on the overlap between them and then combines these values for all ligands and all d orbitals for the complete picture. Both σ and π interactions are considered, and different coordination numbers and geometries can be treated. The term angular overlap is used because the amount of overlap depends strongly on the angles of the metal orbitals and the angle at which the ligand approaches.

In the angular overlap approach, the energy of a metal d orbital in a coordination complex is determined by summing the effects of each of the ligands on that orbital. Some ligands will have a strong effect on a particular d orbital, some a weaker effect, and some no effect at all, because of their angular dependence. Similarly, both σ and π interactions must be taken into account to determine the final energy of a particular orbital. By systematically considering each of the five d orbitals, we can use this approach to determine the overall energy pattern corresponding to the coordination geometry around the metal.

10-4-1 SIGMA-DONOR INTERACTIONS

The strongest σ interaction is between a metal d_{z^2} orbital and a ligand p orbital (or a hybrid ligand orbital of the same symmetry), as shown in Figure 10-19. The strength of all other σ interactions is determined relative to the strength of this reference interaction. Interaction between these two orbitals results in a bonding orbital, which has a larger component of the ligand orbital, and an antibonding orbital, which is largely metal orbital in composition. Although the increase in energy of the antibonding orbital is larger than the decrease in energy of the bonding orbital, we will approximate the molecular orbital energies by an increase in the antibonding (mostly metal d) orbital of e_σ and a decrease in energy of the bonding (mostly ligand) orbital of e_σ.

Similar changes in orbital energy result from other interactions between metal d orbitals and ligand orbitals, with the magnitude dependent on the ligand location and the specific d orbital being considered. Table 10-11 gives values of these energy changes for a variety of shapes. Calculation of the numbers in the table (all in e_σ units) is beyond the
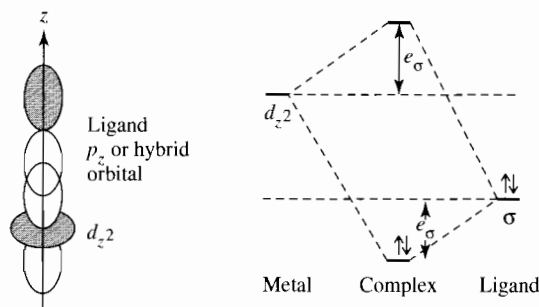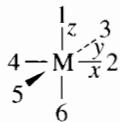

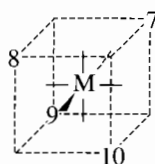**FIGURE 10-19** Sigma Interaction for Angular Overlap.

[17]E. Larsen and G. N. La Mar, *J. Chem. Educ.*, **1974**, *51*, 633. (Note: There are misprints on pp. 635 and 636.)

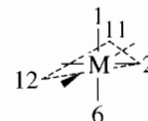[18]J. K. Burdett, *Molecular Shapes*, Wiley-Interscience, New York, 1980.

TABLE 10-11
Angular Overlap Parameters: Sigma Interactions

Octahedral positions

Tetrahedral positions

Trigonal-bipyramidal positions

Sigma Interactions (all in units of e_σ)
Metal d Orbital

CN	Shape	Positions	Ligand Position	z^2	$x^2 - y^2$	xy	xz	yz
2	Linear	1, 6	1	1	0	0	0	0
3	Trigonal	2, 11, 12	2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	T shape	1, 3, 5	3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	Tetrahedral	7, 8, 9, 10	4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	Square planar	2, 3, 4, 5	5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	Trigonal bipyramidal	1, 2, 6, 11, 12	6	1	0	0	0	0
5	Square pyramidal	1, 2, 3, 4, 5	7	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
6	Octahedral	1, 2, 3, 4, 5, 6	8	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
			9	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
			10	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
			11	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
			12	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0

scope of this book, but the reader should be able to justify the numbers qualitatively by comparing the amount of overlap between the orbitals being considered.

The angular overlap approach is best described by example. We will consider first the most common geometry for coordination complexes, octahedral.

EXAMPLE

$[M(NH_3)_6]^{n+}$ $[M(NH_3)_6]^{n+}$ ions are examples of octahedral complexes with only σ interactions. The ammonia ligands have no π orbitals available, either of donor or acceptor character, for bonding with the metal ion. The lone pair orbital is mostly nitrogen p_z orbital in composition, and the other p orbitals are used in bonding to the hydrogens (see Figure 5-31).

In calculating the orbital energies in a complex, the value for a given d orbital is the sum of the numbers for the appropriate ligands in the vertical column for that orbital in Table 10-11. The change in energy for a specific ligand orbital is the sum of the numbers for all d orbitals in the horizontal row for the required ligand position.

Metal d Orbitals d_{z^2} orbital: The interaction is strongest with ligands in positions 1 and 6, along the z axis. Each interacts with the orbital to raise its energy by e_σ. The ligands in positions 2, 3, 4, and 5 interact more weakly with the d_{z^2} orbital, each raising the energy of the orbital by $\frac{1}{4} e_\sigma$. Overall, the energy of the d_{z^2} orbital is increased by the sum of all these interactions, for a total of $3e_\sigma$.

$d_{x^2 - y^2}$ **orbital:**   The ligands in positions 1 and 6 do not interact with this metal orbital. However, the ligands in positions 2, 3, 4, and 5 each interact to raise the energy of the metal orbital by $\frac{3}{4} e_\sigma$, for a total increase of $3e_\sigma$.

d_{xy}, d_{xz}, **and d_{yz} orbitals:**   None of these orbitals interact in a sigma fashion with any of the ligand orbitals, so the energy of these metal orbitals remains unchanged.

FIGURE 10-20 Energies of d Orbitals in Octahedral Complexes: Sigma-Donor Ligands. $\Delta_o = 3e_\sigma$. Metal s and p orbitals also contribute to the bonding molecular orbitals.
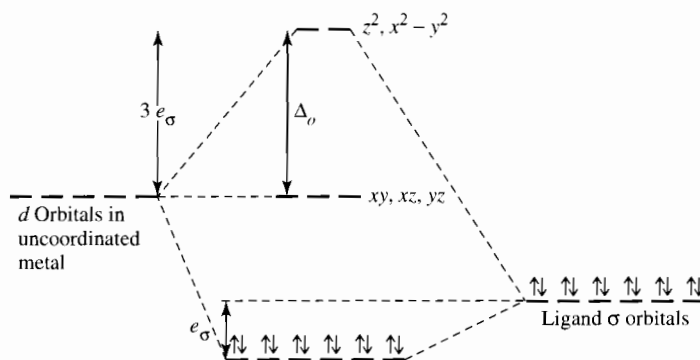
Ligand Orbitals   The energy changes for the ligand orbitals are the same as those above for each interaction. The totals, however, are taken *across a row* of the Table 10-11, including each of the d orbitals.

Ligands in positions 1 and 6 interact strongly with d_{z^2} and are lowered by e_σ. They do not interact with the other d orbitals.

Ligands in positions 2, 3, 4, and 5 are lowered by $\frac{1}{4} e_\sigma$ by interaction with d_{z^2} and by $\frac{3}{4} e_\sigma$ by interaction with $d_{x^2-y^2}$, for a total of e_σ.

Overall, each ligand orbital is lowered by e_σ.

The resulting energy pattern is also shown in Figure 10-20. This result is the same as the pattern obtained from the ligand field approach. Both describe how the metal complex is stabilized: as two of the d orbitals of the metal increase in energy and three remain unchanged, the six ligand orbitals fall in energy, and electron pairs in those orbitals are stabilized in the formation of ligand-metal bonds. The net stabilization is $12e_\sigma$ for the bonding pairs; any d electrons in the upper (e_g) level are destabilized by $3e_\sigma$ each.

The more complete MO picture that includes use of the metal s and p orbitals in the formation of the bonding MOs and the four additional antibonding orbitals was shown in Figure 10-5. There are no examples of complexes with electrons in the antibonding orbitals from s and p orbitals, and these high-energy antibonding orbitals are not significant in describing the spectra of complexes, so we will not consider them further.


EXERCISE 10-8

Using the angular overlap model, determine the relative energies of d orbitals in a metal complex of formula ML_4 having tetrahedral geometry. Assume that the ligands are capable of σ interactions only.

How does this result for Δ_t compare with the value for Δ_o?
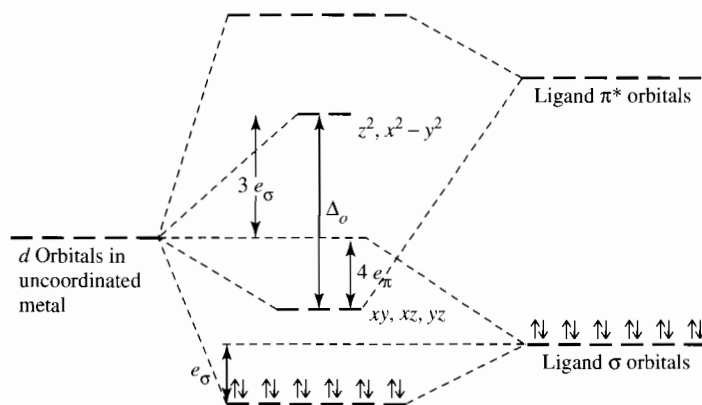

10-4-2 PI-ACCEPTOR INTERACTIONS

Ligands such as CO, CN^-, and phosphines (of formula PR_3) are π acceptors, with empty orbitals that can interact with metal d orbitals in a π fashion. In the angular overlap model, the strongest π interaction is considered to be between a metal d_{xz} orbital and a ligand π^* orbital, as shown in Figure 10-21. Because the ligand π^* orbitals are higher in energy than the original metal d orbitals, the resulting bonding MOs are lower in energy than the metal d orbitals (a difference of e_π) and the antibonding MOs are higher in energy. The d electrons then occupy the bonding MO, with a net energy change of $-4e_\pi$ for each electron, as in Figure 10-22.

Because the overlap for these orbitals is smaller than the σ overlap described in the previous section, $e_\pi < e_\sigma$. The other π interactions are weaker than this reference interaction, with the magnitudes depending on the degree of overlap between the orbitals. Table 10-12 gives values for ligands at the same angles as in Table 10-11.
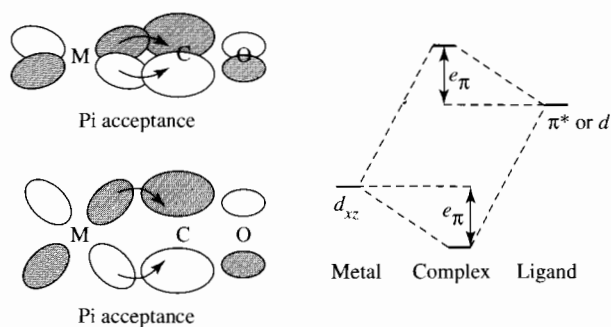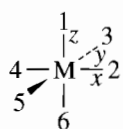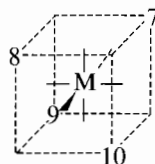
FIGURE 10-21 Pi-Acceptor Interactions.

FIGURE 10-22 Energies of d Orbitals in Octahedral Complexes: Sigma-Donor and Pi-Acceptor Ligands. $\Delta_o = 3e_\sigma + 4e_\pi$. Metal s and p orbitals also contribute to the bonding molecular orbitals.
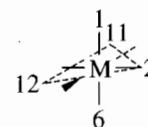
TABLE 10-12
Angular Overlap Parameters: Pi Interactions

Octahedral positions

Tetrahedral positions

Trigonal bipyramidal positions

CN	Shape	Positions
2	Linear	1, 6
3	Trigonal	2, 11, 12
3	T shape	1, 3, 5
4	Tetrahedral	7, 8, 9, 10
4	Square planar	2, 3, 4, 5
5	Trigonal bipyramidal	1, 2, 6, 11, 12
5	Square pyramidal	1, 2, 3, 4, 5
6	Octahedral	1, 2, 3, 4, 5, 6

$Pi\ Interactions\ (all\ in\ units\ of\ e_\pi)$
$Metal\ d\ Orbital$

Ligand Position	z^2	$x^2 - y^2$	xy	xz	yz
1	0	0	0	1	1
2	0	0	1	1	0
3	0	0	1	0	1
4	0	0	1	1	0
5	0	0	1	0	1
6	0	0	0	1	1
7	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
8	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
9	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
10	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
11	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
12	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$

FIGURE 10-23 Pi-Donor Interactions.

EXAMPLE

$[M(CN)_6]^{n-}$ The result of these interactions for $[M(CN)_6]^{n-}$ complexes is shown in Figure 10-22. The d_{xy}, d_{xz}, and d_{yz} orbitals are lowered by $4e_\pi$ each and the six ligand positions have an average increase in orbital energy of $2e_\pi$. The resulting ligand π^* orbitals have high energies and are not involved directly in the bonding. The net value of the t_{2g}-e_g split is $\Delta_o = 3e_\sigma + 4e_\pi$.

10-4-3 PI-DONOR INTERACTIONS

The interactions between occupied ligand p, d, or π^* orbitals and metal d orbitals are similar to those in the π-acceptor case. In other words, the angular overlap model treats π-donor ligands similarly to π-acceptor ligands except that *for π-donor ligands, the signs of the changes in energy are reversed*, as shown in Figure 10-23. The metal d orbitals are raised in energy, whereas the ligand π orbitals are lowered in energy. The overall effect is shown in Figure 10-24.

EXAMPLE

$[MX_6]^{n-}$ Halide ions donate electron density to a metal via p_y orbitals, a σ interaction; the ions also have p_x and p_z orbitals that can interact with metal orbitals and donate additional electron density via π interactions. We will use $[MX_6]^{n-}$ as our example, where X is a halide ion or other ligand that is both a σ and a π donor.

d_{z^2} **and** $d_{x^2-y^2}$ **orbitals:**   Neither of these orbitals has the correct orientation for π interactions; therefore, the π orbitals have no effect on the energies of these d orbitals.

d_{xy}, d_{xz}, **and** d_{yz} **orbitals:**   Each of these orbitals interacts in a π fashion with four of the ligands. For example, the d_{xy} orbital interacts with ligands in positions 2, 3, 4, and 5 with a
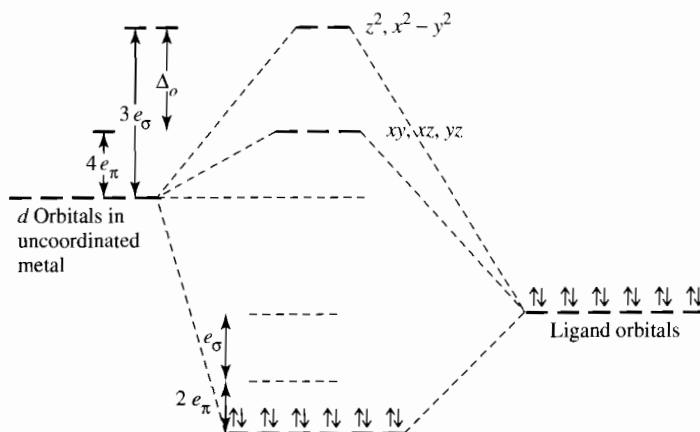

FIGURE 10-24 Energies of d Orbitals in Octahedral Complexes: Sigma-Donor and Pi-Donor Ligands. $\Delta_o = 3e_\sigma - 4e_\pi$. Metal s and p orbitals also contribute to the bonding molecular orbitals.

strength of $1e_\pi$, resulting in a total increase of the energy of the d_{xy} orbital of $4e_\pi$ (the interaction with ligands at positions 1 and 6 is zero). The reader should verify by using Table 10-12 that the d_{xz} and d_{yz} orbitals are also raised in energy by $4e_\pi$.

The overall effect on the energies of the d orbitals of the metal, including both σ and π donor interactions, is shown in Figure 10-24.

EXERCISE 10-9

Using the angular overlap model, determine the splitting pattern of d orbitals for a tetrahedral complex of formula MX_4, where X is a ligand that can act as σ donor and π donor.

In general, in situations involving ligands that can behave as both π acceptors and π donors (such as CO and CN^-), the π-acceptor nature predominates. Although π-donor ligands cause the value of Δ_o to decrease, the larger effect of the π-acceptor ligands cause Δ_o to increase. Pi-acceptor ligands are better at splitting the d orbitals (causing larger changes in Δ_o).

EXERCISE 10-10

Determine the energies of the d orbitals predicted by the angular overlap model for a square-planar complex:

a. Considering σ interactions only.

b. Considering both σ-donor and π-acceptor interactions.

Angular overlap calculations of the energies expected for different numbers of d electrons and different geometries can give us some indication of relative stabilities. Here, we will consider the three major geometries, octahedral, square planar, and tetrahedral. In Chapter 12, similar calculations will be used to help describe reactions at the coordination sites.

Figure 10-27 shows the results of angular overlap calculations for d^0 through d^{10} electron configurations. Figure 10-27(a) compares octahedral and square-planar geometries. Because of the larger number of bonds formed in the octahedral complexes, they are more stable (lower energy) for all configurations except d^8, d^9, and d^{10}. A low-spin square-planar geometry has the same net energy as either a high- or low-spin octahedral geometry for all three of these configurations. This indicates that these configurations are the most likely to have square-planar structures, although octahedral is equally probable from this approach.

Figure 10-27(b) compares square-planar and tetrahedral structures. For strong-field ligands, square planar is preferred in all cases except d^0, d^1, d^2, and d^{10}. In those cases, the angular overlap approach predicts that the two structures are equally probable. For weak-field ligands, tetrahedral and square-planar structures also have equal energies in the d^5, d^6, and d^7 cases.

How accurate are these predictions? Their success is variable, because there are other differences between metals and between ligands. In addition, bond lengths for the same ligand-metal pair depend on the geometry of the complex. One factor that must be included in addition to the d electron energies is the interaction of the s and p orbitals of the metal with the ligand orbitals. The bonding orbitals from these interactions are at a lower energy than those from d orbital interactions and are therefore completely filled. Their overall energy is, then, a combination of the energy of the metal atomic orbitals (approximated by their orbital potential energies) and the ligand orbitals. Orbital potential energies for transition metals become more negative with increasing atomic number. As a result, the formation enthalpy for complexes also becomes more negative with increasing atomic number and increasing ionization energy. This trend provides a downward slope to the baseline under the contributions of the d orbital-ligand interactions shown in Figure 10-27(a). Burdett[25] has shown that the calculated values of enthalpy of hydration can reproduce the experimental values for enthalpy of hydration very well by using this technique. Figure 10-28 shows a simplified version of this, simply adding $-0.3e_\sigma$ (an arbitrary choice) to the total enthalpy for each increase in Z (which equals the number of d electrons). The parallel lines show this slope running through the d^0, d^5, and d^{10} points. Addition of a d electron beyond a completed spin set increases the hydration enthalpy until the next set is complete. Comparison with Figure 10-7, in which the experimental values are given, shows that the approach is at least approximately valid. Certainly other factors need to be included for complete agreement with experiment, but their influence seems small.

As expected from the values shown in Figure 10-27, Cu(II) (d^9) complexes show great variability in geometry. Complicating the simple picture used in this section is the change in bond distance that accompanies change in geometry. Overall, the two regular

[24]N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, pp. 1385–1386.

[25]J. K. Burdett, *J. Chem. Soc. Dalton Trans.*, **1976**, 1725.
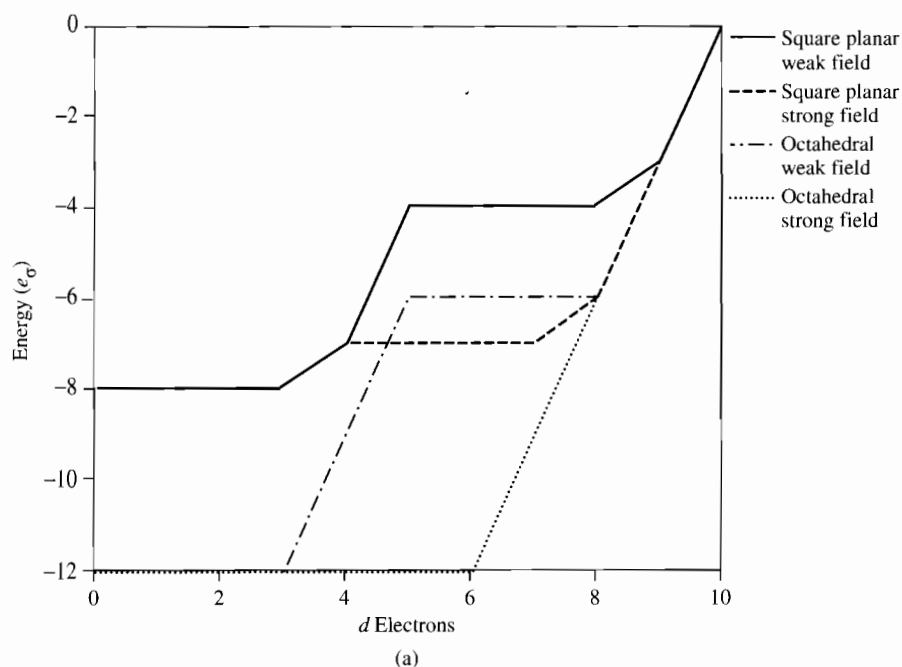
FIGURE 10-27 Angular Overlap Energies of four- and six-Coordinate Complexes. Only σ bonding is considered. (a) Octahedral and square-planar geometries, both strong- and weak-field cases. (b) Tetrahedral and square-planar geometries, both strong- and weak-field cases (there are no known low-spin tetrahedral complexes).
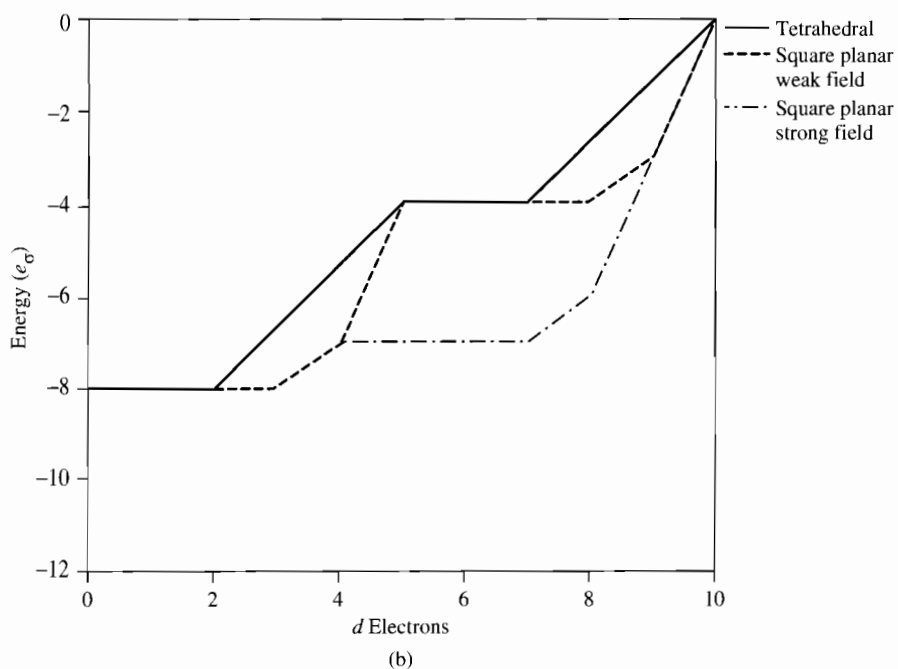
structures most commonly seen are tetragonal (four ligands in a square-planar geometry with two axial ligands at greater distances) and tetrahedral, sometimes flattened to approximately square planar. There are also trigonal-bipyramidal $[CuCl_5]^{3-}$ ions in $[Co(NH_3)_6][CuCl_5]$. By careful selection of ligands, many of the transition metal ions can form compounds with geometries other than octahedral. For d^8 ions, some of the simpler possibilities are the square-planar Au(III), Pt(II), and Pd(II) complexes. Ni(II) forms tetrahedral $[NiCl_4]^{2-}$, octahedral $[Ni(en)_3]^{2+}$, and square-planar $[Ni(CN)_4]^{2-}$ complexes, as well as other special cases such as the square-pyramidal $[Ni(CN)_5]^{3-}$.
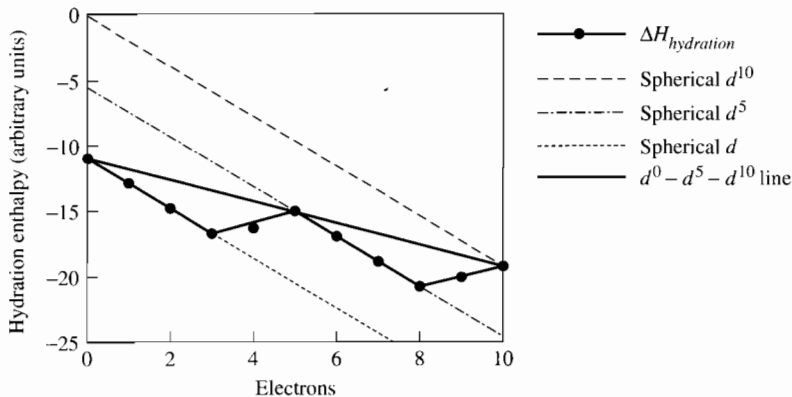
FIGURE 10-28 Simulated Hydration Enthalpies of M^{2+} Transition Metal Ions.

The d^7 Co(II) ion forms tetrahedral blue and octahedral pink complexes ($[CoCl_4]^{2-}$ and $[Co(H_2O)_6]^{2+}$ are simple examples), along with square-planar complexes when the ligands have strong planar tendencies ($[Co(salen)]$), where salen = bis(salicylaldehyde-ethylenediimine) and a few trigonal-bipyramidal structures ($[Co(CN)_5]^{3-}$). Many other examples can be found; descriptive works such as that by Greenwood and Earnshaw[26] should be consulted for these.

Using a square pyramid complex with ligands
that do not have pi interactions as an example.
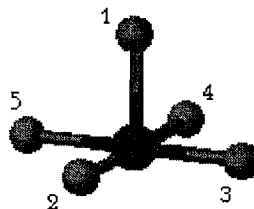
**1. Choose appropriate Structure type and
identify which positions to use from table**

M d orbitals

**2. Start with 5 d orbitals on the metal. Assume
one sigma donating orbital for each ligand.
These are at low energy to start and decrease
in energy upon interaction with the metal
center. They decrease in energy by 1 E_{sigma}
of energy.**

σ donor
5 L orbitals
ML_5 MOs
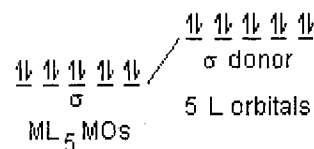
Structure	Atoms
Linear	1 and 6
Trigonal planar	2, 7, and 8
Square planar	2–5
Tetrahedron	9–12
Trigonal bipyramid	1,2,7,8, and 6
Square pyramid	1–5
Octahedron	1–6

Ligand Positions:		Metal ao			
	z^2	x^2-y^2	xz	yz	xy
1 σ	1	0	0	0	0
π	0	0	1	1	0
2 σ	1/4	3/4	0	0	0
π	0	0	1	0	1
3 σ	1/4	3/4	0	0	0
π	0	0	0	0	0
4 σ	1/4	3/4	0	0	1
π	0	0	1	0	0
5 σ	1/4	3/4	0	0	0
π	0	0	0	1	1
6 σ	1	0	0	0	0
π	0	0	1	1	0
7 σ	1/4	3/16	0	0	9/16
π	0	3/4	1/4	3/4	1/4
8 σ	1/4	3/16	0	0	9/16
π	0	3/4	1/4	3/4	1/4
9 σ	0	0	1/3	1/3	1/3
π	2/3	2/3	2/9	2/9	2/9
10 σ	0	0	1/3	1/3	1/3
π	2/3	2/3	2/9	2/9	2/9
11 σ	2/3	2/3	2/9	2/9	2/9
π	0	0	1/3	1/3	1/3
12 σ	0	0	1/3	1/3	1/3
π	2/3	2/3	2/9	2/9	2/9

**3. The d orbitals will be, if anything, sigma
antibonding. To tell how much for each, add
up the values for the sigma lines in the chart
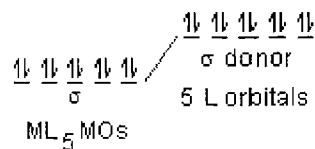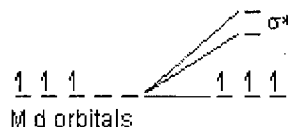for each of the positions that have ligands.**

$dz^2 = 1 + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} = 2$

$dx^2-y^2 = 0 + \frac{3}{4} + \frac{3}{4} + \frac{3}{4} + \frac{3}{4} = 3$

dxy, dxz and dyz all $= 0 + 0 + 0 + 0 + 0 = 0$

(this is antibinding by 2 E_{sigma})
(this is antibonding by 3 E_{sigma})
(these are nonbonding)

**4. Finally, redraw the MO diagram with those
d orbitals that have interaction moving up
in energy by the calculated amount.**

σ^*

M d orbitals

σ donor
5 L orbitals
ML_5 MOs

be overcome if the structure preference energy is greater than 1 e_σ (for observed e_σ).

The structure preference energies are plotted in Figure 9-4(A), from which apparent that the VSEPR/steric forces that favor the T_d geometry are unopposed for d^n ions with $n = 0, 1, 2$, and 10 only. For all others, the magnitude of e_σ is highly tant in determining the preference for D_{4h}. For sufficiently weak ligands (e_σ small spin case) it is clear that VSEPR forces are unopposed for the $n = 5, 6$, and 7 ions $n = 3, 4, 8$, and 9 ions the observed structures are likely to be intermediate flattened tetrahedron, D_{2d}) between square planar and tetrahedral when e_σ is small geometries in Table 9-2 for Cl^- as a ligand are completely explained in this way. stronger ligands NH_3 and CN^- you find examples of a preference for a low spin planar geometry—as predicted by the low spin graph of Figure 9-4(A).

By way of conclusion, *the formation of a T_d or D_{2d} complex is likely for the cases only by ligands that weakly interact with the metal ion because of intrinsic weak M—D bonds and/or because of unusual ligand steric requirements. More basi less hindered ligands will prefer to bind the metal with a planar geometry.*

Some useful conclusions can also be drawn from a comparison of the six- and for coordinate structures. This has been done graphically in Figure 9-4(B) and (C), when it is immediately seen that both high and low spin octahedral complexes are prefer over the high spin tetrahedral structures [Figure 9-4(B)]. This suggests that in addit to the basicity and steric factors just listed for the preparation of tetrahedral comple you must realize that stoichiometry control at a 4:1 ligand-to-metal-ion ratio is important consideration for formation of tetrahedral complexes.
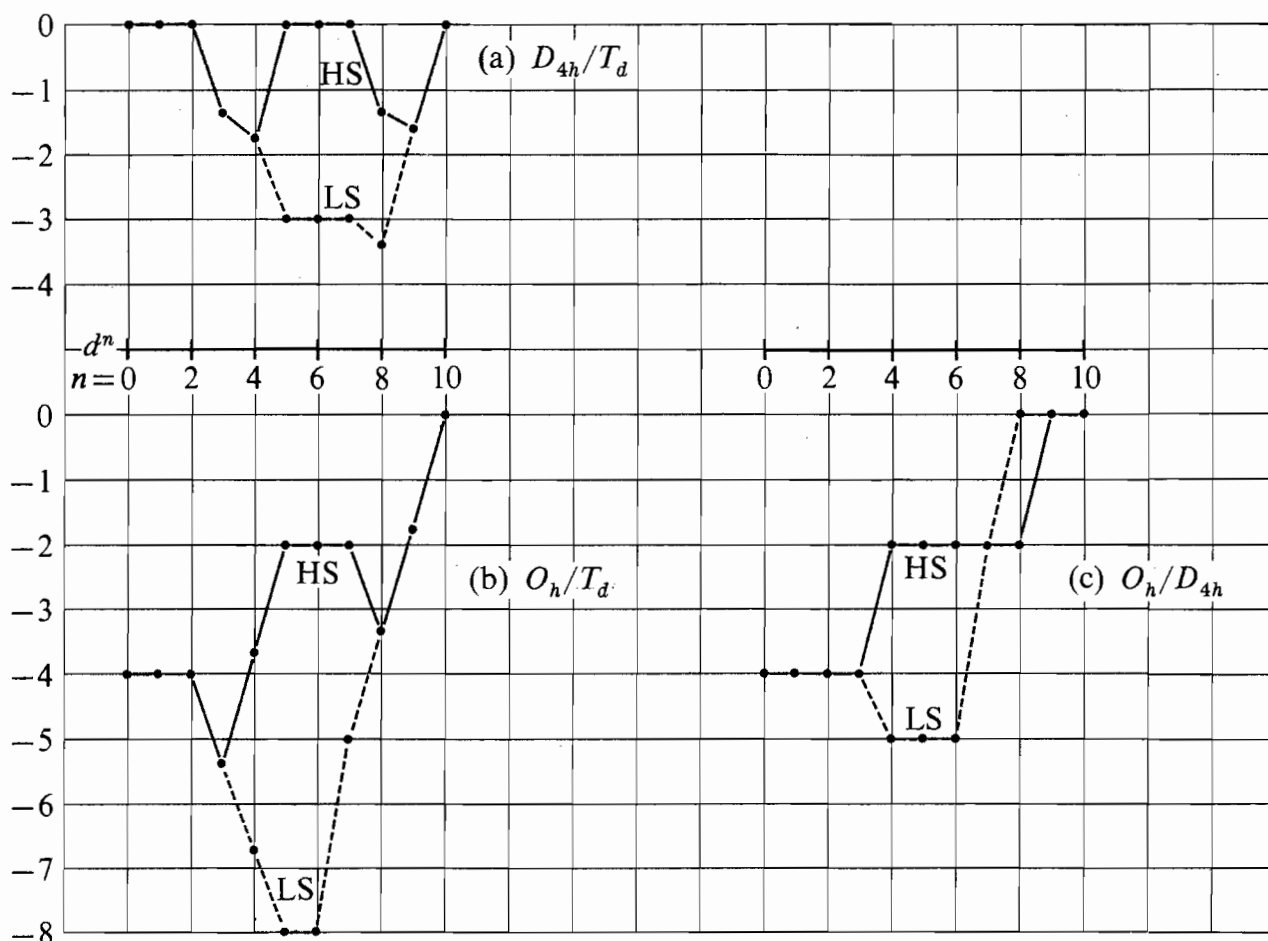

Figure 9-4. Structure preference energies. (A) $E(D_{4h}) - E(T_d)$;
(B) $E(O_h) - E(T_d)$; (C) $E(O_h) - E(D_{4h})$; units $= e_\sigma$. A negative value
means that the first named geometry is preferred.