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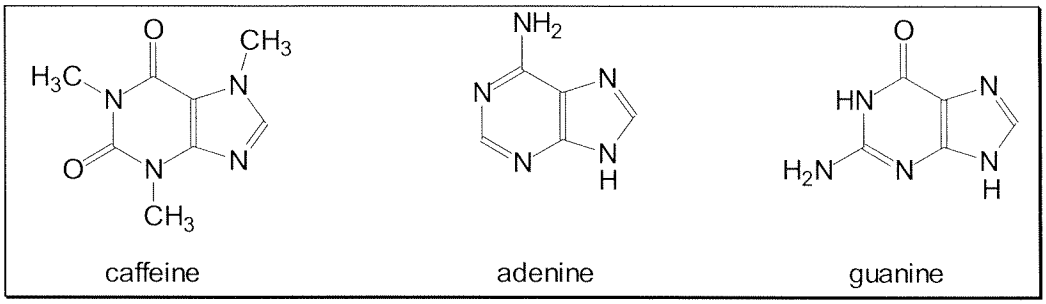
Department of Chemistry
Cairns Edition



CH1012
BOOK
OF
READINGS

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CHEMISTRY

The Molecular Nature of Matter and Change

Second Edition

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14.3 Group 1A(1): The Alkali Metals

The first group of elements in the periodic table is named for the alkal (basic) nature of their oxides and for the basic solutions the elements fo in water. Group 1A(1) provides a perfect example of regular trends with significant exceptions. All the elements in the group—lithium (Li), sodi (Na), potassium (K), rubidium (Rb), cesium (Cs), and rare, radioactive fr cium (Fr)—are very reactive metals. The Family Portrait of Group 1A(1) ments, on pages 548 and 549, is the first in a series that provides an overv of each of the main groups. Atomic and physical properties are summari on the left-hand page; representative reactions and some important co pounds appear on the right-hand page. Refer to these family portraits d ing the discussions because they present supporting information.

Why Are the Alkali Metals Soft, Low Melting, and Lightweight?

Unlike most metals, the alkali metals are soft: Na has the consistency of c butter, and K can be squeezed like clay. The alkali metals also have lo melting and boiling points than any other group of metals. Except for Li, th all melt below 100°C, and Cs melts a few degrees above room temperatu They also have lower densities than most metals: Li floats on lightwei household oil (see Sample Problem 1.5, p. 23).

The unusual physical behavior of the alkali metals can be traced to th atomic size, the largest in their respective periods, and to the ns^1 electr configuration. Because the single valence electron is relatively far from t nucleus, there is only a weak attraction between the delocalized electro and the atom cores. This weak metallic bonding means that the alkali me crystal structure can be easily deformed or broken down, which results in soft consistency and low melting point. These elements also have the low molar masses in their periods, so with their large atomic radii, they have atively low densities.

Why Are the Alkali Metals So Reactive?

The alkali metals are extremely reactive elements. They are *powerful reduc agents* and, thus, always occur in nature as 1+ cations rather than as metals. (As we discuss in Section 22.4, highly endothermic reducti processes are required to prepare the free metals industrially from molten salts.) The alkali metals reduce the halogens and form ionic solid reactions that release large quantities of heat. They reduce the hydrog water, reacting vigorously (Rb and Cs explosively) to form H_2 and me hydroxide solutions. They reduce O_2 in the air, so they tarnish rapi Because of this reactivity, Na and K are usually kept under mineral oil unreactive liquid) in the laboratory, and Rb and Cs are handled with glo under an inert argon atmosphere.

The ns^1 configuration, which you saw is the basis for their physical pro erties, is also the reason these metals form salts so readily. In a Born-H cycle of the reaction between an alkali metal and a nonmetal, for exam the solid metal separates into gaseous atoms, each of the atoms transfe outer electron to the nonmetal, and the resulting cations attract the ani into an ionic solid (Section 9.2). Several properties based on the ns^1 con uration relate to each of these steps.

1. *Low heat of atomization* (ΔH°_{atom}). Consistent with the alkali metals' melting and boiling points, their weak metallic bonding leads to low va

for ΔH°_{atom} (the energy needed to convert the solid into individual gaseous atoms), which decrease down the group:

$$E(s) \longrightarrow E(g) \qquad \Delta H_{atom} \text{ (Li > Na > K > Rb > Cs)*}$$

2. *Low IE and high charge density.* Each alkali metal has the largest size and lowest IE in its period. A great *decrease* in size occurs when the outer electron is lost: the volume of the Li^+ ion is less than 13% that of the Li atom! Thus, E^+ ions are small spheres with high charge density.

3. *High lattice energy.* The small cations can come close to the anions and release large amounts of energy as they crystallize. Thus, the endothermic atomization and ionization steps are easily outweighed by the highly exothermic formation of the solid. For a given anion, the trend in lattice energy is the inverse of the trend in cation size: *as the cation becomes larger, the lattice energy becomes smaller (less negative).* The steady decrease in the magnitude of the lattice energy within the Group 1A(1) and 2A(2) chlorides is shown in Figure 14.2.

4. *Despite the strong ionic attractions in the solid, nearly all Group 1A salts are water soluble.* The high charge density attracts water molecules to create a highly exothermic heat of hydration (ΔH_{hydr}), and a large increase in disorder arises when ions in the organized crystal become randomized and hydrated in solution; together, these factors outweigh the high lattice energy. The magnitude of the hydration energy *decreases* as ionic size increases:

$$E^+(g) \longrightarrow E^+(aq) \qquad \Delta H = -\Delta H_{hydr} \ (Li^+ > Na^+ > K^+ > Rb^+ > Cs^+)$$

Interestingly, the *smaller* ions attract water molecules strongly enough to form *larger hydrated ions*. This size trend has a major effect on the function of nerves, kidneys, and cell membranes because the *sizes* of $Na^+(aq)$ and $K^+(aq)$, the most common cations in cell fluids, influence their movement in and out of cells.

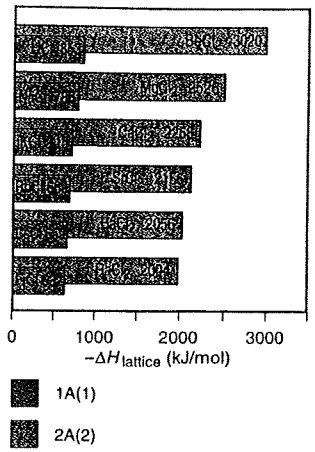


Figure 14.2 Lattice energies of the Group 1A(1) and 2A(2) chlorides. Lattice energies decrease regularly in both groups of metal chlorides as the cations become larger. Lattice energies for the 2A chlorides are greater because the 2A cations have higher charge and smaller size.

The Anomalous Behavior of Lithium

As we noted in discussing Table 14.1, all the Period 2 elements display some anomalous (unrepresentative) behavior within their groups. Even within the regular, predictable trends of Group 1A(1), Li has some atypical properties. It is the only member that forms a simple oxide and nitride, Li_2O and Li_3N, on reaction with O_2 and N_2 in air. Only Li forms molecular compounds with hydrocarbon groups from organic halides:

$$2Li(s) + CH_3CH_2Cl(g) \longrightarrow CH_3CH_2Li(s) + LiCl(s)$$

Organolithium compounds, such as CH_3CH_2Li, are liquids or low-melting solids that dissolve in nonpolar solvents and contain polar covalent $^{\delta-}C—Li^{\delta+}$ bonds. They are important reactants in the synthesis of organic compounds. Because of its small size and thus high charge density, the Li^+ ion can deform nearby electron clouds, which gives many lithium salts significant covalent bond character (Figure 14.3). Thus, LiCl, LiBr, and LiI, for example, are much more soluble in polar organic solvents, such as ethanol and acetone, than are the halides of Na and K, because the lithium halide dipole interacts with these solvents through dipole-dipole forces. The relatively high charge density of Li^+ makes separation of salts into ions more difficult in water; thus, the fluoride, carbonate, hydroxide, and phosphate of Li are much less soluble in water than those of Na and K.

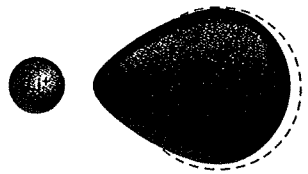


Figure 14.3 The effect of Li^+ charge density on a nearby electron cloud. The ability of the Li^+ ion to deform nearby electron clouds gives rise to many anomalous properties for a Group 1A(1) element. In this case, Li^+ polarizes an I^- ion, which gives some covalent character to lithium iodide, LiI.

*Throughout the chapter, we use E to represent any element in a group.

Some Reactions and Compounds

Important Reactions

The reducing power of the alkali metals (E) is shown in reactions 1 to 4. Some industrial applications of 1A(1) compounds are shown in reactions 5 to 7.

1. The alkali metals reduce H in H_2O from the +1 to the zero oxidation state:

$$2E(s) + 2H_2O(l) \longrightarrow 2E^+(aq) + 2OH^-(aq) + H_2(g)$$

The reaction becomes more vigorous down the group (*see photo*).

Potassium reacting with water

2. Alkali metals reduce oxygen, but the product depends on the metal. Li forms the oxide, Li_2O; Na forms the peroxide, Na_2O_2; K, Rb, and Cs form the superoxide, EO_2:

$$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$$

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

In self-contained breathing units, KO_2 reacts with H_2O and CO_2 in exhaled air to release O_2.

3. The alkali metals reduce hydrogen to form ionic (saltlike) hydrides:

$$2E(s) + H_2(g) \longrightarrow 2EH(s)$$

NaH is an industrial base and reducing agent that is used to prepare other reducing agents, such as $NaBH_4$.

4. The alkali metals reduce halogens to form ionic halides:

$$2E(s) + X_2 \longrightarrow 2EX(s) \qquad (X = F, Cl, Br, I)$$

5. Sodium chloride is the most important alkali halide.

(a) In the Downs process for the production of sodium metal (*Section 22.4*), reaction 4 is reversed by supplying electricity to molten NaCl:

$$2NaCl(l) \xrightarrow{\text{electricity}} 2Na(l) + Cl_2(g)$$

(b) In the chlor-alkali process (*Section 22.5*), NaCl(*aq*) is electrolyzed to form several key industrial chemicals:

$$2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)$$

(c) In its reaction with sulfuric acid, NaCl forms two major products:

$$2NaCl(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2HCl(g)$$

Sodium sulfate is important in the paper industry; HCl is essential in steel, plastics, textiles, and food production.

6. Sodium hydroxide is used in the formation of bleaching solutions:

$$2NaOH(aq) + Cl_2(g) \longrightarrow NaClO(aq) + NaCl(aq) + H_2O(l)$$

7. In an ion-exchange process (*Chemical Connections, Section 13.6*), water is "softened" by removal of dissolved "hard-water" ions, which displace Na^+ from a resin:

$$M^{2+}(aq) + Na_2Z(s) \longrightarrow MZ(s) + 2Na^+(aq)$$
$$(M = Mg, Ca; Z = \text{resin})$$

Important Compounds

...lithium chloride and lithium bromide, LiCl and LiBr. ...ion is so small, Li salts have a high affinity ...ter, a positive heat of solution. Thus, they are ...in dehumidifiers and air-cooling units.

...carbonate, Li_2CO_3. Used to make porcelain ...and lightened glasses and as a drug in the treat... ...depressive disorders.

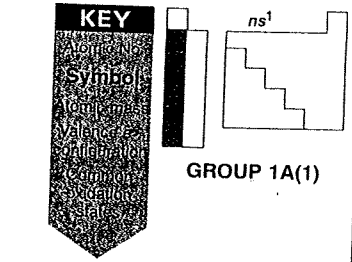
...chloride, NaCl. Millions of tons used in the in... ...duction of Na, NaOH, Na_2CO_3/$NaHCO_3$, Na_2SO_4, ...purified for use as table salt.

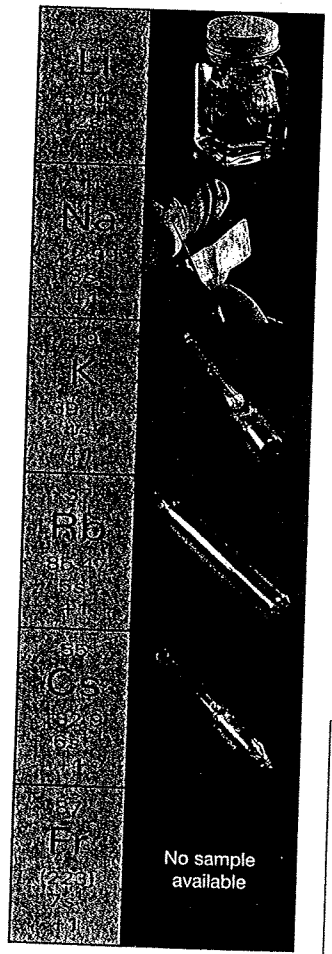
...carbonate and sodium hydrogen carbonate, ...$NaHCO_3$. Carbonate used as an industrial base ...make glass; hydrogen carbonate, which releases CO_2 ...at low temperatures (50° to 100°C), used in baking powder ...fire extinguishers.

5. Sodium hydroxide, NaOH. Most important industrial base; used to make bleach, sodium phosphates, and alcohols.

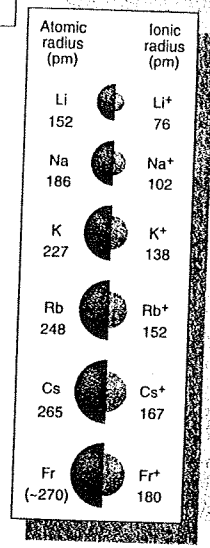
6. Potassium nitrate, KNO_3. Powerful oxidizing agent used in gunpowder and fireworks (*see photo*).

Key Atomic and Physical Properties





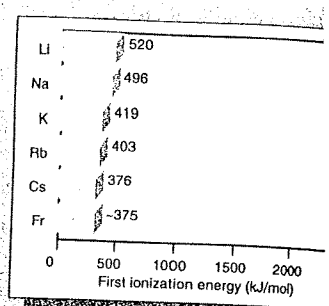
Atomic Properties

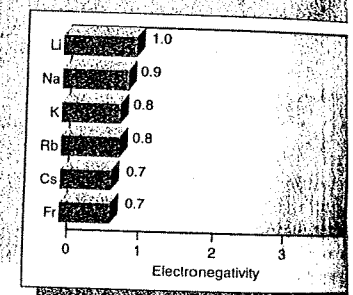


Group electron configuration is ns^1. All members have the +1 oxidation state and form an E^+ ion.

Atoms have the largest size and lowest IE and EN in their periods.

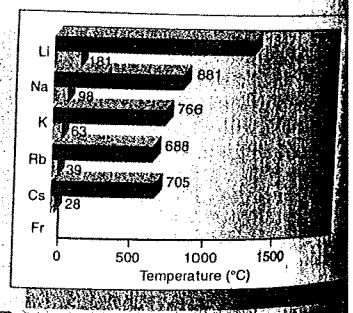
Down the group, atomic and ionic size increase, while IE and EN decrease.

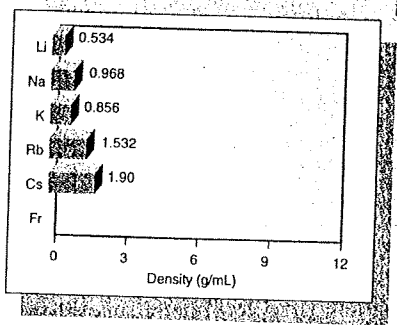




Physical Properties

Metallic bonding is relatively weak because there is only one valence electron. Therefore, these metals are soft with relatively low melting and boiling points. These values decrease down the group because larger atom cores attract delocalized electrons less strongly.





Large atomic size and low atomic mass result in low density, which generally increases down the group because mass increases more than size.

most 2A fluorides, carbonates, phosphates, and sulfates are considered insoluble, unlike the corresponding 1A compounds. Nevertheless, the ion-dipole attraction of 2+ ions for water is so strong that many slightly soluble 2A salts crystallize as hydrates; two examples are Epsom salt, $MgSO_4 \cdot 7H_2O$, used as a soak for inflammations, and gypsum, $CaSO_4 \cdot 2H_2O$, used as the bonding material between the paper sheets in wallboard and as the cement in surgical casts.

The Anomalous Behavior of Beryllium

As the numerous exceptions just mentioned indicate, the Period 2 element Be displays many examples of anomalous behavior, far more than does Li in Group 1A(1). The high charge density of a possible Be^{2+} ion would polarize nearby electron clouds very strongly and cause extensive orbital overlap. In fact, *all Be compounds exhibit covalent bonding.* Even BeF_2, the most ionic Be compound, has a relatively low melting point and, when melted, a low electrical conductivity.

Since Be has only two valence electrons, it does not attain an octet in its simple gaseous compounds (Section 10.1). When it bonds to an electron-rich atom, however, this electron deficiency is overcome as the gas condenses. Consider beryllium chloride ($BeCl_2$) (Figure 14.4). At temperatures greater than 900°C, it consists of linear molecules in which two *sp* hybrid orbitals hold four electrons around the central Be. As it cools, the molecules bond together, solidifying in long chains, with each Be sp^3 hybridized to finally attain an octet.

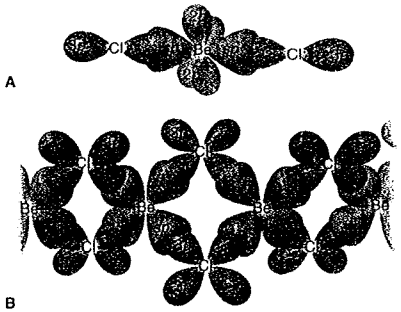


Figure 14.4 **Overcoming electron deficiency in beryllium chloride. A,** At high temperatures, $BeCl_2$ occurs as a gaseous molecule with only four electrons around Be. **B,** In the solid state, $BeCl_2$ occurs in long chains with each Cl bridging two Be atoms, which gives each Be an octet.

Diagonal Relationships: Lithium and Magnesium

One of the clearest ways in which atomic properties influence chemical behavior appears in the **diagonal relationships** of the periodic table, similarities between a Period 2 element and one in Period 3 diagonally down and to the right (Figure 14.5).

The first of these relationships occurs between lithium and magnesium and reflects similarities in atomic and ionic size. Note that *one period down increases atomic (or ionic) size and one group to the right decreases it.* Thus, Li has a radius of 152 pm and Mg has a radius of 160 pm; the Li^+ radius is 76 pm and that of Mg^{2+} is 72 pm. From these similar atomic properties emerge remarkably similar chemical properties. Both elements form nitrides with N_2, hydroxides and carbonates that decompose easily with heat, organic compounds with a polar covalent bond from the metal atom to a hydrocarbon group, and salts with similar solubilities. We will discuss the other two diagonal relationships shown in Figure 14.5—the one between Be and Al, and the one between B and Si—in later sections.

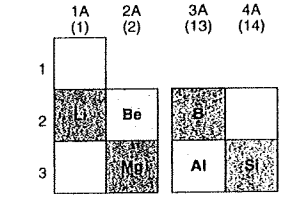


Figure 14.5 **Three diagonal relationships in the periodic table.** Certain Period 2 elements exhibit behaviors that are very similar to those of Period 3 elements immediately below and to the right. Three such diagonal relationships exist: Li and Mg, Be and Al, and B and Si.

Looking Backward and Forward: Groups 1A(1), 2A(2), and 3A(13)

Throughout this chapter, comparing the previous, current, and upcoming groups (Figure 14.6) will help you to keep horizontal trends in mind while examining vertical groups. Not much changes from 1A to 2A, and the elements behave as metals both physically and chemically. With smaller atomic size and stronger metallic bonding, 2A elements are harder, higher melting, and denser than those in 1A. Nearly all 1A and most 2A compounds are ionic. The higher ionic charge in Group 2A (2+ vs. 1+) leads to higher lattice energies and less soluble salts. The range of behavior in 2A is wider than in 1A because of Be and is widened much further in Group 3A from metallic boron to metallic thallium.

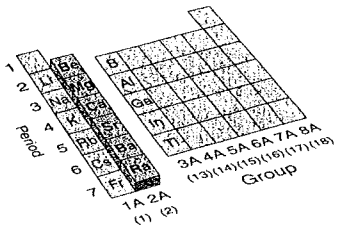


Figure 14.6 **Standing in Group 2A(2), looking backward to 1A(1) and forward to 3A(13).**

Versatile Magnesium Magnesium, second of the alkaline earths, can be rolled, forged, welded, and riveted into virtually any shape, and it forms strong, low-density alloys: some weigh 25% as much as steel but are just as strong. A tough, adherent oxide coating prevents further reaction in air. Alloyed with aluminum and zinc, magnesium is used for everyday objects, such as camera bodies, luggage, and the "mag" wheels of bicycles and sports cars. Alloyed with the lanthanides (first series of inner transition elements), it is used in objects that require great strength at high temperature, such as auto engine blocks and missile parts.

Lime: The Most Useful Metal Oxide Calcium oxide (lime) is a slightly soluble, basic oxide that is among the five most heavily produced industrial compounds in the world; it is made by roasting limestone to high temperatures [Group 2A(2) Family Portrait, reaction 7]. It has essential roles in steelmaking, water treatment, and flue "scrubbing." Lime reacts with carbon to form calcium carbide, which is used to make acetylene, and with arsenic acid (H_3AsO_4) to make insecticides for treating cotton, tobacco, and potato plants. Most glass contains about 12% lime by mass. The paper industry uses lime to prepare the bleach [$Ca(ClO)_2$] that whitens paper. Farmers "dust" fields with lime to "sweeten" acidic soil (see photo). The food industry uses it to neutralize compounds in milk to make cream and butter and to neutralize impurities in crude sugar.

14.4 Group 2A(2): The Alkaline Earth Metals

The Group 2A(2) elements are called *alkaline earth metals* because their ox give basic (alkaline) solutions and melt at such high temperatures that remained as solids ("earths") in the alchemists' fires. The group includ fascinating collection of elements: rare beryllium (Be), common magnes (Mg) and calcium (Ca), less familiar strontium (Sr) and barium (Ba), radioactive radium (Ra). The Group 2A(2) Family Portrait (pp. 552 and 5 presents an overview of these elements.

How Do the Physical Properties of the Alkaline Earth and Alk Metals Compare?

In general terms, the elements in Groups 1A(1) and 2A(2) behave as cl cousins. Whatever differences occur between the groups are those of deg not kind, and are due to the change in electron configuration: ns^2 vs. Two electrons are available for metallic bonding, and the nucleus conta one additional positive charge. These factors make the attraction betw delocalized electrons and atom cores greater. Consequently, 2A melting a boiling points are much higher than for the corresponding 1A metals; in f the 2A elements melt at around the same temperatures that the 1A eleme boil! Compared with transition metals, such as iron and chromium, the elements are soft and lightweight, but they are much harder and more de than their alkali metal neighbors.

How Do the Chemical Properties of the Alkaline Earth and Alk Metals Compare?

The alkaline earth metals display a wider range of chemical behavior th the alkali metals, largely because of the behavior of beryllium, as you'll s shortly. Since the second valence electron lies in the same sublevel as first, it is not shielded from the additional nuclear charge very well, so Z_{ef} greater. Therefore, Group 2A(2) elements have smaller atomic radii a higher ionization energies than Group 1A(1) elements. Despite the high IEs, *all the alkaline earths (except Be) form ionic compounds* as 2+ cations. Ber lium behaves differently because so much energy is needed to remove t electrons from this tiny atom that it never forms discrete Be^{2+} ions, and compounds are polar covalent.

Like the alkali metals, the alkaline earth metals are *strong reducing agen* The elements reduce O_2 in air to form the oxide (Ba also forms the perox ide, BaO_2). Except for Be and Mg, which form adherent oxide coatings, th reduce H_2O at room temperature to form H_2. And, except for Be, they reduc the halogens, N_2, and H_2 to form ionic compounds. The oxides are strong basic (except for amphoteric BeO) and react with acidic oxides to form sal such as sulfites and carbonates; for example,

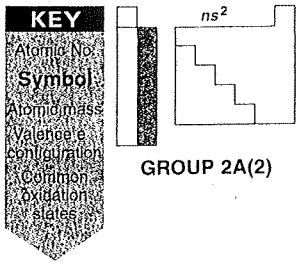
$$SrO(s) + CO_2(g) \longrightarrow SrCO_3(s)$$

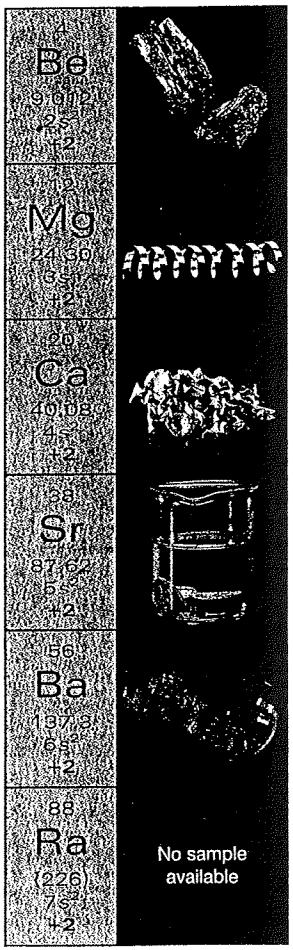
Natural carbonates, such as limestone and marble, are major structural ma rials and the commercial sources for most 2A compounds.

The alkaline earth metals are reactive because the high lattice energies their compounds more than compensate for the large total IE needed to for the 2+ cation (Section 9.2). Group 2A salts have much higher lattice ene gies than those of Group 1A (see Figure 14.2) because the 2A cations smaller and doubly charged.

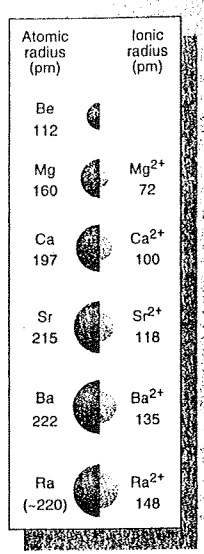
One of the main differences between the two groups is the lower solub ity of 2A salts in water. Their ions are smaller and more highly charged th 1A ions, resulting in much higher charge densities. Even though increases heats of hydration, it increases lattice energies even more. In

Key Atomic and Physical Properties





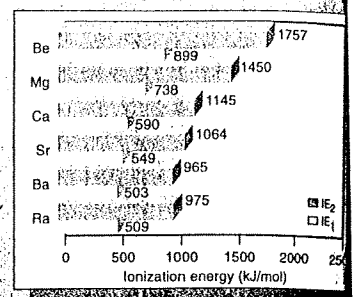
Atomic Properties

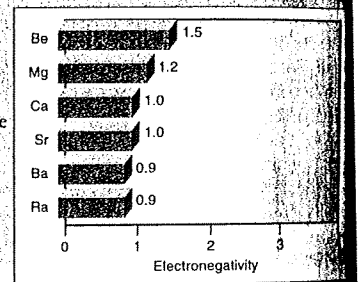


Group electron configuration is ns^2 (filled *ns* sublevel). All members have the +2 oxidation state and, except for Be, form compounds with an E^{2+} ion.

Atomic and ionic sizes increase down the group but are smaller than for the corresponding 1A(1) element.

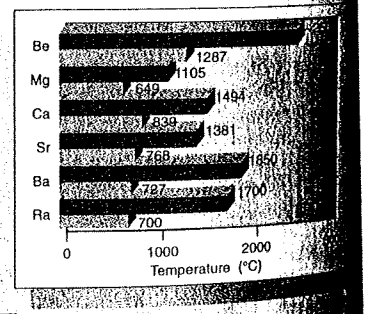
IE and EN decrease down the group but are higher than for the corresponding 1A(1) element.

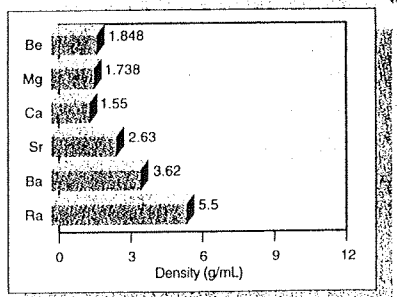




Physical Properties

Metallic bonding involves two valence e^-. These metals are still relatively soft but are much harder than the 1A(1) metals.





Melting and boiling points gene... decrease, and densities general... increase down the group. These ... ues are much higher than for ... and the trend is not as regular.

Some Reactions and Compounds

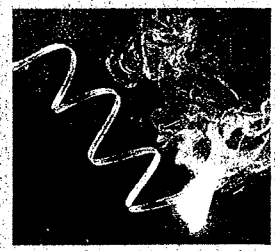
Important Reactions

The elements (E) act as reducing agents in reactions 1 to 5; note the similarity to reactions of Group 1A(1). Reaction 6 shows the general basicity of the oxides; reaction 7 shows the general instability of the carbonates at high temperature.

1. The metals reduce O_2 to form the oxide:

$2E(s) + O_2(g) \longrightarrow 2EO(s)$

Ba forms the peroxide, BaO_2.



Magnesium ribbon burning

2. The larger metals reduce water to form hydrogen gas:

$E(s) + 2H_2O(l) \longrightarrow E^{2+}(aq) + 2OH^-(aq) + H_2(g)$

(E = Ca, Sr, Ba)

Be and Mg form an adherent oxide coating that allows only limited reaction.

3. The metals reduce halogens to form ionic halides:

$E(s) + X_2 \longrightarrow EX_2(s)$ (X = F, Cl, Br, I)

4. Most of the elements reduce hydrogen to form ionic hydrides:

$E(s) + H_2(g) \longrightarrow EH_2(s)$ (E = all except Be)

5. Most of the elements reduce nitrogen to form ionic nitrides:

$3E(s) + N_2(g) \longrightarrow E_3N_2(s)$ (E = all except Be)

6. Except for amphoteric BeO, the oxides are basic:

$EO(s) + H_2O(l) \longrightarrow E^{2+}(aq) + 2OH^-(aq)$

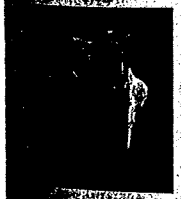
$Ca(OH)_2$ is a component of cement and mortar.

7. All carbonates undergo thermal decomposition to the oxide:

$ECO_3(s) \xrightarrow{\Delta} EO(s) + CO_2(g)$

This reaction is used to produce CaO (lime) in huge amounts from naturally occurring limestone (*see Margin Note, p. 550*).

Important Compounds



1. Beryl, $Be_3Al_2Si_6O_{18}$. Beryl, the industrial source of Be metal, also occurs as a gemstone with a variety of colors (*see photo*). It is chemically identical to emerald, except for the trace of Cr^{3+} that gives emerald its green color.

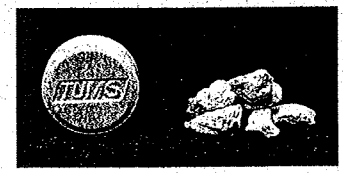
Be... oxide, ...cause of its ... point ... MgO is ... refractory ... for furnace ... (*photo*) and ... lation.

Industrial kiln

3. Alkylmagnesium halides, RMgX (R = hydrocarbon group; X = halogen). These compounds, called *Grignard reagents*, are used to synthesize many organic compounds. Organotin agricultural fungicides are made by treating RMgX with $SnCl_4$:

$3RMgCl + SnCl_4 \longrightarrow 3MgCl_2 + R_3SnCl$

4. Calcium carbonate, $CaCO_3$. Occurs as enormous natural deposits of limestone, marble, chalk, and coral. Used as a building material, to make lime, and, in high purity, as a toothpaste abrasive and an antacid (*see photo*).



Antacid tablet Limestone

14.5 Group 3A(13): The Boron Family

The third family of main-group elements contains some unusual n and some familiar ones, some exotic bonding, and some strange properties. Boron (B) heads the family, but, as you'll see, its proper tainly do not represent the other members. Metallic aluminum (Al) h erties that are more typical of the group, but its great abundance and tance contrast with the rareness of gallium (Ga), indium (In), and t (Tl). The atomic, physical, and chemical properties of these elements a marized in the Group 3A(13) Family Portrait (pp. 556 and 557).

How Do the Transition Elements Influence Group 3A(13) Properties?

Group 3A(13) is the first of the *p* block. If you look at the main grou the elements of this group seem to be just one group away from t Group 2A(2). In Period 4 and higher, however, a large gap separates groups (see Figure 8.10). The gap holds 10 transition elements (*d* bloc in Periods 4, 5, and 6 and an additional 14 inner transition elements (in Period 6. Recall from Section 8.2 that *d* and *f* electrons penetrate tle and spend very little time near the nucleus. Thus, the heavier 3A bers—Ga, In, and Tl—have nuclei with many more protons, but thei (*s* and *p*) electrons are only partially shielded from the much higher charge, so these elements have greater Z_{eff} than the two lighter mem

Many properties of these heavier 3A elements are influenced stronger nuclear attraction. Figure 14.7 compares several properties of 3A(13) with those of Group 3B(3) (the first group of transition eleme which the additional protons of the *d* block and *f* block have *not* been Note the regular changes exhibited by the 3B elements in contrast irregular patterns for those in 3A. The deviations for Ga reflect the *contraction in size* and can be explained by limited shielding by the *d* el of the 10 additional protons of the first transition series. Similarly, th ations for Tl reflect the *f*-block (lanthanide) contraction and can be ex by limited shielding by the *f* electrons of the 14 additional protons of t inner transition series.

Physical properties are influenced by the type of bonding that oc the element. Boron is a network covalent metalloid—black, hard, an high melting. The other group members are metals—shiny and relativ and low melting. Aluminum's low density and three valence electron it an exceptional conductor: for a given mass, aluminum conducts a twice as effectively as copper. Gallium has the largest liquid temp range of any element: it melts in your hand but does not boil until (see Figure 9.22). Its metallic bonding is too weak to keep the Ga atom when the solid is warmed, but it is strong enough to keep them from ing the molten metal until it is very hot. ◆

What New Features Appear in the Chemical Properties of 3A(13)?

Looking down Group 3A(13), we see a wide range of chemical be Boron, the anomalous member from Period 2, is the first metalloid encountered so far and the only one in the group. It is much less rea room temperature than the other members and forms covalent bond sively. Although aluminum acts like a metal physically, its halides exi gas phase as covalent dimers—molecules formed by joining two smaller molecules (Figure 14.8)—and its oxide is amphoteric rat basic. Most of the other 3A compounds are ionic, but they have mo lent character than similar 2A compounds. Because the 3A ions are

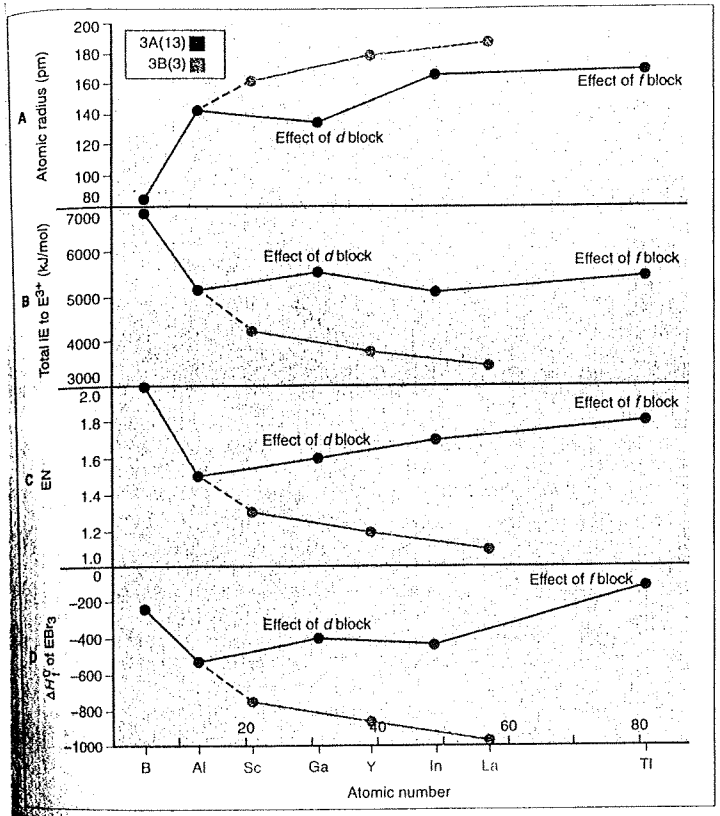


Figure 14.7 **The effect of transition elements on properties: Group 3B(3) vs. Group 3A(13).** The additional protons in the nuclei of transition elements exert an exceptionally strong attraction because *d* and *f* electrons shield the nuclear charge poorly. This greater effective nuclear charge affects the *p*-block elements in Periods 4 to 6, as can be seen by comparing properties of Group 3B(3), the first group after the *s* block, with 3A(13), the first group after the *d* block. **A,** Atomic size. In Group 3B, size increases smoothly, whereas in 3A, Ga and Tl are smaller than expected. **B,** Total ionization energy for E^{3+}. The deviations in size lead to deviations in total IE ($IE_1 + IE_2 + IE_3$). Note the regular decrease for Group 3B and the unexpectedly higher values for Ga and Tl in 3A. **C,** Electronegativity. The deviations in size also make Ga and Tl more electronegative than expected. **D,** Heat of formation of EBr_3. The higher IE values for Ga and Tl mean less heat is released upon ionic-compound formation, thus the smaller-than-expected ΔH_f° values for $GaBr_3$ and $TlBr_3$.

Gallium Arsenide: The Next Wave of Semiconductors An important modern use of gallium is in the production of gallium arsenide (GaAs) semiconductors. One of the factors limiting the efficiency of computer chips is the speed with which electrons can move, and they move 10 times faster through GaAs than through Si-based chips. GaAs chips also have novel optical properties: absorbing light creates a current and, conversely, supplying a current emits light. GaAs devices are already used in light-powered calculators, wristwatches, and solar panels. In addition, GaAs-based lasers are much smaller and more powerful than normal types.

more highly charged, they polarize the anion electron cloud more effec-

Our first glimpse of multiple oxidation states occurs in this group, and it ovides a chance to note some general principles that appear in Groups (13) to 6A(16):

Increasing prominence of the lower oxidation state. When a group exhibits re than one oxidation state, *the lower state becomes more prominent down the* In Group 3A(13), for instance, all members exhibit the +3 state, but +1 state first appears with some compounds of gallium and becomes the important state of thallium.

Explanation of the inert-pair effect. Many of the larger elements in these ps also have an important oxidation state *two lower than the A-group num-* The lower state occurs when the atoms lose their *np* electrons, but not two *ns* electrons. This fact is often called the *inert-pair effect* (Section 8.5), has nothing to do with any inertness of *ns* electrons; in fact, the 6*s* ons in Tl are lost *more* easily than the 4*s* electrons in Ga. The reason for mmon appearance of the lower state involves bond energies of the unds. Bond energy decreases as atomic size, and therefore bond length, ses. Since the Tl—Cl bond, for instance, is relatively long and weak, it ore energy to remove the two 6*s* electrons from Tl^+ to make Tl^{3+}

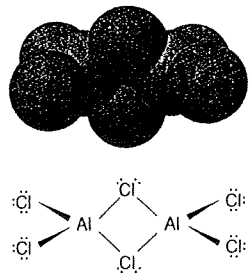


Figure 14.8 **The dimeric structure of gaseous aluminum chloride.** Despite its name, aluminum trichloride actually exists in the gas phase as a dimer of separate Al_2Cl_6 molecules.

Some Reactions and Compounds

Important Reactions

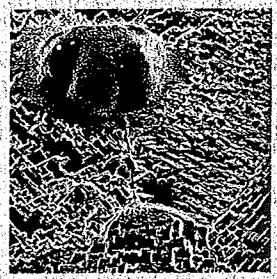
In reactions 1 to 3, note that the elements (E) usually require higher temperatures to react than those of Groups 1A(1) and 2A(2); note the lower oxidation state of Tl. Reactions 4 to 6 show some compounds in key industrial processes.

1. The elements react sluggishly, if at all, with water:

$$2E(s) + 6H_2O(hot) \longrightarrow 2Ga^{3+}(aq) + 6OH^-(aq) + 3H_2(g)$$

$$2Tl(s) + 2H_2O(steam) \longrightarrow 2Tl^+(aq) + 2OH^-(aq) + H_2(g)$$

Al becomes covered with a layer of Al_2O_3 that prevents further reaction (*see* Figure 13.1).



Scanning electron micrograph of Ga coating on Al surface

2. When strongly heated in pure O_2, all members form oxides:

$$4E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s) \quad (E = B, Al, Ga, In)$$

$$4Tl(s) + O_2(g) \xrightarrow{\Delta} 2Tl_2O(s)$$

Oxide acidity decreases down the group: B_2O_3 (weakly acidic) > Al_2O_3 > Ga_2O_3 > In_2O_3 > Tl_2O (strongly basic), and the +1 oxide is more basic than the +3 oxide.

3. All members reduce halogens (X_2):

$$2E(s) + 3X_2 \longrightarrow 2EX_3 \quad (E = B, Al, Ga, In)$$

$$2Tl(s) + X_2 \longrightarrow 2TlX(s)$$

BX_3 are volatile covalent molecules. Trihalides of Al, Ga, and In are (mostly) ionic solids but occur as covalent dimers in the gas phase; in this way, the 3A atom attains a filled outer level.

4. Acid treatment of Al_2O_3 is important in water purification:

$$Al_2O_3(s) + 3H_2SO_4(l) \longrightarrow Al_2(SO_4)_3(s) + 3H_2O(l)$$

In water, $Al_2(SO_4)_3$ and CaO form a colloid that aids in removing suspended particles.

5. The overall reaction in the production of aluminum metal is a redox process:

$$2Al_2O_3(s) + 3C(s) \longrightarrow 4Al(s) + 3CO_2(g)$$

This process is carried out electrochemically in the presence of cryolite (Na_3AlF_6), which lowers the melting point of the reactant mixture and takes part in the change (*Section 22.4*).

6. A displacement reaction produces gallium arsenide, GaAs (*see Margin Note, p. 554*):

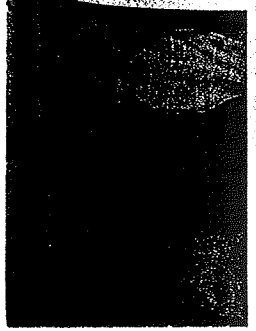
$$(CH_3)_3Ga(g) + AsH_3(g) \longrightarrow 3CH_4(g) + GaAs(s)$$

Important Compounds

Boron oxide, B_2O_3. Used in the production of borosilicate glass (*see Margin Note, p. 558*).

Borax, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$. Major mineral source of boron compounds and B_2O_3. Used as a fireproof insulation material, as a washing powder (20-Mule Team Borax), and as H_3BO_3 [or $B(OH)_3$]. Used as external disinfectant, wash, and insecticide.

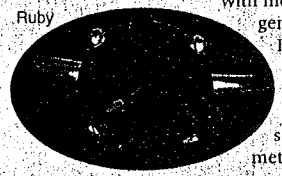
Diborane, B_2H_6. A powerful reductant for possible use as rocket fuel. Used to synthesize higher boranes, compounds that led to theories of chemical bonding.



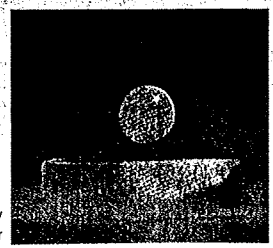
5. Aluminum sulfate (alum), $Al_2(SO_4)_3\cdot 18H_2O$. Used in purifying water, tanning leather, sizing paper, as a fixative for dyeing cloth (*see photo*), and as an antiperspirant.

6. Aluminum oxide, Al_2O_3. Major compound in natural source (bauxite) of Al metal. Used as abrasive in sandpaper, sanding and cutting tools, and toothpaste. Large crystals with metal ion impurities often of gemstone quality (*see photo*). Inert support for chromatography. In fibrous forms, woven into heat-resistant fabrics; also used to strengthen ceramics and metals.

Ruby

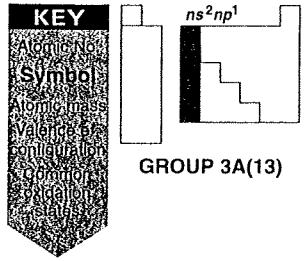


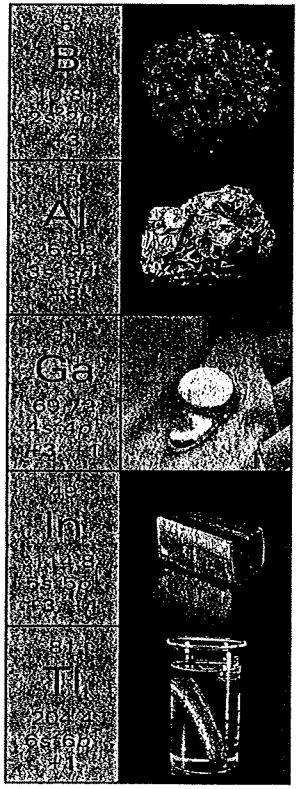
7. $Tl_2Ba_2Ca_2Cu_3O_{10}$. Becomes a high-temperature superconductor at 125 K, which is readily attained with liquid N_2 (*see photo*).



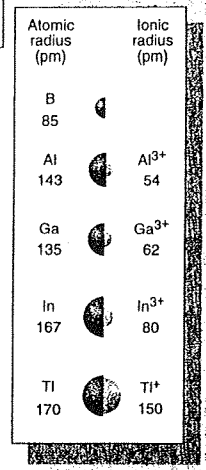
Magnet levitated by superconductor

Key Atomic and Physical Properties





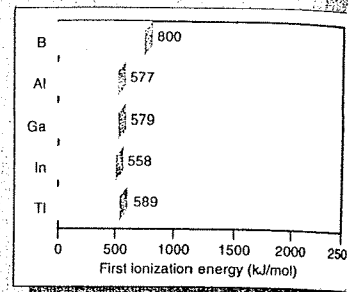
Atomic Properties

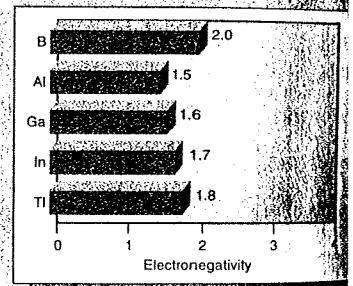


Group electron configuration is ns^2np^1. All except Tl commonly display the +3 oxidation state. The +1 state becomes more common down the group.

Atomic size is smaller and EN is higher than for 2A(2) elements, but IE is lower because it is easier to remove e^- from the higher energy *p* sublevel.

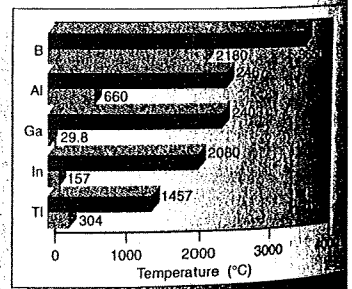
Atomic size, IE, and EN do not change as expected down the group because there are intervening transition and inner transition elements.

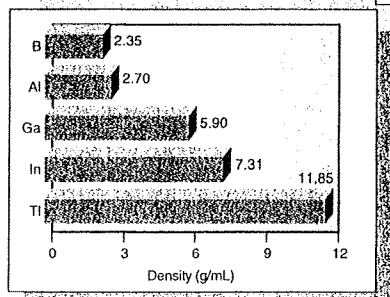




Physical Properties

Bonding changes from network covalent in B to metallic in rest of group. Thus, B has a much higher melting point than the others, but there is no overall trend. Boiling points decrease down the group.





Densities increase down the group.

than is released when two more weak Tl—Cl bonds form in $TlCl_3$. In fac
$TlCl_3$ is so unstable that it decomposes readily to Cl_2 gas and TlCl.

3. *Relative basicity of oxides.* In general, *lower state oxides are more basic th*
higher state oxides. A good example in Group 3A is that In_2O is more bas
than In_2O_3. In general, when an element has more than one oxidation sta
it acts more like a metal in its lower state, and this, too, is related to ionic char
density. In this case, the lower charge of In^+ does not polarize the O^{2-} i
as much as the higher charge of In^{3+} does. Thus, in compounds of gene
formula E_2O, the E-to-O bonding is more ionic than in E_2O_3, so the O^{2-} i
is more available to act as a base (Interchapter, Topic 4).

Highlights of Boron Chemistry

Like the other Period 2 members, the chemical behavior of boron is str
ingly different from that of the other members of its group. As pointed o
earlier, *all boron compounds are covalent,* and unlike the other 3A(13) membe
boron forms network covalent compounds or large molecules with metals,
O, N, and C. The unifying feature of many B compounds is their *electron d*
ciency, but B adopts two strategies to fill its outer level: accepting a bondi
pair from an electron-rich atom and forming bridge bonds with electron-p
atoms.

Accepting a Bonding Pair from an Electron-Rich Atom In gaseous bor
trihalides (BX_3), the B atom is electron deficient, with only six electro
around it (Section 10.1). To attain an octet, the B atom accepts a lone p
of electrons from an electron-rich atom and forms a covalent bond:

$$BF_3(g) + :NH_3(g) \longrightarrow F_3B{-}NH_3(g)$$

(Such reactions, in which one reactant accepts an electron pair from anot
to form a covalent bond, are very widespread in inorganic, organic, and b
chemical processes. They are known as *Lewis acid-base reactions,* and we'll d
cuss them in Chapters 18 and 23 and see examples of them throughout
second half of the text.)

Similarly, B has only six electrons in boric acid, $B(OH)_3$ (sometimes w
ten as H_3BO_3). In water, the acid itself does not release a proton. Rathe
accepts an electron pair from the O in H_2O, forming a fourth bond and rel
ing an H^+ ion:

$$B(OH)_3(s) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$$

Boron's outer shell is filled in the wide variety of borate salts, such as
mineral borax (sodium borate), $Na_2[B_4O_5(OH)_4]{\cdot}8H_2O$, used for decades
household cleaning agent. ◆

Boron also attains an octet in several nitrogen compounds whose structu
are amazingly similar to that of elemental carbon and some of its organic c
pounds (Figure 14.9). These similarities are due to the fact that the size
and EN of C are between those of B and N (see Table 14.1). Moreover, C
four valence electrons, whereas B has three and N has five, so the $\cdot\dot{C}{-}\dot{C}\cdot$
$\cdot\dot{B}{-}\dot{N}\cdot$ groupings have the same number of valence electrons. Theref
$H_3C{-}CH_3$ (ethane) and $H_3B{-}NH_3$ are isoelectronic, as are benzene
borazine (Figure 14.9A and B). Boron nitride (Figure 14.9C) has a struc
consisting of hexagons fused into sheets very similar to that of graphite; H
ever, its π electrons are localized into separate double bonds, whereas t
electrons in graphite are highly delocalized through resonance. As a re
boron nitride is an electrical insulator, whereas graphite is an electrical
ductor. At high pressure and temperature, boron nitride forms borazon (F
14.9D), which has a crystal structure like that of diamond and is extre
hard and abrasive.

◆ Borates in Your Labware Strong heating of boric acid (or borate salts) drives off water molecules and gives molten boron oxide: $2B(OH)_3(s) \longrightarrow B_2O_3(l) + 3H_2O(g)$. The molten oxide dissolves metal oxides to form borate glasses. When mixed with silica (SiO_2), it forms borosilicate glass. Its transparency and small change in size when heated or cooled make borosilicate glass useful in cookware and in the glassware you use in the lab.

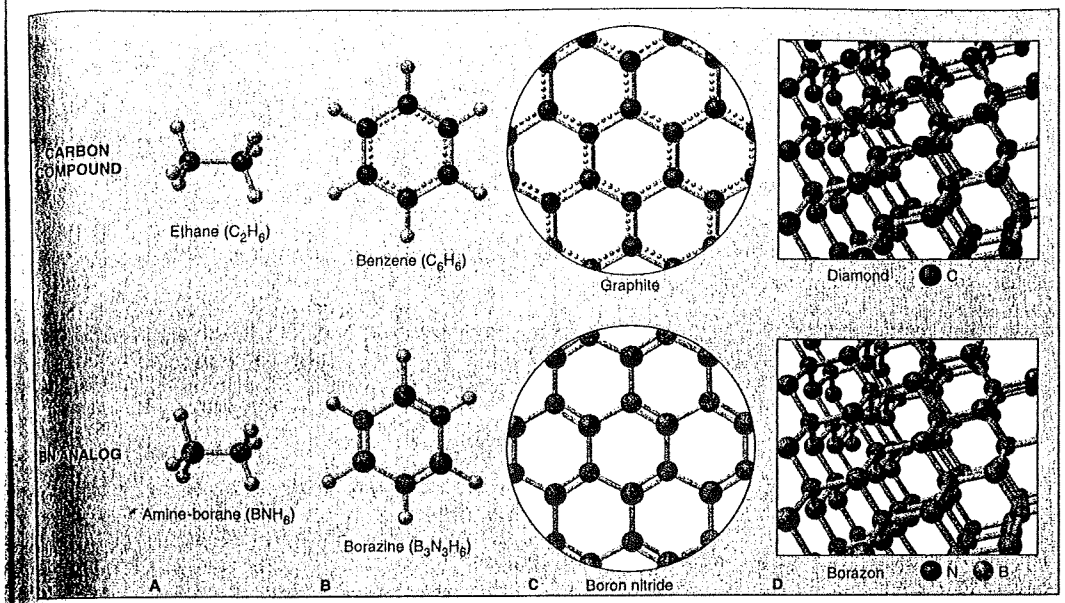


Figure 14.9 Similarities between substances with C—C bonds and those with B—N bonds. Note that in each case, B attains an octet of electrons by bonding with electron-rich N. **A,** Ethane and its BN analog. **B,** Benzene and borazine, which is often referred to as "inorganic" benzene. **C,** Graphite and the similar extended hexagonal structure of boron nitride. **D,** Diamond and borazon have the same crystal structure and are among the hardest substances known.

Forming Bridge Bonds with Electron-Poor Atoms In elemental boron and its many hydrides (boranes), there is no electron-rich atom to supply boron with electrons. In these substances, boron attains an octet through some unusual bonding. In diborane (B_2H_6) and many larger boranes, for example, two types of B—H bonds exist. The first type is a typical electron-pair bond. The valence bond picture in Figure 14.10 shows an sp^3 orbital of B overlapping the H 1*s* orbital in each of the four terminal B—H bonds, using two of the three electrons in the valence shell of each B atom.

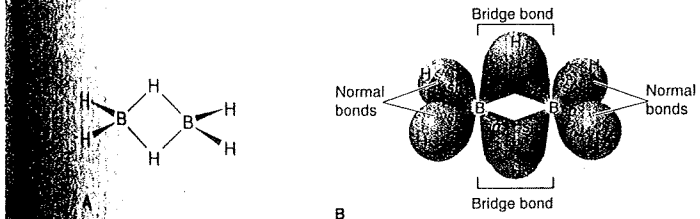
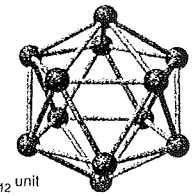
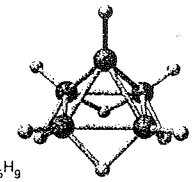


Figure 14.10 The two types of covalent bonding in diborane. A, A perspective diagram of B_2H_6 shows the unusual B—H—B bridge bond and the tetrahedral arrangement around each B atom. **B,** A valence bond depiction shows sp^3-hybridized B forming normal covalent bonds at the four terminal B—H bonds and bridge bonds, in which two electrons bind three atoms at the two central B—H—B groupings.



A B_{12} unit



B B_5H_9

Figure 14.11 The boron icosahedron and a larger borane. A, The icosahedron structural unit of elemental boron. **B,** The structure of B_5H_9, one of many boranes.

The other type of bond is a hydride **bridge bond** (or three-center, tw electron bond), in which *each B—H—B grouping is held together by only two e trons.* An sp^3 orbital from *each* B overlaps an H 1*s* orbital between them. T electrons move through this extended bonding orbital—one from one of t B atoms and the other from the H atom—and join the two B atoms via t H atom bridge. Notice that *each B atom is surrounded by eight electrons:* four fr the two normal B—H bonds and four from the two B—H—B bridge bon In many boranes and in elemental boron (Figure 14.11), one B atom bridg two others in a three-center, two-electron B—B—B bond.

Diagonal Relationships: Beryllium and Aluminum

Beryllium in Group 2A(2) and aluminum in Group 3A(13) are the next pa of diagonally related elements. Both form oxoanions in strong base: bery late, $Be(OH)_4^{2-}$, and aluminate, $Al(OH)_4^-$. Both have bridge bonds in the hydrides and chlorides. Both form oxide coatings impervious to reaction wi water, and both oxides are amphoteric, extremely hard, and high meltin Although their atomic and ionic sizes differ, the small, highly charged Be^{2+} and Al^{3+} ions polarize nearby electron clouds strongly. Therefore, some compounds and all Be compounds have significant covalent character.

14.6 Group 4A(14): The Carbon Family

The whole range of elemental behavior occurs within Group 4A(14): nor metallic carbon (C) leads off, followed by the metalloids silicon (Si) and ge manium (Ge), with metallic tin (Sn) and lead (Pb) at the bottom of the grou Information about the compounds of C and of Si fills libraries: organic chem istry, most polymer chemistry, and biochemistry are based on carbo whereas geochemistry is based on silicon. There are also some extreme important polymer and electronic technologies based on silicon. The Gro 4A(14) Family Portrait (pp. 562 and 563) summarizes atomic, physical, a chemical properties.

How Does the Bonding in an Element Affect Physical Properties?

The elements of Group 4A(14) and their neighbors in Groups 3A(13) an 5A(15) illustrate how physical properties, such as melting point and heat fusion (ΔH^0_{fus}), depend on the type of bonding in an element (Table 14.2 Within Group 4A, the large decrease in melting point between the C and covalent networks is due to longer, weaker bonds in the Si structure

Table 14.2 Bond Type and the Melting Process in Groups 3A(13) to 5A(15)

Period	Group 3A(13) Element	Bond Type	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Group 4A(14) Element	Bond Type	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Group 5A(15) Element	Bond Type	Melting Point (°C)	ΔH_{fus} (kJ/mol)
2	B		2180	23.6	C		4100	Very high	N		−210	0.7
3	Al		660	10.5	Si		1420	50.6	P		44.1	2.5
4	Ga		30	5.6	Ge		945	36.8	As		816	27.7
5	In		157	3.3	Sn		232	7.1	Sb		631	20.0
6	Tl		304	4.3	Pb		327	4.8	Bi		271	10.5

Key: Metallic; Covalent network; Covalent molecular; Metal; Metalloid; Nonmetal

large decrease between Ge and Sn is due to the change from covalent network to metallic bonding. Similarly, looking horizontally, the large increases in melting point and ΔH^0_{fus} across a period between Al and Si and between Ga and Ge reflect the change from metallic bonding to covalent networks. Note the abrupt rises in these properties from the values for metallic Al, Ga, and Sn to those for the network-covalent metalloids Si, Ge, and Sb, and note the abrupt drops from the covalent networks of C and Si to the individual molecules of N and P in Group 5A.

Allotropism: Different Forms of an Element Striking changes in physical properties often appear among **allotropes,** different crystalline or molecular forms of a substance. One allotrope is usually more stable than another at a particular pressure and temperature. Group 4A provides the first dramatic example of allotropism, in the forms of carbon. It is difficult to imagine two substances made entirely of the same atom that are more different than graphite and diamond. Graphite is a black electrical conductor that is soft and "greasy," whereas diamond is a colorless electrical insulator that is extremely hard. Graphite is the standard state of carbon, the more stable form at ordinary temperature and pressure, as the phase diagram in Figure 14.12 shows. Fortunately for jewelry owners, diamond changes to graphite at a negligible rate under normal conditions.

In the mid-1980s, interest arose about a newly discovered allotrope of carbon. Mass spectrometric analysis of soot had shown evidence for a soccer ball–shaped molecule of formula C_{60} (Figure 14.13A; see also the Gallery, p. 383). More recent findings reveal the molecule in geological samples formed by meteorite impact, even the one that occurred around the time the dinosaurs became extinct. The molecule has been dubbed *buckminsterfullerene* (informally called a *bucky ball*) after the architect-engineer R. Buckminster Fuller, who designed structures with similar shapes. Excitement rose in 1990, when scientists learned how to prepare multigram quantities of C_{60} and related fullerenes, enough to study macroscopic behavior and possible applications. Since then, metal atoms have been incorporated into the structure and compounds have been prepared with many different groups attached (fluorine, hydroxyl, sugars, etc.) that have a range of useful properties.

Then, in 1991, scientists passed an electric discharge through graphite rods sealed in a container with helium gas and obtained extremely thin (~1 nm diameter) graphite-like tubes with fullerene ends (Figure 14.13B). These "nanotubes" are rigid and, on a mass basis, much stronger than steel along their long axis. They also conduct electricity along this axis because of the delocalized electrons. Reports about fullerenes and nanotubes appear almost daily in scientific journals. With potential applications in ultraminiature electronics, catalysis, polymers, and medicine, fullerene and nanotube chemistry will receive increasing attention well into the next century.

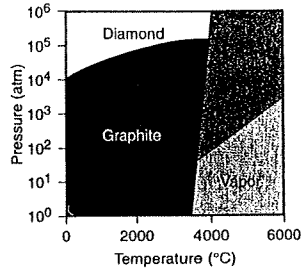
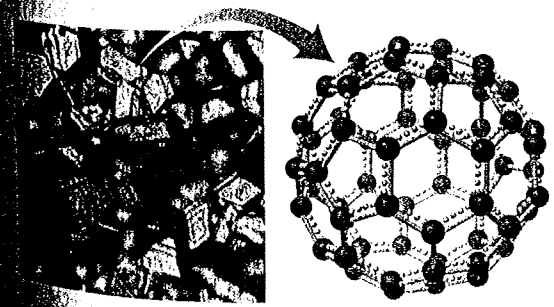


Figure 14.12 Phase diagram of carbon. Graphite is the more stable form at ordinary conditions (*small red circle at extreme lower left*). Diamond is more stable at very high pressure.



B

Figure 14.13 Buckyballs and nanotubes. A, Crystals of buckminsterfullerene (C_{60}) are shown leading to a ball-and-stick model. The parent of the fullerenes, the "bucky ball," is a soccer ball–shaped molecule of 60 carbon atoms. **B,** Nanotubes are single or, as shown in this electron micrograph, concentric graphite-like tubes with fullerene ends (see the Gallery, p. 383).

Some Reactions and Compounds

eactions

ertain to all the elements (E); reactions 3
rial uses for compounds of C and Si.
e oxidized by halogen:

$X_2 \longrightarrow EX_4$ (E = C, Si, Ge)

more stable for tin and lead, SnX_2 and

e oxidized by O_2:

$) \longrightarrow EO_2$ (E = C, Si, Ge, Sn)

idé, PbO. Oxides become more basic
ie reaction of CO_2 and H_2O provides the
ural unpolluted waters:

$\rightleftharpoons [H_2CO_3(aq)] \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

assed over hot coke produce gaseous fuel
gas and water gas):

$(g) \longrightarrow CO(g) + CO_2(g) + N_2(g) + H_2(g)$ [not balanced]

eact with O_2 to form CO_2 and H_2O. The
ie is adapted to yield heat or electricity:

$2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

Oxyacetylene torch

5. Certain metal carbides react with water to produce acetylene:

$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + C_2H_2(g)$

The gas is used to make other organic compounds and as a fuel in welding (*see photo*).

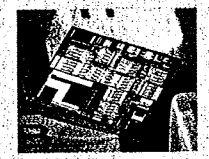
6. Freons (chlorofluorocarbons) are formed by fluorinating carbon tetrachloride:

$CCl_4(l) + HF(g) \longrightarrow CFCl_3(g) + HCl(g)$

Production of trichlorofluoromethane (Freon-11), the major refrigerant in the world, is being eliminated because of its severe effects on the environment (*see Margin Note, p. 565*).

7. Silica is reduced to form elemental silicon:

$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$



This crude silicon is made ultrapure through zone refining (*see Gallery, Section 13.5*) for manufacture of computer chips (*see photo*).

Computer chip

ompounds

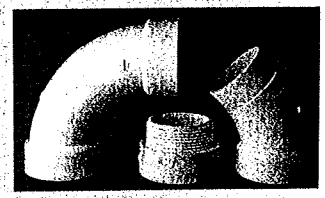
de, CO. Used as a gaseous fuel, as a pre-
on organic compounds, and as a reactant
of nickel. Formed in internal combustion
ed as a toxic air pollutant.
CO_2. Atmospheric component used by
nts to make carbohydrates and O_2. The
duct of all C-based fuels; its increase in
ay lead to
sed indus-
nt gas,
re extin-
escent
e photo).
to form
and plas-

Used as a fuel and in the production of
pounds. Major component of natural gas.
bic decomposition of plants (swamp gas)
termites and certain mammals. May
l warming.

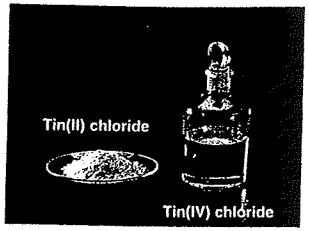
4. Silicon dioxide, SiO_2. Occurs in many amorphous (glassy) and crystalline forms, quartz being the most common. Used to make glass and as an inert chromatography support material.

5. Silicon carbide, SiC. Known as carborundum, a major industrial abrasive and a highly refractory ceramic for tough, high-temperature uses. Can be doped to form a high-temperature semiconductor.

6. Organotin compounds, R_4Sn. Used to stabilize PVC, poly(vinyl chloride) plastics (*see photo*), and to cure silicone rubbers. Agricultural biocide for insects, fungi, and weeds.



7. Tetraethyl lead, $(C_2H_5)_4Pb$. Once used as a gasoline additive to improve fuel efficiency, but now removed because of its inactivation of auto catalytic converters. Major source of lead as a toxic air pollutant.



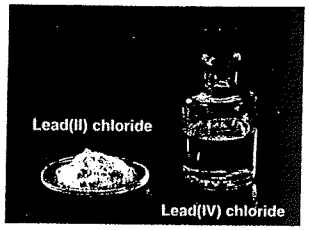


Figure 14.14 **The greater metallic character of tin and lead in the lower oxidation state.** Metals with more than one oxidation state exhibit more metallic behavior in the lower state. Tin(II) and lead(II) chlorides are white, crystalline, saltlike solids. In contrast, tin(IV) and lead(IV) chlorides are volatile liquids, indicating the presence of individual molecules.

Tin has two allotropes. White β-tin is stable at room temperature an above, whereas gray α-tin is the more stable form below 13°C (56°F). Whe white tin is kept for long periods at a low temperature, some converts microcrystals of gray tin. The random formation and growth of these regio of gray tin, which has a different crystal structure, weaken the metal an make it crumble. In the unheated cathedrals of medieval northern Europe tin pipes of magnificent organs sometimes crumbled as a result of "tin dis ease" caused by this allotropic transition from white to gray tin.

How Does the Type of Bonding Change in Group 4A(14) Compounds?

The 4A(14) elements display a wide range of chemical behavior, from th covalent compounds of carbon to the ionic compounds of lead. Carbon' intermediate EN of 2.5 ensures that it virtually always forms covalent bonds but the larger members of Group 4A form bonds with increasing ionic char acter. With nonmetals, Si and Ge form strong polar covalent bonds, such a the Si—O bond, one of the strongest of any Period 3 element (368 kJ/mol) This bond is responsible for the physical and chemical stability of the Earth's solid surface, as we discuss later in this section. Although individual ions rarely exist, Sn and Pb bonding to nonmetals has more ionic character.

The patterns of elements with more than one oxidation state that we first observed in Group 3A(13) appear here as well. After silicon, the shift to greater importance of the lower oxidation state occurs: Si compounds of the +4 state are much more stable than those of the +2 state, whereas Pb compounds of the +2 state are more stable than those of the +4 state. The elements also behave more like metals in the lower state. Consider the chlorides and oxides of Sn and Pb. Figure 14.14 shows that the +2 chlorides $SnCl_2$ and $PbCl_2$ are white, relatively high-melting, water-soluble crystals—typical properties of a salt. In contrast, $SnCl_4$ is a volatile, benzene-soluble liquid, and $PbCl_4$ is a thermally unstable oil. The +2 oxides SnO and PbO are more basic than the +4 oxides SnO_2 and PbO_2 because the +2 metals are less able to polarize the O^{2-} ion, so the E-to-O bonding is more ionic.

Highlights of Carbon Chemistry

Like the other Period 2 elements, carbon is an anomaly in its group; indeed it may be an anomaly in the entire periodic table. Carbon forms bonds with the smaller Group 1A(1) and 2A(2) metals, many transition metals, the halogens, and its neighbors B, Si, N, O, P, and S. This versatile element exhibits every oxidation state possible for its group, from +4 in CO_2 and halides like CCl_4 through −4 in CH_4.

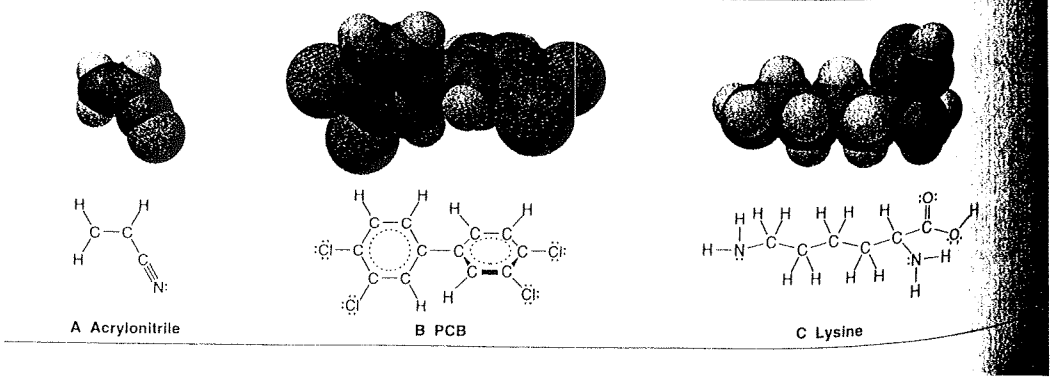


Figure 14.15 **Three of the several million known organic compounds of carbon.** **A,** Acrylonitrile (precursor of acrylic fibers). **B,** One of numerous PCBs (polychlorinated biphenyls). **C,** Lysine (an amino acid).

Two features stand out in the chemistry of carbon: its ability to bond to itself, a process known as *catenation*, and its ability to form multiple bonds. As a result of its small size and its capacity for four bonds, carbon can form chains, branches, and rings that lead to myriad structures. Add a lot of H, some O and N, a bit of S, P, halogen, and a few metals, and you have the whole organic world! Figure 14.15 shows three of the several million organic compounds known. Multiple bonding is common in carbon structures because the C—C bond is short enough for sideways overlap of half-filled $2p$ orbitals to form p,p-π bonds. (In Chapter 15, we discuss in detail how the atomic properties of carbon give rise to the diverse structure and reactivity of organic compounds.)

Because the other 4A members are larger, E—E bonds become longer and weaker down the group; thus, in terms of bond strength, C—C > Si—Si > Ge—Ge. The empty d orbitals of these larger atoms make the chains much more susceptible to chemical attack. Thus, some compounds with long Si chains are known but they are very reactive, and the longest Ge chain has only eight atoms. Moreover, longer bonds do not typically allow sufficient overlap for p,p-π bonding. Only very recently have compounds with π bonds between Si atoms and between Ge atoms been prepared, but they too are extremely reactive.

In contrast to its organic compounds, carbon's inorganic compounds are simple. Metal carbonates are the main mineral form. Marble, limestone, chalk, coral, and several other types are found in enormous deposits throughout the world. Many of these compounds are remnants of fossilized marine organisms. Carbonates are used in several common antacids because they react with the HCl in stomach acid [see Group 2A(2) Family Portrait, compound 4]:

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Identical net ionic reactions with sulfuric and nitric acids protect lakes bounded by limestone deposits from the harmful effects of acid rain.

Unlike the solid network or ionic oxides of the other 4A members, carbon forms two common gaseous oxides, CO_2 and CO. Carbon dioxide is essential to all life as the primary source of carbon in plants and animals through its role in photosynthesis. Its aqueous solution is the cause of acidity in natural waters. However, its atmospheric buildup from deforestation and excessive use of fossil fuels may severely affect the global climate. Carbon monoxide forms when carbon or its compounds burn in an inadequate supply of O_2:

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

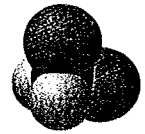
Carbon monoxide is a key component of syngas fuels (see Chemical Connections, p. 247) and is widely used in the production of methanol, formaldehyde, and other major industrial compounds.

CO binds strongly to many transition metals. When inhaled in cigarette smoke or polluted air, it enters the blood and binds strongly to the Fe(II) in hemoglobin, preventing the normal binding of O_2, and to other iron-containing proteins. The cyanide ion (CN^-) is *isoelectronic* with CO:

$$[:C{\equiv}N:]^- \quad \text{same electronic structure as} \quad :C{\equiv}O:$$

Cyanide binds to many of the same iron-containing proteins and is also toxic.

Monocarbon halides (or halomethanes) are tetrahedral molecules whose stability to heat and light decreases as the size of the halogen atom increases (the C—X bond becomes longer (weaker) (see Interchapter, Topic 2). The chlorofluorocarbons (CFCs, or Freons) have important industrial uses, but in short, strong carbon-halogen bonds are exceptionally stable, and the environmental persistence of these compounds has created major problems. ◆



CFCs: The Good, the Bad, and the Strong

The strengths of the C—F and C—Cl bonds make CFCs, such as Freon-12 shown here, both useful and harmful. Chemically and thermally stable, nontoxic, and nonflammable, they are excellent cleaners for electronic parts, coolants in refrigerators and air conditioners, and propellants in aerosol cans. However, these bond strengths also mean they decompose *very* slowly near the Earth's surface. In the lower atmosphere, they contribute to climate warming, absorbing infrared radiation 16,000 times as effectively as CO_2. Once in the stratosphere, however, they are bombarded by ultraviolet (UV) photons, which break the otherwise stable C—Cl bonds, releasing free Cl atoms that initiate ozone-destroying reactions (Chapter 16).

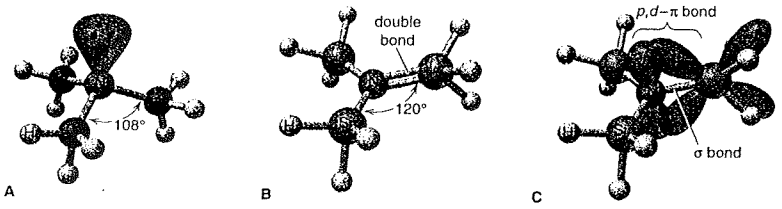


Figure 14.16 **The impact of *p,d*-π bonding on the structure of trisilylamine.** **A,** The molecular shape of trimethylamine is trigonal *pyramidal*, as in ammonia. **B,** Trisilylamine, the silicon analog, has a trigonal *planar* shape because of the formation of a double bond between N and Si. The ball-and-stick model shows one of three resonance forms. **C,** The lone pair in an unhybridized *p* orbi of N overlaps with an empty *d* orbital of Si to give a *p,d*-π bond. I the resonance hybrid, a *d* orbital on each Si is involved in the π bond.

Highlights of Silicon Chemistry

Silicon halides are more reactive than carbon halides because Si has emp *d* orbitals that are available for chemical attack. Surprisingly, the Si halid have longer yet *stronger* bonds than the corresponding C halides (see Tabl 9.2 and 9.3). One explanation for this unusual strength is that the Si— bond has some double-bond character because of the presence of a σ bo *and* a different type of π bond, called a *p,d-π bond.* This bond arises fro sideways overlap of an Si *d* orbital and a halogen *p* orbital. A similar type *p,d*-π bonding leads to the trigonal planar molecular shape of trisilylamin in contrast to the trigonal pyramidal shape of trimethylamine, shown in Fi ure 14.16.

To a great extent, the chemistry of silicon is the chemistry of the *silico oxygen bond.* Just as carbon forms unending C—C chains, the —Si—O— grouping repeats itself endlessly in a wide variety of **silicates,** the mo important minerals on the planet, and in **silicones,** synthetic polymers wi many applications:

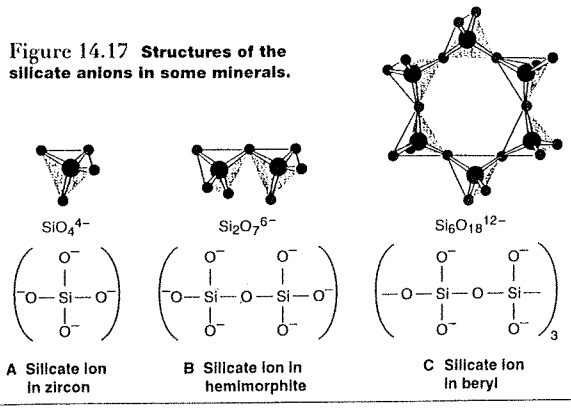
1. *Silicate minerals.* From common sand and clay to semiprecious amethy and carnelian, silicate minerals are the dominant form of matter in the non living world. Oxygen, the most abundant element on Earth, and silicon, t next most abundant, compose these minerals and thus account for four every five atoms on the surface of the planet!

The silicate building unit is the *orthosilicate* grouping, $-SiO_4-$, a tetra dral arrangement of four oxygens around a central silicon. Several we known minerals contain SiO_4^{4-} ions or small groups of them linked toget The gemstone zircon ($ZrSiO_4$) contains one unit; hemimorph $[Zn_4(OH)_2Si_2O_7 \cdot H_2O]$ contains two units linked through an oxygen cor and beryl ($Be_3Al_2Si_6O_{18}$), the major source of beryllium, contains six joined into a cyclic ion (Figure 14.17). As you'll see in a moment, in a tion to these separate ions, SiO_4 units are linked more extensively to cr much of the planet's mineral structure.

2. *Silicone polymers.* Unlike the naturally occurring silicates, silicone po mers are manufactured substances consisting of alternating Si and O at with two organic groups bound to the Si atoms. A key starting materia formed by the reaction of silicon with methyl chloride:

$$Si(s) + 2CH_3Cl(g) \xrightarrow[\sim 300°C]{\text{Cu catalyst}} (CH_3)_2SiCl_2(g)$$

Figure 14.17 **Structures of the silicate anions in some minerals.**



Although the corresponding carbon compound $[(CH_3)_2CCl_2]$ is inert in water, the empty *d* orbitals in Si make this compound reactive:

$$(CH_3)_2SiCl_2(l) + 2H_2O(l) \longrightarrow (CH_3)_2Si(OH)_2(l) + 2HCl(g)$$

The product reacts with itself to form water and a silicone chain molecule called a *polydimethylsiloxane:*

$$n(CH_3)_2Si(OH)_2 \longrightarrow \left[-O-\overset{CH_3}{\underset{CH_3}{Si}}-\right]_n + nH_2O$$

Silicones have properties of both plastics and minerals. The organic groups ive them the flexibility and weak intermolecular forces between chains of a lastic, while the O—Si—O backbone confers the thermal stability and non-lammability of a mineral. In the upcoming Gallery, note the structural sim-larities of silicates and silicones.

iagonal Relationships: Boron and Silicon

he final diagonal relationship that we consider occurs between the metal-oids B and Si. Both exhibit the electrical properties of a semiconductor (Sec-ion 12.6). Both elements and their mineral oxoanions, borates and silicates, ccur in extended covalent networks. Both boric acid $[B(OH)_3]$ and silicic id $[Si(OH)_4]$ are weakly acidic and occur in layers with widespread H bond-ng. Both elements form flammable, low-melting compounds with hydro-—the boranes and silanes—that act as reducing agents.

ooking Backward and Forward: Groups 3A(13), 4A(14), nd 5A(15)

ading in Group 4A(14), we look back at Group 3A(13) as the tran-ion from the *s* block of metals to the *p* block of mostly metalloids nd nonmetals (Figure 14.18). Major changes occur in physical behav-rs we move across from metals to covalent networks. Changes in mical behavior occur as well, as cations give way to covalent tetra-dra. Looking ahead to Group 5A(15), we find covalent bonding and NNs increase) the expanded valence shells of nonmetals occurring e often, as well as the first appearance of monatomic anions.

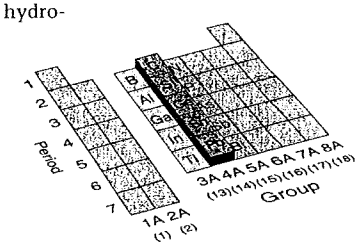


Figure 14.18 **Standing in Group 4A(14), looking backward to 3A(13) and forward to 5A(15).**

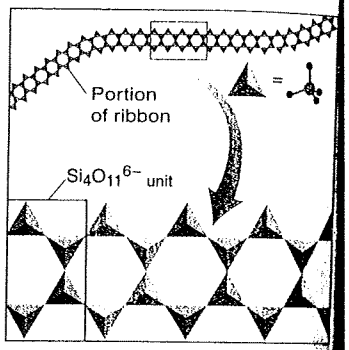
Silicate Minerals and Silicone Polymers

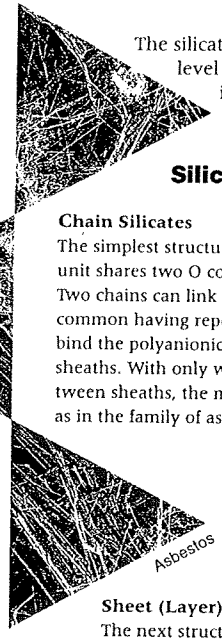
The silicates and silicones show beautifully how organization at the molecular level manifests itself in the properties of macroscopic substances. Interestingly, the major types of both materials exhibit the same three structural classes: chains, sheets, and frameworks.

Silicate Minerals

Chain Silicates

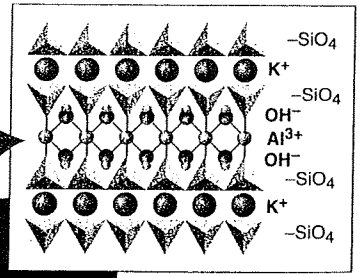
The simplest structural class occurs when each SiO_4 unit shares two O corners and links into a chain. Two chains can link laterally into a ribbon, the most common having repeating $Si_4O_{11}^{6-}$ units. Metal ions bind the polyanionic ribbons together into neutral sheaths. With only weak intermolecular forces between sheaths, the material occurs in fibrous strands, as in the family of asbestos minerals.

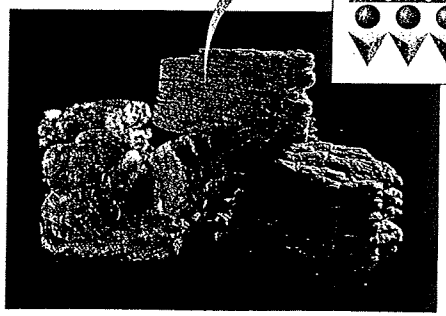




Sheet (Layer) Silicates

The next structural class arises when each SiO_4 unit shares three of its four O corners to form a sheet; double sheets arise when the fourth O is shared with another sheet. In talc, the softest mineral, the sheets interact through weak forces, so talcum powder feels slippery. If Al substitutes for some Si, or if $Al(OH)_3$ layers interleave with silicate sheets, an aluminosilicate results, such as the clay kaolinite. Different substitutions and/or interlayering of ions give the micas. In muscovite mica, ions lie between aluminosilicate double layers. Mica flakes when the ionic attractions are overcome.

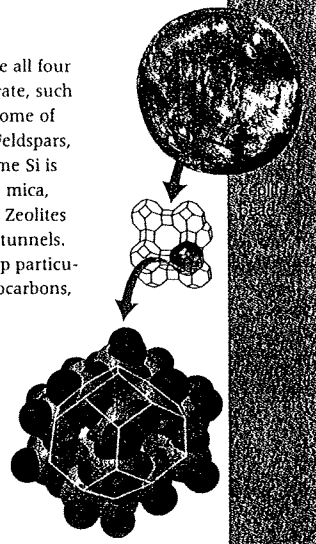




Muscovite mica

Framework Silicates

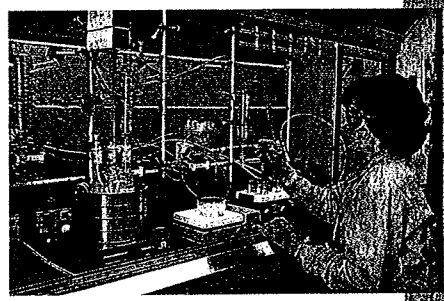
The final structural class arises when SiO_4 units share all four O corners to give a three-dimensional framework silicate, such as silica (SiO_2), which occurs most often as α-quartz. Some of silica's 12 crystalline forms exist as semiprecious gems. Feldspars, which comprise 60% of the Earth's crust, result when some Si is replaced by Al; granite consists of microcrystals of feldspar, mica, and quartz. Eons of weathering convert feldspars into clays. Zeolites have open frameworks of polyhedra that give rise to minute tunnels. Synthetic zeolites are made with cavities of specific sizes to trap particular molecules; they are used to dry gas mixtures, separate hydrocarbons, and prepare catalysts.

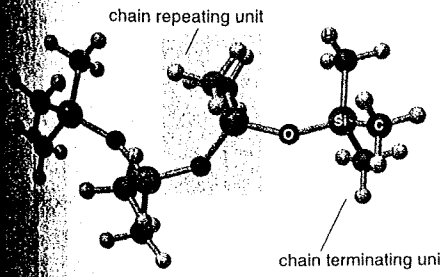


Silicone Polymers

Polymer Chemistry

The design, synthesis, and production of polymers forms one of the largest branches of modern chemical science. Nearly half of all industrial chemists and chemical engineers are involved in this pursuit. A major branch of polymer chemistry is devoted to exploring the properties and countless uses of silicones.





Chain Silicones: Oils and Greases

The simplest structural class is the polysiloxane chain, in which each $(CH_3)_2Si(OH)_2$ unit uses both OH groups to link two others. A chain-terminating compound with a third organic group, such as $(CH_3)_3SiOH$, is added to control chain length. Polysiloxanes are unreactive, oily liquids with high viscosity and low surface tension. They are used as hydraulic oils and lubricants, as anti-foam agents in frying potato chips, and as components of suntan oil, car polish, digestive aids, and makeup.

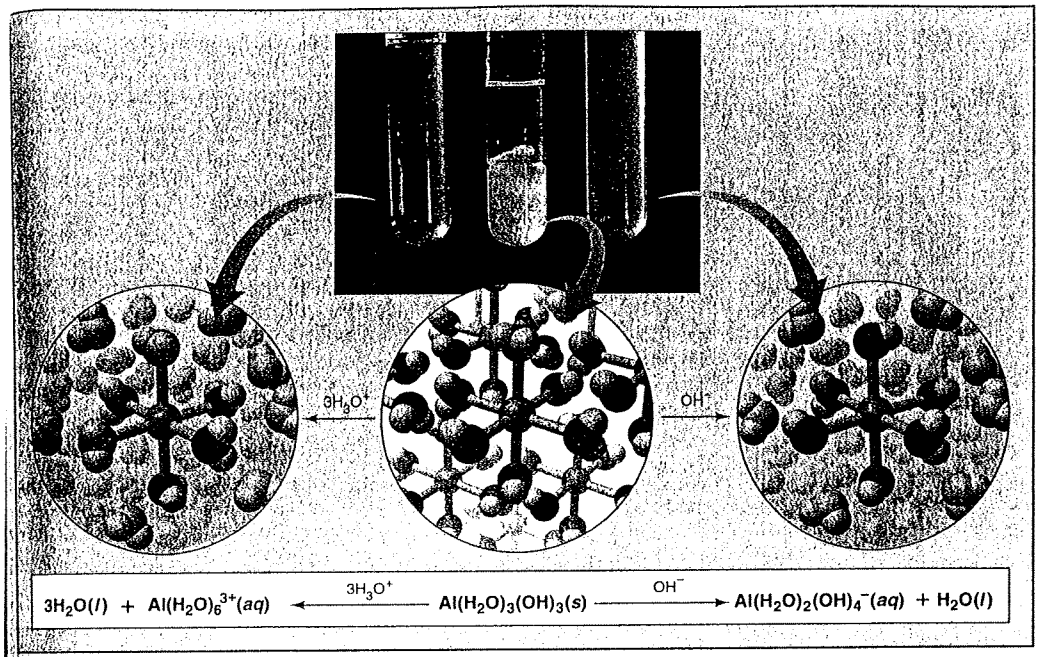


Figure 19.14 **The amphoteric behavior of aluminum hydroxide.** When solid $Al(OH)_3$ is treated with H_3O^+ (*left*) or with OH^- (*right*), it dissolves as a result of the formation of soluble complex ions. The molecular views show that $Al(OH)_3$ is actually the neutral species $Al(H_2O)_3(OH)_3$. (The extensive OH bridging that occurs between Al^{3+} ions throughout the solid is not shown.) Addition of OH^- (*right*) forms the soluble $Al(H_2O)_2(OH)_4^-$ ion; addition of H_3O^+ (*left*) forms the soluble $Al(H_2O)_6^{3+}$ ion.

Figure 19.14 shows this amphoteric behavior but includes some unexpected formulas for the species. Let's see how these species arise. When we dissolve a soluble aluminum salt, such as $Al(NO_3)_3$, in water and then slowly add a strong base, a white precipitate first forms and then dissolves as more base is added. What reactions are occurring? The formula for the hydrated Al^{3+} ion is $Al(H_2O)_6^{3+}(aq)$. It acts as a weak polyprotic acid and reacts with OH^- ions in a stepwise manner:

$$Al(H_2O)_6^{3+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_5OH^{2+}(aq) + H_2O(l)$$
$$Al(H_2O)_5OH^{2+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_4(OH)_2^+(aq) + H_2O(l)$$
$$Al(H_2O)_4(OH)_2^+(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_3(OH)_3(s) + H_2O(l)$$

At this point, the white precipitate has formed. It is the insoluble hydroxide $Al(H_2O)_3(OH)_3(s)$, often written as $Al(OH)_3(s)$. (It exists as a solid because of extensive bridging from one Al^{3+} ion to another by OH^- ions.) Now you can see that the precipitate is actually the hydrated Al^{3+} ion with an H^+ removed from each of three bound H_2O molecules. Addition of H_3O^+ protonates the OH groups and re-forms the hydrated Al^{3+} ion.

Further addition of OH^- removes a fourth H^+ and forms the soluble ion $Al(H_2O)_2(OH)_4^-(aq)$, which we usually write as $Al(OH)_4^-(aq)$:

$$Al(H_2O)_3(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(H_2O)_2(OH)_4^-(aq) + H_2O(l)$$

In other words, this complex ion is not created by ligands substituting for bound water molecules but through an acid-base reaction in which added OH^- ions titrate bound water molecules.

Several other slightly soluble hydroxides, such as those of Cr^{3+}, Zn^{2+}, Pb^{2+}, and Sn^{2+}, are amphoteric and exhibit similar reactions:

$$Zn(H_2O)_2(OH)_2(s) + OH^-(aq) \rightleftharpoons Zn(H_2O)(OH)_3^-(aq) + H_2O(l)$$

Transition Metals as Essential Dietary Trace Elements

Living things consist primarily of water and complex organic compounds of four key elements: carbon, oxygen, hydrogen, and nitrogen. All known organisms also contain seven other elements, known as *macro*nutrients because they occur in fairly high concentrations. In order of increasing atomic number, they are sodium, magnesium, phosphorus, sulfur, chlorine, potassium, and calcium. In addition, organisms contain a surprisingly large number of elements in much lower concentrations, and most of these *micro*nutrients, or *trace elements*, are transition metals.

With the exception of scandium and titanium, all of the Period 4 transition elements are essential for organisms, and plants require molybdenum (from Period 5) as well. Within the organism, the transition metal ion usually occurs at a bend of a protein chain covalently bonded to surrounding amino acid groups whose N and O atoms act as ligands. Despite the structural complexity of biomolecules, the principles of bonding and *d*-orbital splitting are the same as in simple inorganic systems. Table 23.A lists the Period 4 transition metals known, or thought, to be essential in human nutrition. We focus here on iron and zinc.

Iron plays a crucial role in oxygen transport in all vertebrates. The oxygen-transporting protein hemoglobin (Figure 23.A, *A*) consists of four protein chains called *globins*, each cradling the iron-containing complex *heme*. Heme is a porphyrin, a complex derived from a metal ion and the tetradentate ring ligand known as *porphin*. Iron(II) is centered in the plane of the porphin ring through coordinate covalent bonds with four N lone pairs, resulting in a square planar complex. When heme is bound in hemoglobin (Figure 23.A, *B*), the complex is *octahedral*, with the fifth ligand of iron(II) being an N atom from a nearby amino acid (histidine), and the sixth an O atom from either an O_2 (shown) or an H_2O molecule.

Hemoglobin exists in two forms, depending on the nature of the sixth ligand. In the blood vessels of the lungs, where O_2 concentration is high, heme binds O_2 to form *oxyhemoglobin*, which is transported in the arteries to O_2-depleted tissues. There, the O_2 is released and replaced by an H_2O molecule to form *deoxyhemoglobin*, which is transported in the veins back to the lungs. Since H_2O is a weak-field ligand, the d^6 Fe^{2+} ion in deoxyhemoglobin is part of a high-spin complex. Because of the relatively small *d*-orbital splitting, deoxyhemoglobin absorbs light at the red (low-energy) end of the spectrum and looks purplish blue, which accounts for the dark color of venous blood. On the other hand, O_2 is a strong-field ligand, so it increases the splitting energy. For this reason, oxyhemoglobin absorbs at the blue (high-energy) end of the spectrum, which accounts for the bright-red color of arterial blood.

The position of the Fe^{2+} ion relative to the plane of the porphin ring also depends on this sixth ligand. Bound to O_2, Fe^{2+} is *in* the porphin plane; bound to H_2O, it moves *out of* the plane slightly. This tiny (~70 pm = 7×10^{-11} m) change in Fe^{2+} position on release or attachment of O_2 influences the shape of its globin chain, which in turn alters the shape of a neighboring globin chain, triggering the release or attachment of *its* O_2, and so on to the other two globin chains. The very survival of vertebrate life is the result of this cooperative "teamwork" by the four globin chains because it allows hemoglobin to pick up O_2 rapidly from the lungs and unload it rapidly in the tissues.

Table 23.A Some Transition Metal Trace Elements in Humans

Element	Biomolecule Containing Element	Function of Biomolecule
Vanadium	Protein (?)	Redox couple in fat metabolism (?)
Chromium	Glucose tolerance factor	Glucose utilization
Manganese	Isocitrate dehydrogenase	Cell respiration
Iron	Hemoglobin and myoglobin	Oxygen transport
	Cytochrome *c*	Cell respiration; ATP formation
	Catalase	Decomposition of H_2O_2
Cobalt	Cobalamin (vitamin B_{12})	Development of red blood cells
Copper	Ceruloplasmin	Hemoglobin synthesis
	Cytochrome oxidase	Cell respiration; ATP formation
Zinc	Carbonic anhydrase	Elimination of CO_2
	Carboxypeptidase A	Protein digestion
	Alcohol dehydrogenase	Metabolism of ethanol

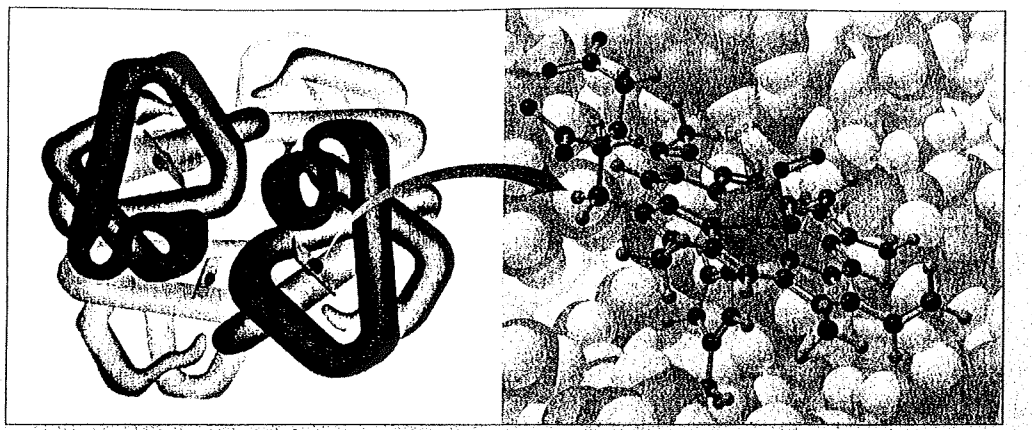


Figure 23.A **Hemoglobin and the octahedral complex n heme. A,** The structure of hemoglobin consists of four protein hains, each with a bound heme. **B,** In oxyhemoglobin, the octahedral complex in heme has iron(II) at the center surrounded by the four N atoms of the porphin ring, a fifth N from histidine *(below)*, and an O_2 molecule *(above)*. (Copyright Irving Geis; The estate of Irving Geis)

Carbon monoxide is highly toxic because it binds to the Fe^{2+} ion in heme about 200 times more tightly than O_2, hereby eliminating that heme group from functioning in the irculation. Like O_2, CO is a strong-field ligand and produces a right red, "healthy" look in the individual. Because heme inding is an equilibrium process, CO poisoning can be reersed by breathing extremely high concentrations of O_2, vhich effectively displaces CO from the heme:

$$\text{Heme—CO} + O_2 \rightleftharpoons \text{Heme—}O_2 + \text{CO}$$

Porphin rings are among the most common biological ligands. Chlorophyll, the photosynthetic pigment of green plants, is a porphyrin with Mg^{2+} at the center of the porphin ring, and vitamin B_{12} has Co^{3+} at the center of a very similar ring system. Heme itself is found not only in hemoglobin, but also in several redox proteins involved in energy metabolism (see Chemical Connections, Section 21.7).

The zinc ion occurs in many enzymes, the protein catalysts of cells (see Chemical Connections, Section 16.8). With its d^{10} configuration, Zn^{2+} is typically surrounded tetrahedrally by the N atoms of three amino acid groups, and the fourth position is free to interact with the molecule whose reaction is being catalyzed (Figure 23.B). In every case studied, the Zn^{2+} ion acts as a Lewis acid, accepting a lone pair from the reactant as a key step in the catalytic process. Consider the enzyme carbonic anhydrase, which catalyzes the essential reaction between H_2O and CO_2 during respiration:

$$CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The Zn^{2+} ion at the active site binds three histidine N atoms and the H_2O reactant as the fourth ligand. By withdrawing electron density from the O—H bonds, the Zn^{2+} makes the H_2O acidic enough to lose a proton. In the rate-determining step, the resulting bound OH^- ion attacks the partially positive C atom of CO_2 much more vigorously than could the lone pair of a free water molecule, so the reaction rate is higher. One reason the Cd^{2+} ion is toxic is that it competes with Zn^{2+} for fitting into the carbonic anhydrase active site.

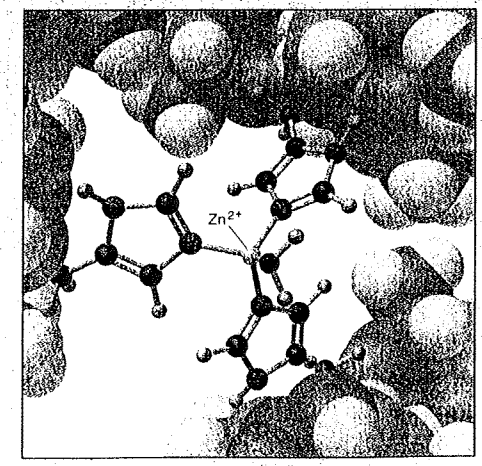


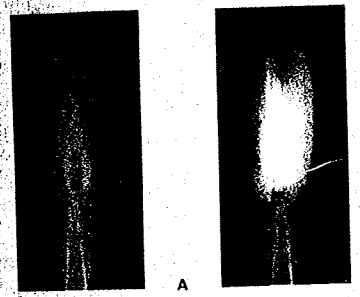
Figure 23.B **The tetrahedral Zn^{2+} complex in carbonic anhydrase.**

Spectrophotometry in Chemical Analysis

The use of spectral data to identify and quantify substances is essential to modern chemical analysis. The terms *spectroscopy, spectrometry,* and **spectrophotometry** denote a large group of instrumental techniques that obtain spectra corresponding to a substance's atomic and molecular energy levels.

The two types of spectra most often obtained are emission and absorption spectra. An **emission spectrum,** such as the H atom line spectrum, is produced when atoms in an excited state *emit* photons characteristic of the element as they return to lower energy states. Some elements produce a very intense spectral line (or several closely spaced ones) that serves as a marker of the element's presence. Such an intense line is the basis of **flame tests,** rapid qualitative procedures performed by placing a granule of an ionic compound or a drop of its solution in a flame (Figure 7.A, part A). Some of the colors of fireworks and flares are due to emissions from the same elements shown in the flame tests: crimson from strontium salts and blue-green from copper salts (Figure 7.A, part B). The characteristic colors of sodium-vapor and mercury-vapor streetlamps, seen in many towns and cities, are due to one or a few prominent lines in their emission spectra.

An **absorption spectrum** is produced when atoms *absorb* photons of certain wavelengths and become excited from lower to higher energy states. Therefore, the absorption spectrum of an element appears as dark lines against a bright background. When white light passes through sodium vapor, for example, it gives rise to a sodium absorption spectrum, and the dark lines appear at the same wavelengths where yellow-orange lines appear in the sodium emission spectrum (Figure 7.B). *(continued)*



A

B

Figure 7.A **Flame tests and fireworks. A,** In general, the color of the flame is created by a strong emission in the line spectrum of the element and therefore is often taken as preliminary evidence of the presence of the element in a sample. Shown here are the crimson of strontium and the blue-green of copper. **B,** The same emissions from compounds that contain these elements often appear in the brilliant displays of fireworks.

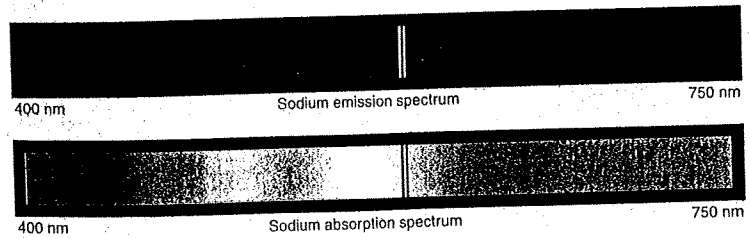


Figure 7.B **Emission and absorption spectra of sodium atoms.** The wavelengths of the bright emission lines correspond to those of the dark absorption lines because both are created by the same energy change: $\Delta E_{\text{emission}} = -\Delta E_{\text{absorption}}$. (Only the two most intense lines in the sodium atomic spectra are shown here.)

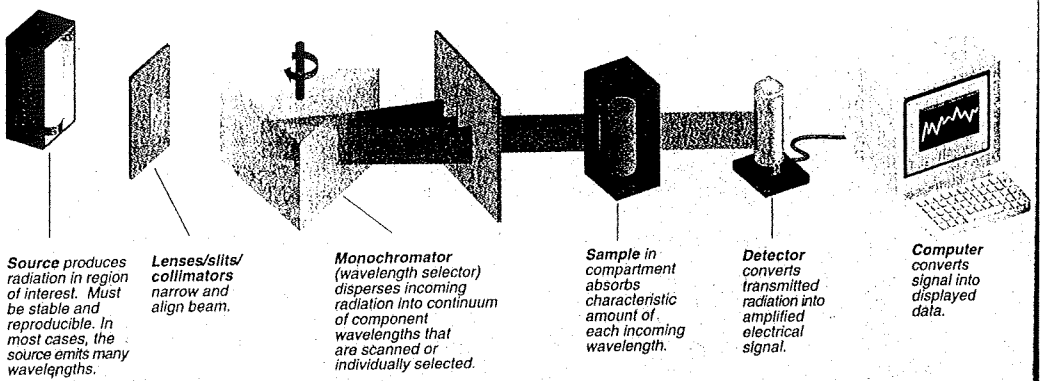


Figure 7.C The main components of a typical spectrometer.

Instruments based on absorption spectra are much more common than those based on emission spectra, for several reasons. When a solid, liquid, or dense gas is excited, it *emits* so many lines that the spectrum is a continuum (recall the continuum of colors in sunlight). Absorption is also less destructive of fragile organic and biological molecules.

Despite differences that depend on the region of the electromagnetic spectrum used to irradiate the sample, all modern spectrometers have components that perform the same basic functions (Figure 7.C). (We discuss infrared spectroscopy and nuclear magnetic resonance spectroscopy in later chapters.)

Visible light is often used to study colored substances, which absorb only some of the wavelengths from white light. A leaf looks green, for example, because its chlorophyll absorbs red and blue wavelengths strongly and green weakly, so most of the green is reflected. The absorption spectrum of chlorophyll *a* in ether solution appears in Figure 7.D.

The overall shape of the curve and the wavelengths of the major peaks are characteristic of chlorophyll *a*, so its spectrum serves as a means of identifying it from an unknown source. The curve varies in height because chlorophyll absorbs incoming wavelengths to different extents. The absorptions appear as broad bands, rather than as the distinct lines we saw earlier for individual gaseous atoms, because dissolved substances, as well as pure solids and liquids, absorb many more wavelengths due to the greater numbers and types of energy levels within a molecule, among molecules, and between molecules and solvent.

In addition to identifying a substance, a spectrometer can be used to measure its concentration because *the absorbance, the amount of light of a given wavelength absorbed by a substance, is proportional to the number of molecules.* Suppose you want to determine the concentration of chlorophyll in an ether solution of leaf extract. You select a strongly absorbed wavelength from the chlorophyll spectrum (such as 663 nm in Figure 7.D), measure the absorbance of the leaf-extract solution, and compare it with the absorbances of a series of ether solutions with known chlorophyll concentrations.

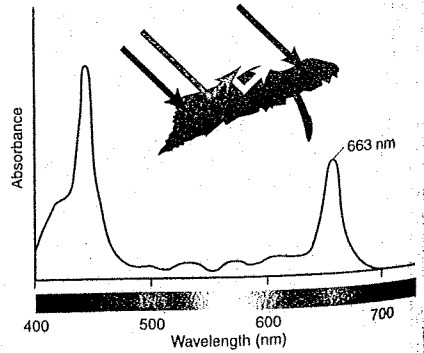
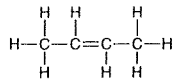
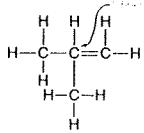
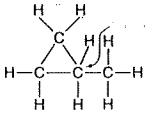


Figure 7.D The absorption spectrum of chlorophyll *a*.
Chlorophyll *a* is one of several leaf pigments. It absorbs red and blue wavelengths strongly but almost no green or yellow wavelengths. Thus, leaves containing large amounts of chlorophyll *a* appear green. The strong absorption at 663 nm can be used to quantify the amount of chlorophyll *a* present in a plant extract.

In **(b):** C—C—C=C is the same skeleton as C=C—C—C
since the double bond restricts rotation, another possible structure is



Too many bonds in 

In **(c):** Too many bonds in 

Follow-up Problem 15.4 Draw all hydrocarbons that have different atom arrangements with
(a) Seven C atoms, no multiple bonds, and no rings (nine arrangements)
(b) Five C atoms, one triple bond, and no rings (three arrangements)

The enormous number of hydrocarbons can be classified into four main groups. For the remainder of this section, we examine some structural features and physical properties of each group. Later, we discuss the chemical behavior of the hydrocarbons.

Alkanes: Hydrocarbons with Only Single Bonds

A hydrocarbon that contains only single bonds is an **alkane** (general formula C_nH_{2n+2}, where n is an integer). For example, if $n = 5$, the formula is $C_nH_{(2\times5)+2}$, or C_5H_{12}. These compounds comprise a **homologous series,** one in which each member differs from the next by a $-CH_2-$ (methylene) group. In alkanes, each C is sp^3 hybridized. Since each C is bonded to the *maximum number of other atoms* (C or H), alkanes are referred to as **saturated hydrocarbons.**

Naming Alkanes You learned the names of the first ten unbranched alkanes in Chapter 2 (see Table 2.7). Here we discuss general rules for naming any alkane and, by extension, other organic compounds as well. The key point to remember is that *each chain, branch, or ring has a name based on the number of C atoms.* The entire name of the compound has three portions:

PREFIX + ROOT + SUFFIX

Root: the root tells the number of C atoms in the longest *continuous* chain in the molecule. The roots are shown in Table 15.1. Recall that there are special roots for compounds of one to four C atoms; roots of longer chains are based on Greek numbers.

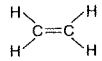
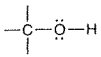
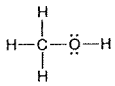
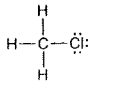
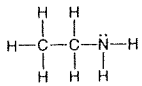
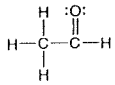
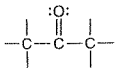
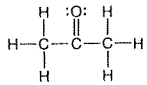
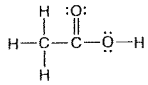
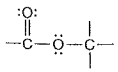
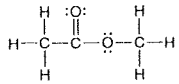
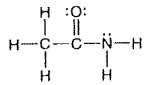
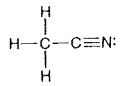
Prefix: each prefix tells the *group attached to the main chain* and the number of the carbon to which it is attached. Prefix names are the same as root names (Table 15.1) but take a *-yl* ending. Each prefix is placed *before* the root.

Suffix: the suffix tells the *type of organic compound* to which the molecule belongs, that is, the functional group the molecule possesses. The suffix is generally placed *after* the root.

Table 15.1 Numerical Roots for Carbon Chains and Branches

Root	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Table 15.5 Important Functional Groups in Organic Compounds

Functional Group	Compound Type	Suffix or Prefix of Name	Example	Systematic Name (Common Name)
	alkene	-ene		ethene (ethylene)
	alkyne	-yne		ethyne (acetylene)
	alcohol	-ol		methanol (methyl alcohol)
 (X=halogen)	haloalkane	halo-		chloromethane (methyl chloride)
	amine	-amine		ethylamine
	aldehyde	-al		ethanal (acetaldehyde)
	ketone	-one		2-propanone (acetone)
	carboxylic acid	-oic acid		ethanoic acid (acetic acid)
	ester	-oate		methyl ethanoate (methyl acetate)
	amide	-amide		ethanamide (acetamide)
	nitrile	-nitrile		ethanenitrile (acetonitrile, methyl cyanide)

Tools of the Chemistry Laboratory

Basic Separation Techniques

Some of the most challenging and time-consuming laboratory procedures involve separating mixtures and purifying the components. Several common separation techniques are described here. Note that all these methods depend on the *physical properties* of the substances in the mixture; no chemical changes occur.

Filtration separates the components of a mixture on the basis of *differences in particle size.* It is used most often to separate a liquid (smaller particles) from a solid (larger particles). Figure 2.D shows simple filtration of a solid reaction product. In vacuum filtration, reduced pressure within the flask speeds the flow of the liquid through the filter. Filtration is a key step in the purification of the tap water you drink.

Figure 2.D **Filtration.**

Crystallization is based on *differences in solubility.* The *solubility* of a substance is the amount that dissolves in a fixed volume of solvent at a given temperature. The procedure shown in Figure 2.E applies the fact that many substances are more soluble in hot solvent than in cold. Purified compound is shown crystallizing out of the solution as it is cooled. Essential substances in computer chips and other modern electronic devices are purified by a type of crystallization.

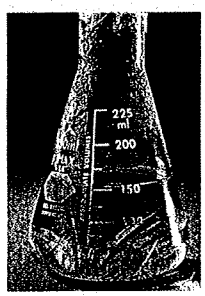


Figure 2.E **Crystallization.**

Distillation separates components through *differences in volatility,* the tendency of a substance to become a gas. Ether, for example, is more volatile than water, which is much more volatile than sodium chloride. As the mixture boils, the vapor is richer in the more volatile component, which can be condensed and collected separately. The simple distillation apparatus shown in Figure 2.F is used to separate components with *large* differences in volatility, such as water from dissolved ionic compounds. Separating components with small volatility differences requires many vaporization-condensation steps (as discussed in Chapter 13).

Extraction is also based on *differences in solubility.* In a typical procedure, a natural (often plant or animal) material is ground in a blender with a solvent that extracts (dissolves) soluble compound(s) embedded in insoluble material. This extract is separated further by the addition of a second solvent

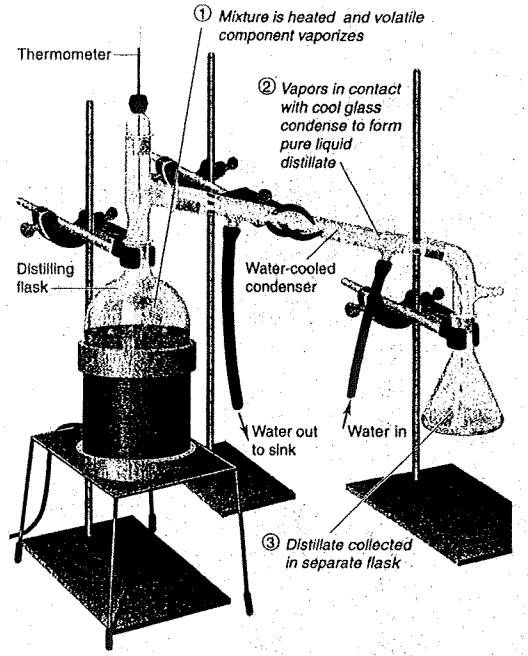


Figure 2.F **Distillation.**

that does not dissolve in the first. After shaking in a separatory funnel, some components are extracted into the new solvent. Figure 2.G shows the extraction of plant pigments from water into hexane, an organic solvent.

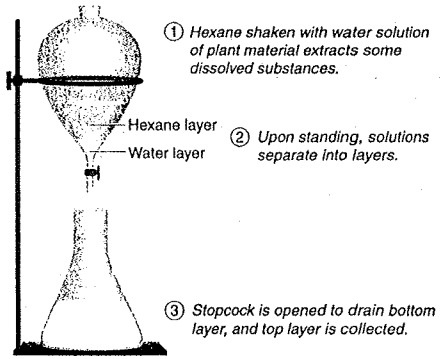


Figure 2.G **Extraction.**

Chromatography is a third technique based on *differences in solubility.* The mixture is dissolved in a gas or liquid called the *mobile phase,* and the components are separated as this phase moves over a solid (or viscous liquid) surface called the *stationary phase.* A component with low solubility in the stationary phase spends less time there, thus moving faster, than a component that is highly soluble in it. Figure 2.H depicts the separation of a mixture of pigments in ink. Many types of chromatography are used to separate a wide variety of substances, from simple gases to biological macromolecules. In *gas-liquid chromatography (GLC),* the mobile phase is an inert gas, such as helium, that carries the previously vaporized components into a long tube that contains the stationary phase (Figure 2.I, part A). The components emerge separately and reach a detector to create a chromatogram. A typical chromatogram has numerous peaks of specific position and height, each of which represents the amount of a given component (Figure 2.I, part B). The principle of *high-performance (high-pressure) liquid chromatography (HPLC)* is very similar, but the mixture is not vaporized, so a more diverse group of mixtures, which may include nonvolatile compounds, can be separated (Figure 2.J).

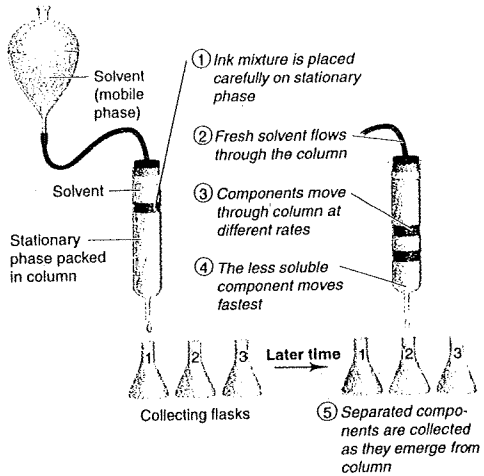
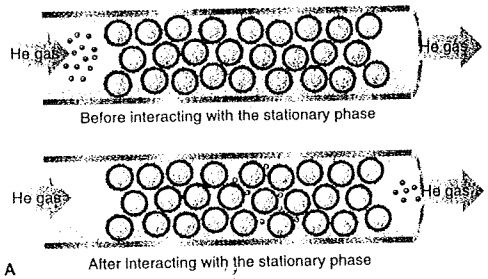


Figure 2.H **Procedure for column chromatography.**



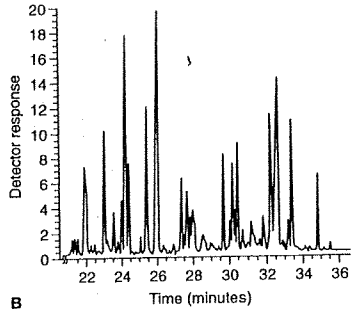


Figure 2.I **Principle of gas-liquid chromatography (GLC).** **A,** The moblile phase *(purple arrow)* carries the sample mixture into a tube packed with the stationary phase *(gray outine on yellow spheres),* and each component dissolves in the stationary phase to a different extent. A component *(red)* that dissolves less readily than another *(blue)* emerges from the tube sooner. **B,** A typical gas-liquid chromatogram displays each component as a peak.

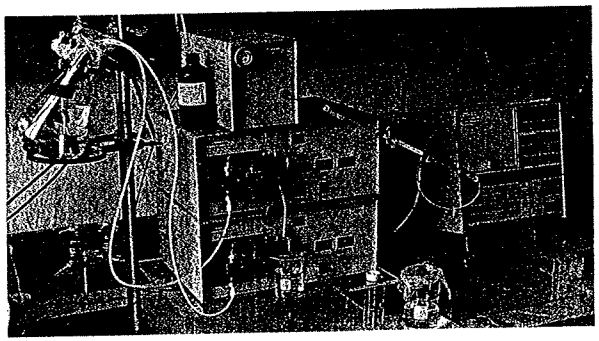


Figure 2.J **A high-performance liquid chromatograph.**

Mass Spectrometry

Mass spectrometry, the most powerful technique for measuring the mass and abundance of charged particles, is an outgrowth of electric and magnetic deflection studies on particles formed in cathode ray experiments. When a high-energy electron collides with an atom of neon-20, for example, one of the atom's electrons is knocked away and the resulting particle has one positive charge, Ne^+ (Figure 2.A). Therefore, its mass/charge ratio (*m/e*) equals the mass divided by 1+. These *m/e* values are measured to identify the masses of different isotopes of an element.

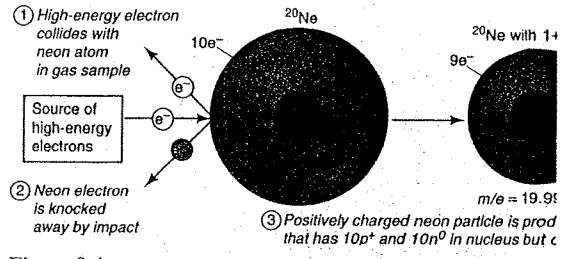


Figure 2.A **Formation of a positively charged neon (Ne) particl**

Figure 2.B depicts the core of one type of mass spectrometer and the data it provides. The sample is introduced and vaporized (if liquid or solid), then bombarded by high-energy electrons to form positively charged particles. These are attracted toward a series of negatively charged plates with slits in them, and some particles pass through into an evacuated tube exposed to a magnetic field. As the particles zoom through this region, they are deflected according to their *m/e*: the lightest particles are deflected most and the heaviest particles least. At the enc magnetic region, the particles strike a detector, which their relative position and abundance. For extremely work, such as determining isotopic masses and abun the instrument is calibrated with a substance of amount and mass.

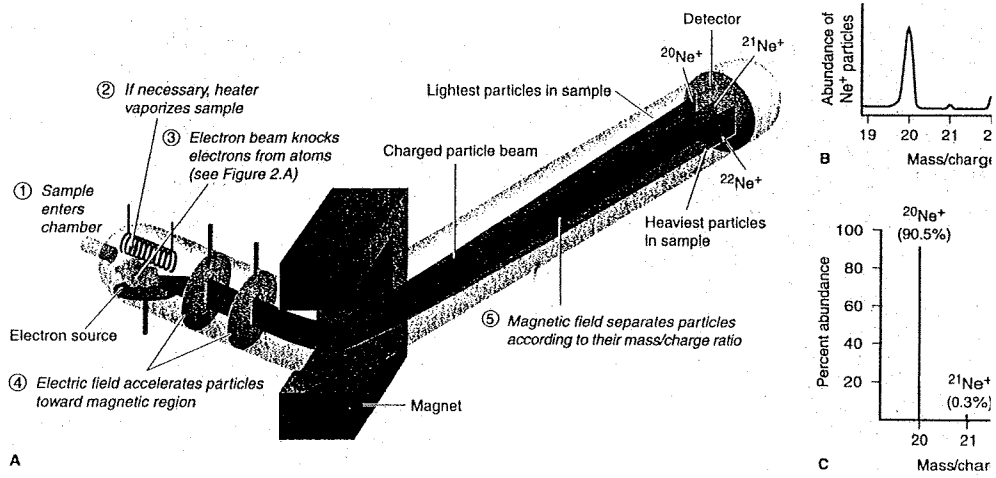
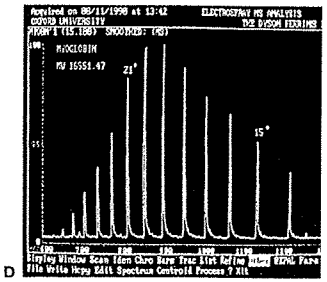


Figure 2.B **The mass spectrometer and its data.** **A,** The instrument separates charged particles on the basis of their mass/charge ratios (*m/e*). Atmospheric neon is the sample. In very exact work, the spectrometer can be tuned to measure *m/e* values to six decimal places. **B,** Mass spectral data from the sample show the abundance of each particle present. The three peaks correspond to three neon isotopes. **C,** The data are recalculated to show the percent abundance of each particle. **D,** The mass spectrum of a protein molecule.



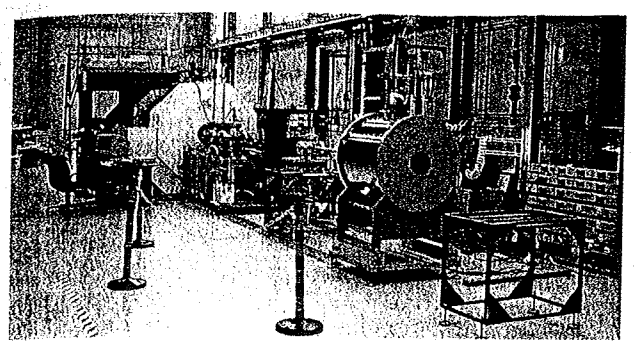


Figure 2.C **A modern mass spectrometer.** Some modern instruments have extremely powerful magnets that allow measurement of the masses of large molecules in the 10^5 amu range to an accuracy of better than 1 amu. Even the masses of single molecules in the 10^8 amu range have been measured. The instrument shown is a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer located at the NSF-sponsored National High Magnetic Field Laboratory.

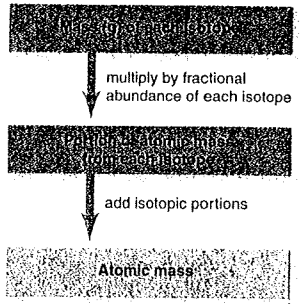
Mass spectrometry is also used in structural chemistry and separations science to measure the mass of virtually any atom, molecule, or fragment of a molecule (Figure 2.C). Among its many applications, mass spectrometry is employed by biochemists determining protein structures, materials scientists examining catalyst surfaces, forensic chemists analyzing criminal evidence, organic chemists designing new drugs, and industrial chemists investigating petroleum components.

Sample Problem 2.3 Calculating the Atomic Mass of an Element

PROBLEM Silver (Ag; $Z = 47$) has 46 known isotopes, but only two occur naturally, ^{107}Ag and ^{109}Ag. Given the following mass spectrometric data, calculate the atomic mass of silver:

ISOTOPE	MASS (amu)	ABUNDANCE (%)
^{107}Ag	106.90509	51.84
^{109}Ag	108.90476	48.16

PLAN From the mass and abundance of the two Ag isotopes, we have to find the atomic mass of Ag (weighted average of the isotopic masses). We multiply each isotopic mass by its fractional abundance to find the portion of the atomic mass contributed by each isotope. The sum of the isotopic portions is the atomic mass.



SOLUTION Finding the portion of the atomic mass from each isotope:

Portion of atomic mass from ^{107}Ag: = isotopic mass × fractional abundance
= 106.90509 amu × 0.5184 = 55.42 amu

Portion of atomic mass from ^{109}Ag: = 108.90476 amu × 0.4816 = 52.45 amu

Finding the atomic mass of silver:

Atomic mass of Ag = 55.42 amu + 52.45 amu = 107.87 amu

CHECK The individual portions seem right: ~100 amu × 0.50 = 50 amu. The portions are almost the same because the two isotopic abundances are almost the same. We rounded each portion to four significant figures because that is the number of significant figures in the abundance values. This is the correct atomic mass (to two decimal places), as shown in the list of elements.

COMMENT Averages must be interpreted carefully. The number of children in an average American family in 1985 was 2.4. Just as you know that no family actually has 2.4 children, you should also know that no individual silver atom has a mass of 107.87 amu. But for most laboratory purposes, we consider the sample to consist of atoms with this average mass.

Follow-up Problem 2.3 Boron (B; $Z = 5$) has two naturally occurring isotopes. Calculate the percent abundances of ^{10}B and ^{11}B from the following: atomic mass of B = 10.81 amu; isotopic mass of ^{10}B = 10.0129 amu; isotopic mass of ^{11}B = 11.0093 amu. (*Hint:* The sum of the fractional abundances is 1. If x = abundance of ^{10}B, then $1 - x$ = abundance of ^{11}B.)

Tools of the Chemistry Laboratory

Infrared Spectroscopy

Infrared (IR) spectroscopy is an instrumental technique used primarily for measuring the absorption of IR radiation by covalently bonded molecules. It plays a major role in our understanding of molecular structure and bonding. IR spectrometers are found in most research laboratories, particularly where organic molecules are studied, and are essential aids in identifying unknown substances. Their key components are the same as those of any spectrometer (see Tools of the Chemistry Laboratory, Section 7.2). The source emits radiation of many wavelengths, and those in the IR region are selected and directed at the sample. Certain wavelengths are absorbed more than others, and the IR spectrum of the compound is generated.

What property of a molecule is displayed in its IR spectrum? All molecules, whether in a gas, liquid, or solid, undergo continual rotations and vibrations. Consider, for instance, a sample of ethane gas. The $H_3C—CH_3$ molecules zoom throughout the container, colliding with the walls and each other. If we could look closely at one molecule, however, and disregard its motion through space, we would see the molecule rotating and its two CH_3 groups rotating relative to each other about the C—C bond. The bonded atoms also vibrate, that is, move back and forth as though their bonds were flexible springs: stretching and compressing, twisting, bending, rocking, and wagging (Figure 9.A). (Thus, the length of a given bond even within a given substance is actually the *average* distance between nuclei, analogous to the average length of a spring when it is stretching and compressing.)

Each vibrational motion has its own natural frequency, which is based on the type of motion, the masses of the atoms, and the strengths of the bonds between them. These frequen-

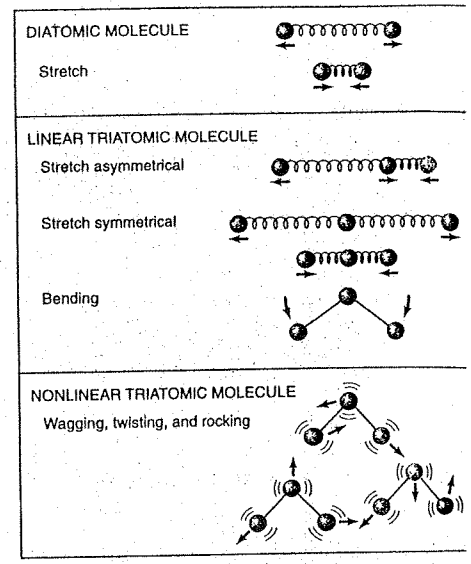


Figure 9.A **Some vibrational motions in general diato and triatomic molecules.**

Section Summary

A shared pair of valence electrons attracts the nuclei of two atoms and h them together in a covalent bond while making each atom's outer shell c plete. The number of shared pairs between the two atoms is the bond or For a given type of bond, the bond energy is the average energy require completely separate the bonded atoms; the bond length is the average tance between their nuclei. For a given pair of bonded atoms, bond ord directly related to bond energy and inversely related to bond length. stances that consist of separate molecules are generally soft and low me because of the weak *noncovalent* forces between molecules. Those together throughout by covalent bonds are extremely hard and high m ing. Most covalent substances have low electrical conductivity because trons are localized and ions are absent. The atoms in a covalent bond vib and the energy of these vibrations can be studied with IR spectroscopy.

cies correspond to wavelengths between 2.5 and 25 μm, which make up a part of the IR region of the electromagnetic spectrum (see Figure 7.3). The energy of each of these vibrations is quantized. Just as an atom can absorb a photon whose energy corresponds to the difference between two quantized *electron* energy levels, a molecule can absorb an IR photon whose energy corresponds to the difference between two of its quantized *vibrational* energy levels.

The IR spectrum is important in compound identification because of two related factors. First, *each kind of bond has a characteristic range of IR wavelengths it can absorb.* For example, a C—C bond absorbs IR photons of different wavelength range from those absorbed by a C=C bond, a C—H bond, a C=O bond, and so forth. Second, the exact wavelength and quantity of IR radiation absorbed by a given bond depend on the *overall structure* of the molecule. This means that *each compound has a characteristic IR spectrum* that can be used to identify it, much as a fingerprint identifies a person. The spectrum appears as a series of downward pointing peaks, varying in depth and sharpness, that correspond to absorption frequencies across the IR region scanned. Figure 9.B shows the IR spectrum of acrylonitrile, a compound that is used to manufacture synthetic rubber and plastics; no other compound has exactly the same IR spectrum.

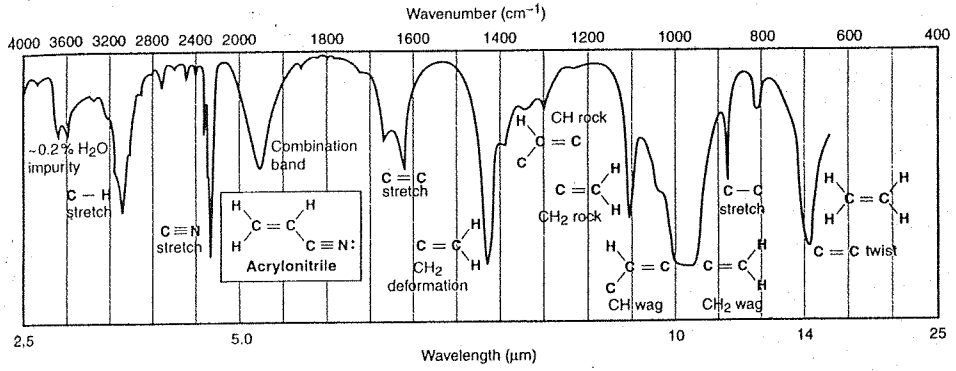


Figure 9.B The infrared (IR) spectrum of acrylonitrile. The IR spectrum of acrylonitrile is typical of a molecule with several types of covalent bonds. There are many absorption bands (peaks) of differing depth and sharpness. Most peaks correspond to a particular type of vibration in a particular group of bonded atoms. Some broad peaks (for example, "combination band") represent a variety of vibrational types that are overlapping. The spectrum is reproducible and unique for acrylonitrile. (The top axis shows wavenumbers, the inverse of wavelength, so its units are those of length^{-1}. The scale expands to the right of 2000 cm^{-1}.)

9.4 Between the Extremes: Electronegativity and Bond Polarity

Scientific models are idealized descriptions of reality. As we've discussed them so far, the ionic and covalent bonding models portray compounds as being formed by *either* complete electron transfer *or* complete electron sharing. However, the great majority of compounds have bonds that are more accurately thought of as partially ionic and partially covalent. Now that you're familiar with the ideal models, we can explore the actual continuum in bonding that lies between these extremes.

Electronegativity

One of the most important concepts in chemical bonding is **electronegativity (EN)**, the relative ability of a bonded atom to attract the shared

Nuclear Magnetic Resonance (NMR) Spectroscopy

Chemists rely on a battery of instrumental methods to determine the complex structures of organic molecules. Earlier we discussed mass spectrometry (Chapter 2) and infrared (IR) spectroscopy (Chapter 9). One of the most useful tools is **nuclear magnetic resonance (NMR) spectroscopy,** which measures the environments of certain nuclei in a molecule to elucidate its structure.

In Chapter 8, we saw that an electron can spin in either of two directions, each of which creates a tiny magnetic field. Several types of nuclei behave in a similar way. The most important of these are ^{1}H, ^{13}C, ^{19}F, and ^{31}P. In this discussion we focus primarily on the proton, ^{1}H, the nucleus of the most common isotope of hydrogen, and therefore refer to ^{1}H-NMR spectroscopy. Generally, the magnetic fields of all the protons in a sample of compound are oriented randomly. When placed in a strong external magnetic field (H_0), however, the proton fields become aligned with it (parallel) or against it (antiparallel). The parallel orientation is slightly lower in energy, with the energy difference (ΔE) between the two energy states (spin states) lying in the radio frequency (rf) region of the spectrum.

The protons in the sample oscillate rapidly between the two spin states, and in a process known as *resonance,* the rf value is varied until it matches the frequency of this oscillation. At this point, the protons are "in resonance" with the rf radiation and they absorb and reemit the energy, which is detected by the rf receiver of the NMR spectrometer (Figure 15.B). If all the protons in a sample required the same ΔE for resonance, an NMR spectrum would have only one peak and be useless. However, the ΔE between the two states depends on the *actual* magnetic field felt by each proton, which is affected by the tiny magnetic fields of the *electrons* on atoms adjacent to that proton. Thus, the ΔE of each proton depends on the electrons in the adjacent atoms—C atoms, electronegative atoms, multiple bonds, and aromatic rings—in other words,

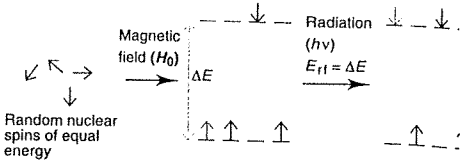


Figure 15.B The basis of proton spin resonance. The randomly oriented magnetic fields of protons in a sample become aligned in a strong external field (H_0), with slightly more protons in the lower spin state. In a process called *resonance,* the spin flips when the proton absorbs a photon with energy equal to ΔE (radio frequency region).

on the specific molecular environment. Therefore, the NM spectrum is *unique* to that compound.

The NMR spectrum of a compound is a series of peaks th represents the resonance of each proton as a function changing magnetic field. The *chemical shift* is the frequency which resonance occurs for a given proton, that is, where peak appears. The chemical shifts are shown relative to that an added standard, tetramethylsilane [$(CH_3)_4Si$, TMS], whi has 12 protons bonded to four C atoms that are bonded to o Si atom. Because the shape of TMS is tetrahedral around t Si, the protons are in identical environments, so they produ one peak. Figure 15.C shows the ^{1}H-NMR spectrum of ac tone. The six protons of acetone also have identical enviro ments—bonded to two C atoms that are bonded to the C at in a C=O bond—so they also produce one peak, but at a d ferent position from that of TMS. (The axes need not conc us.) The spectrum of dimethoxymethane in Figure 15 shows *two* peaks in addition to the TMS peak. The taller one due to the six CH_3 protons, and the shorter is due to the t

Isomers are compounds with the same molecular formula but differen properties. Structural isomers have different atom arrangements. Stereoiso mers (optical and geometric) have the same arrangement of atoms, but the atoms are oriented differently in space. Optical isomers cannot be superim posed on each other because they are asymmetric, with four different group bonded to the C that is the chiral center. They have identical physical an chemical properties except in their rotation of plane-polarized light and the reaction with chiral reactants. Geometric (*cis-trans*) isomers have groups or ented differently around a C=C bond, which restricts rotation. Light con verts *cis*-retinal to *trans*-retinal, which initiates the visual response. ^{1}H-NMR spectroscopy indicates the relative numbers of H atoms in the various envi ronments within an organic molecule.

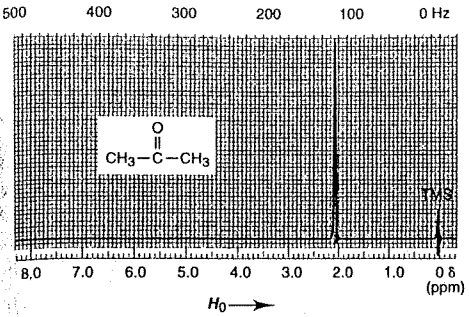


Figure 15.C **The ^{1}H-NMR spectrum of acetone.** Since the six CH_3 protons are in identical environments, they produce one peak, which has a different chemical shift from the 12 protons of the TMS standard.

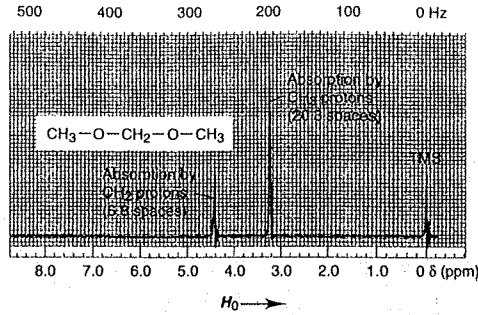


Figure 15.D **The ^{1}H-NMR spectrum of dimethoxymethane.** The two peaks represent the chemical shifts of protons in two different environments. The area under each peak is proportional to the number of protons in each environment.

CH_2 protons. The area under each peak (given here in units of chart-paper spaces) is proportional to *the number of protons in a given environment* and is determined by the instrument. Note that the area ratio is 20.3:6.8 ≈ 3:1, the same as the ratio of six CH_3 protons:two CH_2 protons. Thus, by analyzing the chemical shifts and peak areas, the chemist learns the type and number of each ^{1}H in the compound.

Newer NMR methods measure the resonance of other nuclei and have many applications in biochemistry and medicine. ^{13}C-NMR is used to monitor changes in protein and nucleic acid shape and function, and ^{31}P-NMR can determine the health of various organs. For example, the extent of damage from a heart attack can be learned by using ^{31}P-NMR to measure the concentrations of specific phosphate-containing molecules involved in energy utilization by cardiac muscle tissue. Most recently, computer-aided magnetic resonance imaging (MRI) has allowed visualization of damage to organs and greatly assists physicians in medical diagnosis. For example, an MRI scan of the head (Figure 15.E) can show various levels of metabolic activity in different regions of the brain.

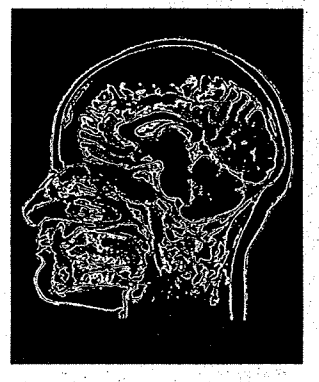


Figure 15.E **Magnetic resonance imaging (MRI) of a human head.** Colors indicate a range from high (*red*) to low (*blue*) metabolic activity.

15.3 Some Important Classes of Organic Reactions

In Chapter 4, we classified chemical reactions based on the chemical process involved (precipitation, acid-base, or redox) and then briefly included a classification based on the number of reactants and products (combination, decomposition, or displacement). We take a similar approach here with organic reactions.

From here on, we use the notation of an upper-case R with a single bond, such as to signify a general organic group attached to the atoms shown; you can usually picture R— as an **alkyl group,** a saturated hydrocarbon chain with one bond available. Thus, R—CH_2—Br has an alkyl group attached to a CH_2 group bearing a Br atom; R—CH=CH_2 is an alkene with an alkyl

Introduction to
ORGANIC CHEMISTRY

SECOND EDITION

William H. Brown
Beloit College

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Compounds containing a halogen atom covalently bonded to an sp^3 hybridized carbon atom are named haloalkanes or, in the common system of nomenclature, alkyl halides. The general symbol for an **alkyl halide** is R—X, where —X may be —F, —Cl, —Br, or —I.

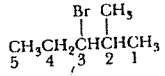
A haloalkane
(an alkyl halide)

In this chapter, we study two characteristic reactions of haloalkanes: nucleophilic substitution and β-elimination. By these reactions, alkyl halides can be converted to alcohols, ethers, thiols, amines, and alkenes. Thus, an understanding of nucleophilic substitution and β-elimination opens entirely new areas of organic chemistry for you.

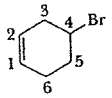
7.1 NOMENCLATURE

A. IUPAC System

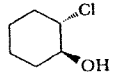
IUPAC names for haloalkanes are derived according to the rules given in Section 3.3A. The parent chain is located and numbered from the direction that gives the substituent encountered first the lower number. Halogen substituents are indicated by the prefixes fluoro-, chloro-, bromo-, and iodo- and are listed in alphabetical order along with other substituents. The location of each halogen atom on the parent chain is given by a number preceding the name of the halogen.



3-Bromo-2-methylpentane



4-Bromocyclohexene



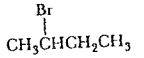
trans-2-Chlorocyclohexanol

In haloalkenes, numbering the parent hydrocarbon is determined by the location of the carbon-carbon double bond. In molecules containing functional groups designated by a suffix (for example, -ol, -al, -one, -oic acid), numbering is determined by the location of the functional group indicated by the suffix.

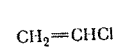
B. Common Names

Common names of haloalkanes consist of the common name of the alkyl group followed by the name of the halide as a separate word. Hence, the name **alkyl halide** is a common name for this class of compounds. In the following examples, the IUPAC name of the compound is given first and then, in parentheses, its common name.

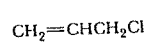
Alkyl halide A compound containing a halogen atom covalently bonded to an alkyl group; given the symbol RX.



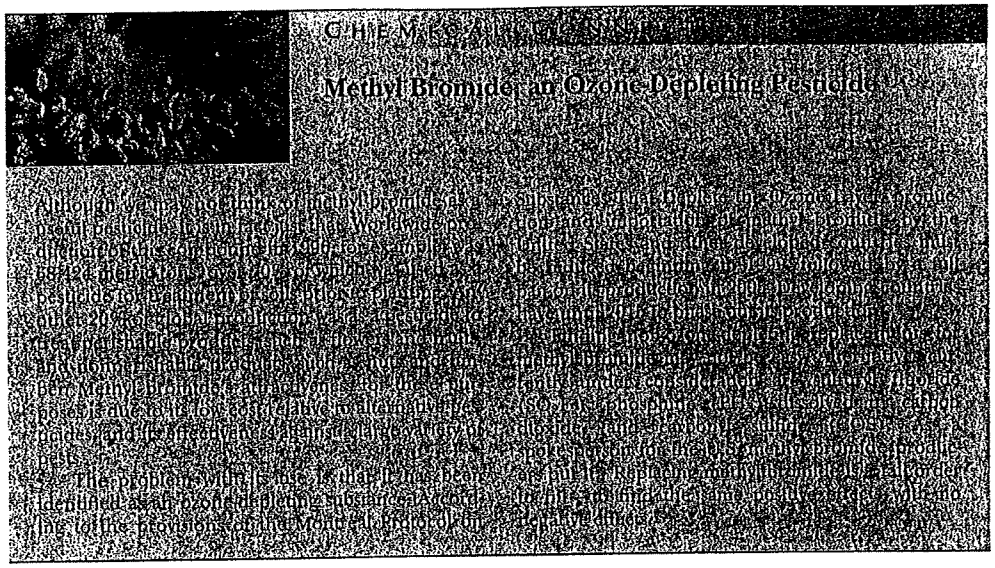
2-Bromobutane
(*sec*-Butyl bromide)



Chloroethene
(Vinyl chloride)



3-Chloropropene
(Allyl chloride)

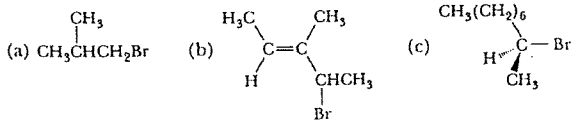


Several of the polyhalomethanes are common solvents and are generally referred to by their common, or trivial, names. Dichloromethane (methylene chloride) is the most widely used haloalkane solvent. Compounds of the type CHX_3 are called **haloforms**. The common name for $CHCl_3$, for example, is chloroform. It is from the name chloroform that the common name methyl chloroform is derived for the compound CH_3CCl_3. Methyl chloroform and trichloroethylene are common solvents for commercial dry cleaning.

CH_2Cl_2	$CHCl_3$	CH_3CCl_3	$CCl_2{=}CHCl$
Dichloromethane (Methylene chloride)	Trichloromethane (Chloroform)	1,1,1-Trichloroethane (Methyl chloroform)	Trichloroethylene (Trichlor)

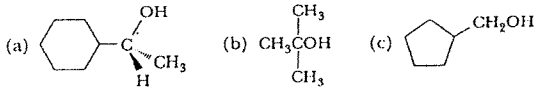
EXAMPLE 7.1

Write the IUPAC name for each compound.



EXAMPLE 8.2

Classify each alcohol as primary, secondary, or tertiary.

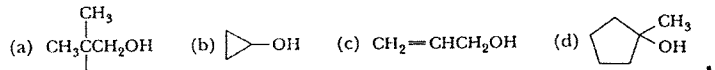


SOLUTION

(a) Secondary (2°) (b) Tertiary (3°) (c) Primary (1°)

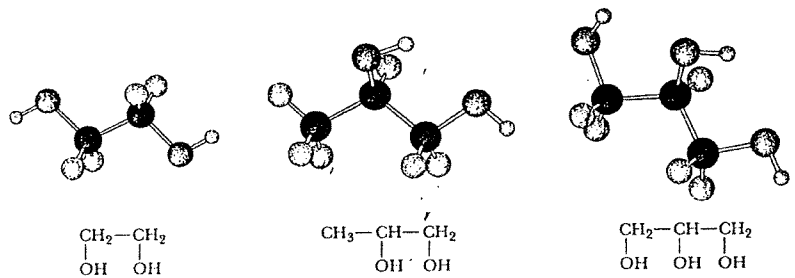
Practice Problem 8.2

Classify each alcohol as primary, secondary, or tertiary.



In the IUPAC system, a compound containing two hydroxyl groups is named as a **diol,** one containing three hydroxyl groups is named as a **triol,** and so on. In IUPAC names for diols, triols, and so on, the final -e (the suffix) of the parent alkane name is retained, as for example in the name 1,2-ethanediol. As with many organic compounds, common names for certain diols and triols have persisted. Compounds containing two hydroxyl groups on adjacent carbons are often referred to as **glycols** (Section 6.4B). Ethylene glycol and propylene glycol are synthesized from ethylene and propylene, respectively, hence their common names.

Glycol A compound with two hydroxyl (—OH) groups on adjacent carbons.



1,2-Ethanediol (Ethylene glycol)

1,2-Propanediol (Propylene glycol)

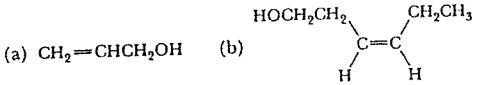
1,2,3,-Propanetriol (Glycerol, Glycerin)

Compounds containing —OH and C=C groups are often referred to as **unsaturated alcohols** because of the presence of the carbon-carbon double bond. In the IUPAC system, the parent alkane is numbered to give the —OH group the lowest possible number. The double bond is shown by changing the infix of the parent alkane from -an- to -en- (Section 3.5), and the alcohol is shown by changing

the suffix of the parent alkane from -e to -ol. Numbers must be used to show the location of both the carbon-carbon double bond and the hydroxyl group. In numbering the parent chain of these difunctional molecules, priority is given to the functional group indicated by the suffix over the one indicated by an infix.

EXAMPLE 8.3

Write the IUPAC name for each unsaturated alcohol.



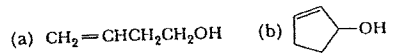
SOLUTION

(a) 2-Propen-1-ol. Its common name is allyl alcohol.

(b) *cis*-3-Hexen-1-ol. It is sometimes called leaf alcohol because of its occurrence in leaves of fragrant plants, including trees and shrubs (*The Merck Index,* 12th ed., #4737).

Practice Problem 8.3

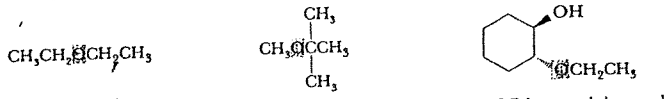
Write the IUPAC name for each unsaturated alcohol.



B. Ethers

In the IUPAC system, ethers are named by selecting the longest carbon chain as the parent alkane and naming the —OR group attached to it as an **alkoxy group.** Common names are derived by listing the alkyl groups attached to oxygen in alphabetical order and adding the word "ether." Following are the IUPAC names and, in parentheses, common names for three low-molecular-weight ethers.

Alkoxy group An —OR group, where R is an alkyl group.



Ethoxyethane (Diethyl ether)

2-Methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE)

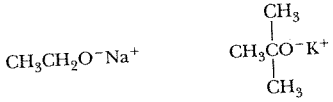
trans-2-Ethoxycyclohexanol

Chemists almost invariably use common names for low-molecular-weight ethers. For example, although ethoxyethane is the IUPAC name for $CH_3CH_2OCH_2CH_3$, it is rarely called that but rather, diethyl ether, ethyl ether, or even more commonly, simply ether. The abbreviation for *tert*-butyl methyl ether, an ether that is becoming increasingly important as an octane-improving additive to gasolines, is MTBE after the common name of methyl *tert*-butyl ether.

Cyclic ether An ether in which the ether oxygen is one of the atoms of a ring.

Cyclic ethers are heterocyclic compounds in which the ether oxygen is one of the atoms in a ring. These ethers are generally known by their common names.

used in organic reactions requiring a strong base in a nonaqueous solvent, as for example sodium ethoxide in ethanol.



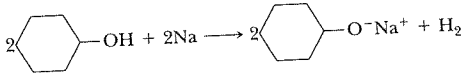
Sodium ethoxide

Potassium *tert*-butoxide

EXAMPLE 8.7

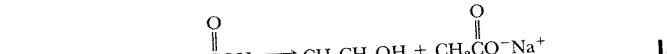
Write a balanced equation for the reaction of cyclohexanol with sodium metal.

SOLUTION



Practice Problem 8.7

Predict the position of equilibrium for this acid-base reaction. (*Hint:* Review Section 2.4.)

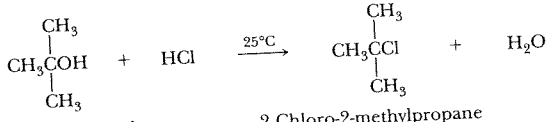


D. Conversion to Alkyl Halides

Conversion of an alcohol to an alkyl halide involves substitution of halogen for —OH at a saturated carbon. The most common reagents for this conversion are the halogen acids and $SOCl_2$. These reactions are examples of **nucleophilic aliphatic substitutions** (Section 7.2).

Reaction with HCl, HBr, and HI

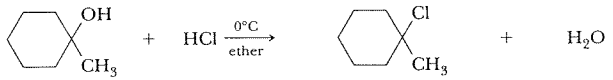
Water-soluble tertiary alcohols react very rapidly with HCl, HBr, and HI. Mixing a tertiary alcohol with concentrated hydrochloric acid for a few minutes at room temperature results in conversion of the alcohol to an alkyl chloride. Reaction is evident by formation of a water-insoluble chloroalkane that separates from the aqueous layer. Low-molecular-weight, water-soluble primary and secondary alcohols are unreactive under these conditions.



2-Methyl-2-propanol

2-Chloro-2-methylpropane

Water-insoluble tertiary alcohols are converted to tertiary halides by bubbling gaseous HX through a solution of the alcohol dissolved in diethyl ether or tetrahydrofuran (THF).



1-Methylcyclohexanol

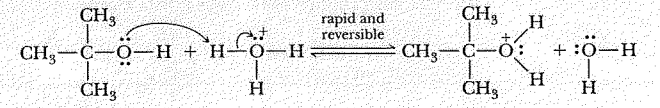
1-Chloro-1-methylcyclohexane

Water-insoluble primary and secondary alcohols react only slowly under these conditions.

To account for the reaction between a tertiary alcohol and HX, chemists propose an S_N1 mechanism. Step 1 is a rapid, reversible proton transfer from HX (or H_3O^+ when aqueous acid is used) to the hydroxyl group to give an oxonium ion. This is followed in Step 2 by loss of a molecule of water (the leaving group) to give a 3° carbocation intermediate. The 3° carbocation intermediate then reacts with halide ion in Step 3 to give the product. Formation of the carbocation intermediate in Step 2 is the rate-limiting step.

MECHANISM Reaction of a Tertiary Alcohol with HCl: An S_N1 Reaction

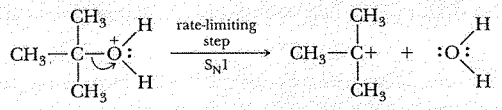
Step 1: Rapid and reversible proton transfer to the OH group gives an oxonium ion.



2-Methyl-2-propanol (*tert*-Butyl alcohol)

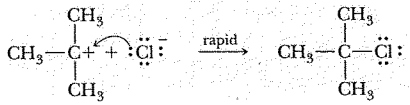
An oxonium ion

Step 2: Loss of water from the oxonium ion gives a 3° carbocation intermediate.



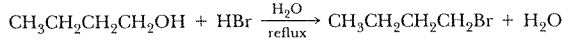
A 3° carbocation intermediate

Step 3: Reaction of the 3° carbocation intermediate (a Lewis acid) with chloride ion (a Lewis base) gives the product.



2-Chloro-2-methylpropane (*tert*-Butyl chloride)

Primary and secondary alcohols are converted to bromoalkanes and iodoalkanes by treatment with hydrobromic and hydroiodic acids. For example, when heated to reflux with concentrated HBr, 1-butanol is converted to 1-bromobutane.



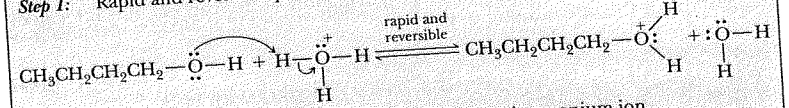
1-Butanol

1-Bromobutane

To account for the conversion of primary alcohols to alkyl bromides and iodides, chemists propose an S_N2 mechanism. Step 1 is a rapid, reversible reaction of the hydroxyl group with H_3O^+ to form an oxonium ion. In Step 2, halide ion reacts at the carbon bearing the oxonium ion to displace oxygen and to form a C—X bond. Displacement by halide ion is from the side of the primary carbon opposite that of the leaving oxonium ion. Step 2 is rate limiting.

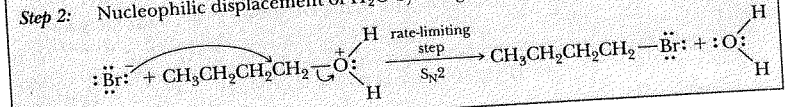
MECHANISM Reaction of a Primary Alcohol with HBr: An S_N2 Mechanism

Step 1: Rapid and reversible proton transfer to the OH group gives an oxonium ion.



An oxonium ion

Step 2: Nucleophilic displacement of H_2O by Br^- gives the alkyl bromide.



Why do tertiary alcohols react with HX by formation of a 3° carbocation intermediate, whereas primary alcohols react by direct displacement of —OH (more accurately, displacement of $—OH_2^+$)? The answer is a combination of the same two factors involved in nucleophilic substitution reactions of alkyl halides (Section 7.4B).

1. *Electronic factors* Tertiary carbocations are the most stable (lowest activation energy for their formation), whereas primary carbocations are the least stable (highest activation energy for their formation). Therefore, tertiary alcohols are most likely to react by carbocation formation; secondary alcohols are intermediate, and primary alcohols rarely, if ever, react by carbocation formation.
2. *Steric factors* To form a new carbon-halogen bond, halide ion must approach the substitution center and begin to form a new covalent bond to it. If we compare the ease of approach to the substitution center of a primary alcohol to that of a tertiary alcohol, we see that approach is considerably easier in the case of a primary alcohol. The backside of the substitution center of a primary alcohol is screened by two hydrogen atoms and one alkyl group, whereas the backside of the substitution center of a tertiary alcohol is screened by three alkyl groups.

Rate of direct displacement of H_2O → governed by steric factors (S_N2)

3° alcohol 2° alcohol 1° alcohol

governed by electronic factors (S_N1) ← Rate of substitution by carbocation formation

Reaction with Thionyl Chloride

The most widely used reagent for the conversion of primary and secondary alcohols to alkyl chlorides is thionyl chloride, $SOCl_2$. The by-products of this nucleophilic substitution reaction are HCl and SO_2, both given off as gases.

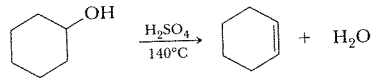
$$\underset{\text{1-Heptanol}}{CH_3(CH_2)_5CH_2OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{1-Chloroheptane}}{CH_3(CH_2)_5CH_2Cl} + \underset{\text{Sulfur dioxide}}{SO_2} + HCl$$

E. Acid-Catalyzed Dehydration of Alcohols to Alkenes

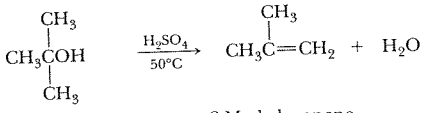
Dehydration Elimination of a molecule of water from a compound.

An alcohol can be converted to an alkene by elimination of a molecule of water from adjacent carbon atoms. Elimination of water is called **dehydration.** In the laboratory, dehydration of an alcohol is most often brought about by heating it with either 85% phosphoric acid or concentrated sulfuric acid. Primary alcohols are the most difficult to dehydrate and generally require heating in concentrated sulfuric acid at temperatures as high as 180°C. Secondary alcohols undergo acid-catalyzed dehydration at somewhat lower temperatures. Acid-catalyzed dehydration of tertiary alcohols often requires temperatures only slightly above room temperature.

$$CH_3CH_2OH \xrightarrow[180°C]{H_2SO_4} CH_2{=}CH_2 + H_2O$$



Cyclohexanol Cyclohexene



2-Methyl-2-propanol (*tert*-Butyl alcohol) 2-Methylpropene (Isobutylene)

Thus, the ease of acid-catalyzed dehydration of alcohols is in this order:

1° alcohol < 2° alcohol < 3° alcohol

Ease of dehydration of alcohols →

When isomeric alkenes are obtained in the acid-catalyzed dehydration of an alcohol, the alkene having the greater number of substituents on the double bond generally predominates; that is, acid-catalyzed dehydration of alcohols follows **Zaitsev's rule** (Section 7.6).

$$\underset{\text{2-Butanol}}{CH_3CH_2\underset{OH}{C}HCH_3} \xrightarrow[\text{heat}]{85\%\ H_3PO_4} \underset{\text{2-Butene (80\%)}}{CH_3CH{=}CHCH_3} + \underset{\text{1-Butene (20\%)}}{CH_3CH_2CH{=}CH_2}$$

TABLE 11.1 Increasing Order of Precedence of Six Functional Groups

Functional Group	Suffix if Higher in Precedence	Prefix if Lower in Precedence
$-CO_2H$	-oic acid	—
$-CHO$	-al	oxo-
$>C{=}O$	-one	oxo-
$-OH$	-ol	hydroxy-
$-NH_2$	-amine	amino-
$-SH$	-thiol	mercapto-

SOLUTION

(a) An aldehyde is of higher precedence than a ketone. The presence of the carbonyl group of the ketone is indicated by the prefix oxo-. The IUPAC name of this compound is 3-oxobutanal.

(b) The carboxyl group is of higher precedence. The presence of the amino group is indicated by the prefix amino-. The IUPAC name is 4-aminobenzoic acid. Alternatively, it may be named *p*-aminobenzoic acid, abbreviated PABA. PABA, a growth factor of microorganisms, is required for the synthesis of folic acid (*The Merck Index*, 12th ed., #443).

(c) The C=O group has higher precedence than the —OH group. The —OH group is indicated by the prefix hydroxy-. The IUPAC name of this compound is (R)-5-hydroxy-2-hexanone.

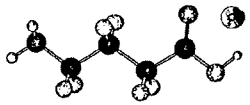
Practice Problem 11.3

Write IUPAC names for these compounds, each of which is important in intermediary metabolism. Below each is the name by which it is more commonly known in the biological sciences.

(a) $CH_3CH(OH)CO_2H$, Lactic acid (product of anaerobic glycolysis)

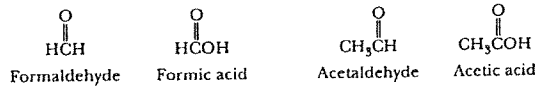
(b) CH_3CCO_2H (O), Pyruvic acid (product of anaerobic glycolysis)

(c) $H_2NCH_2CH_2CH_2CO_2H$, γ-Aminobutyric acid (a neurotransmitter)



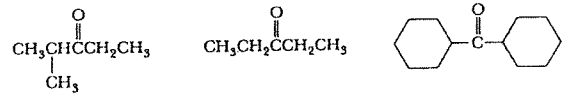
C. Common Names

The common name for an aldehyde is derived from the common name of the corresponding carboxylic acid by dropping the word "acid" and changing the suffix -ic or -oic to -aldehyde. Because we have not yet studied common names for carboxylic acids, we are not in a position to discuss common names for aldehydes. We can, however, illustrate how they are derived by reference to two common names of carboxylic acids with which you are familiar. The name formaldehyde is derived from formic acid; the name acetaldehyde is derived from acetic acid.



Formaldehyde — Formic acid — Acetaldehyde — Acetic acid

Common names for ketones are derived by naming each alkyl or aryl group attached to the carbonyl group as a separate word, followed by the word "ketone."



Ethyl isopropyl ketone — Diethyl ketone — Dicyclohexyl ketone

11.3 PHYSICAL PROPERTIES

Oxygen is more electronegative than carbon (3.5 compared with 2.5; Table 1.5); therefore, a carbon-oxygen double bond is polar, with oxygen bearing a partial negative charge and carbon bearing a partial positive charge.

Polarity of a carbonyl group

Because of the polarity of the carbonyl group, aldehydes and ketones are polar compounds and have higher boiling points than do nonpolar compounds of comparable molecular weight. Table 11.2 lists boiling points of six compounds of comparable molecular weight.

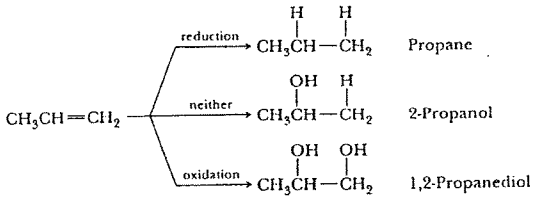
Pentane and diethyl ether have the lowest boiling points of these six compounds. Both butanal and 2-butanone are polar compounds, and, because of the intermolecular attraction between carbonyl groups, their boiling points are higher than those of pentane and diethyl ether. Alcohols (Section 8.3A) and carboxylic

TABLE 11.2 Boiling Points of Six Compounds of Comparable Molecular Weight

Name	Structural Formula	Molecular Weight	bp (°C)
diethyl ether	$CH_3CH_2OCH_2CH_3$	74	34
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36
butanal	$CH_3CH_2CH_2CHO$	72	76
2-butanone	$CH_3CH_2COCH_3$	72	80
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	117
propanoic acid	$CH_3CH_2CO_2H$	72	141

A. How to Recognize Oxidation-Reduction

In the following reactions, propene is transformed into three different compounds by reactions we study in this chapter. The first reaction involves reduction, the third involves oxidation, whereas the second involves neither oxidation nor reduction. These equations are not complete because they do not specify any reactant other than propene; that is, they do not specify what reagents are necessary to bring about the particular transformation. Each does specify, however, that the carbon atoms of the products are derived from those of propene.



It is possible to decide if transformations such as these involve oxidation, reduction, or neither by using **balanced half-reactions.** To write a balanced half-reaction:

1. Write a half-reaction showing the organic reactant(s) and product(s).
2. Complete a material balance—that is, balance the number of atoms on each side of the half-reaction. To balance the number of oxygens and hydrogens for a reaction taking place in acid solution, use H_2O for oxygens and then H^+ for hydrogens. For a reaction taking place in basic solution, use OH^- and H_2O.
3. Complete a charge balance—that is, balance the charge on both sides of the half-reaction. To balance the charge, add electrons, e^-, to one side or the other. The equation completed in this step is a balanced half-reaction.

Oxidation is the loss of electrons. If electrons appear on the right side of a balanced half-reaction, the reactant has given up electrons and has been oxidized. **Reduction** is the gain of electrons. If electrons appear on the left side of a balanced half-reaction, the reactant has gained electrons and has been reduced. If no electrons appear in the balanced half-reaction, then the transformation involves neither oxidation nor reduction. Let us apply these steps to the transformation of propene to propane.

Step 1: Half-reaction.

$$CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_3$$

Step 2: Material balance.

$$CH_3CH{=}CH_2 + 2H^+ \longrightarrow CH_3CH_2CH_3$$

Step 3: Balanced half-reaction.

$$CH_3CH{=}CH_2 + 2H^+ + 2e^- \longrightarrow CH_3CH_2CH_3$$

Because two electrons appear on the left side of the balanced half-reaction (Step 3), conversion of propene to propane is a two-electron reduction. To bring it about requires use of a reducing agent.

Oxidation The loss of electrons.

Reduction The gain of electrons.

Following is a balanced half-reaction for the transformation of propene to 2-propanol:

Balanced half-reaction: $CH_3CH{=}CH_2 + H_2O \longrightarrow CH_3\overset{\overset{OH}{|}}{C}HCH_3$

Propene — 2-Propanol

Because no electrons are required to achieve an electrical balance, conversion of propene to 2-propanol is neither oxidation nor reduction.

A balanced half-reaction for the transformation of propene to 1,2-propanediol requires two electrons on the right side of the equation for a charge balance; this transformation is a two-electron oxidation.

Balanced half-reaction: $CH_3CH{=}CH_2 + 2H_2O \longrightarrow CH_3\overset{\overset{HO}{|}}{C}H\overset{\overset{OH}{|}}{C}H_2 + 2H^+ + 2e^-$

Propene — 1,2-Propanediol

It is important to realize that this strategy for recognizing oxidation and reduction is only that, a strategy. In no way does it indicate how a particular oxidation or reduction might be carried out in the laboratory. For example, the balanced half-reaction for the transformation of propene to propane requires $2H^+$ and $2e^-$. Yet by far the most common laboratory procedure for reducing propene to propane does not involve H^+ at all; rather it involves molecular hydrogen, H_2, and a transition metal catalyst (Section 6.5).

We use this method of balanced half-reactions throughout the text to recognize transformations that involve oxidation, those that involve reduction, and those that involve neither oxidation nor reduction.

EXAMPLE 6.7

Balance each half-reaction to show that each transformation involves an oxidation.

(a) $CH_3CH_2CH_2OH \longrightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}H$

(b) $CH_3CH{=}CH_2 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}H + H\overset{\overset{O}{\|}}{C}H$

SOLUTION

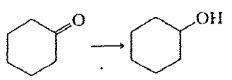
First complete a material balance and then a charge balance. Part (a) is a 2-electron oxidation; part (b) is a 4-electron oxidation. To bring each about requires an oxidizing agent.

(a) $CH_3CH_2CH_2OH \longrightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}H + 2H^+ + 2e^-$

(b) $CH_3CH{=}CH_2 + 2H_2O \longrightarrow CH_3\overset{\overset{O}{\|}}{C}H + H\overset{\overset{O}{\|}}{C}H + 4H^+ + 4e^-$

Practice Problem 6.7

Balance each half-reaction to show that each transformation involves a reduction.

(a) 

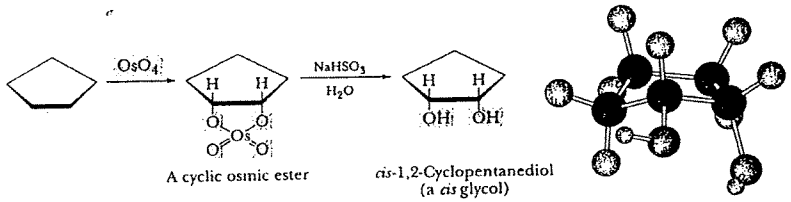
(b) $CH_3CH_2\overset{O}{\overset{\|}{C}}OH \longrightarrow CH_3CH_2CH_2OH$

B. OsO_4—Oxidation of an Alkene to a Glycol

Certain transition metal oxides, in particular osmium tetroxide, OsO_4, are effective oxidizing agents for the conversion of an alkene to a **glycol**, a compound with two hydroxyl groups on adjacent carbons. Oxidation of an alkene by osmium tetroxide is stereoselective in that it involves **syn addition** (addition from the same side) of —OH groups to the carbons of the double bond. For example, oxidation of cyclopentene by OsO_4 gives *cis*-1,2-cyclopentanediol, a **cis glycol.** Note that both cis and trans isomers are possible for this glycol.

Glycol A compound with two hydroxyl (—OH) groups on adjacent carbons.

Syn addition Addition of atoms or groups of atoms from the same side or face of a carbon-carbon double bond.

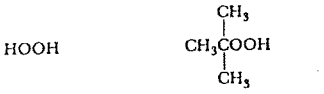


A cyclic osmic ester

cis-1,2-Cyclopentanediol (a *cis* glycol)

The stereoselectivity of osmium tetroxide oxidation of alkenes is accounted for by the formation of a cyclic osmic ester in which oxygen atoms of OsO_4 form new covalent bonds with each carbon of the double bond in such a way that the five-membered osmium-containing ring is fused in a cis configuration to the original alkene. Osmic esters can be isolated and characterized. Usually, however, they are treated directly with a reducing agent, such as $NaHSO_3$, which cleaves osmium-oxygen bonds to give the cis glycol and reduced forms of osmium.

The drawbacks of OsO_4 are that it is both expensive and highly toxic. One strategy to circumvent the high cost of OsO_4 is to use it in catalytic amounts along with stoichiometric amounts of another oxidizing agent, which reoxidizes the reduced forms of osmium and thus recycles the osmium reagent. Oxidizing agents commonly used for this purpose are hydrogen peroxide and *tert*-butyl hydroperoxide. When this procedure is used, there is no need for a reducing step using $NaHSO_3$.

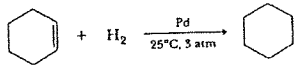


Hydrogen peroxide

tert-Butyl hydroperoxide (*t*-BuOOH)

6.5 Reduction of Alkenes—Formation of Alkanes

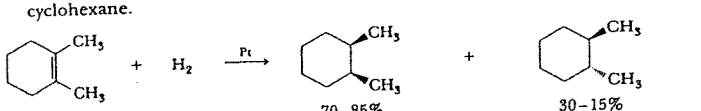
Virtually all alkenes react quantitatively with molecular hydrogen, H_2, in the presence of a transition metal catalyst to give alkanes. Commonly used transition metal catalysts include platinum, palladium, ruthenium, and nickel. Because conversion of an alkene to an alkane involves reduction by hydrogen in the presence of a catalyst, the process is called **catalytic reduction** or, alternatively, **catalytic hydrogenation.**



Cyclohexene Cyclohexane

The metal catalyst is used as a finely powdered solid, which may be supported on some inert material such as powdered charcoal or alumina. Reaction is carried out by dissolving the alkene in ethanol or another nonreacting organic solvent, adding the solid catalyst, and exposing the mixture to hydrogen gas at pressures from 1 to 100 atm. Alternatively, the metal may be complexed with certain organic molecules and used in the form of a soluble complex.

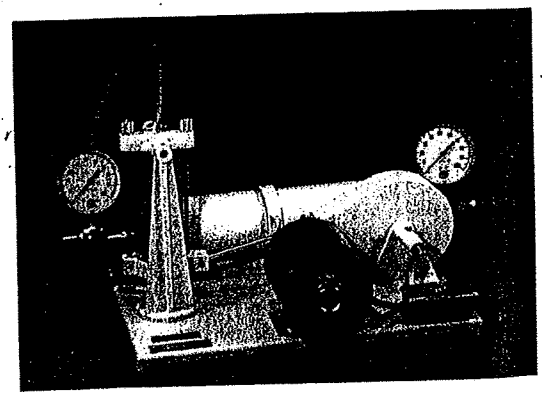
The most common pattern in catalytic reduction of an alkene is syn addition of hydrogens to the carbon-catalyst double bond. Catalytic reduction of 1,2-dimethylcyclohexene, for example, yields predominantly *cis*-1,2-dimethylcyclohexane. Along with the cis isomer are formed lesser amounts of *trans*-1,2-dimethylcyclohexane.



1,2-Dimethylcyclohexene

70–85% *cis*-1,2-Dimethylcyclohexane

30–15% *trans*-1,2-Dimethylcyclohexane



Paar shaker-type hydrogenation apparatus. *(Paar Instrument Co., Moline, IL)*

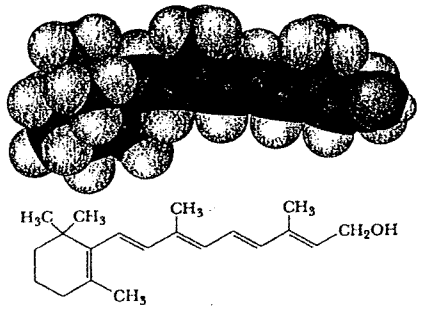
SOLUTION

Cis-trans isomerism is possible about both double bonds. Four isomers are possible.

Practice Problem 5.7

The sex pheromone of the silkworm is (10E,12Z)-10,12-hexadecadien-1-ol. Draw a structural formula for this compound.

An example of a biologically important compound for which a number of cis-trans isomers is possible is vitamin A. There are four carbon-carbon double bonds in the chain of carbon atoms attached to the substituted cyclohexene ring, and each has the potential for cis-trans isomerism. There are $2^4 = 16$ cis-trans isomers possible for this structural formula. Vitamin A is the all-trans isomer.

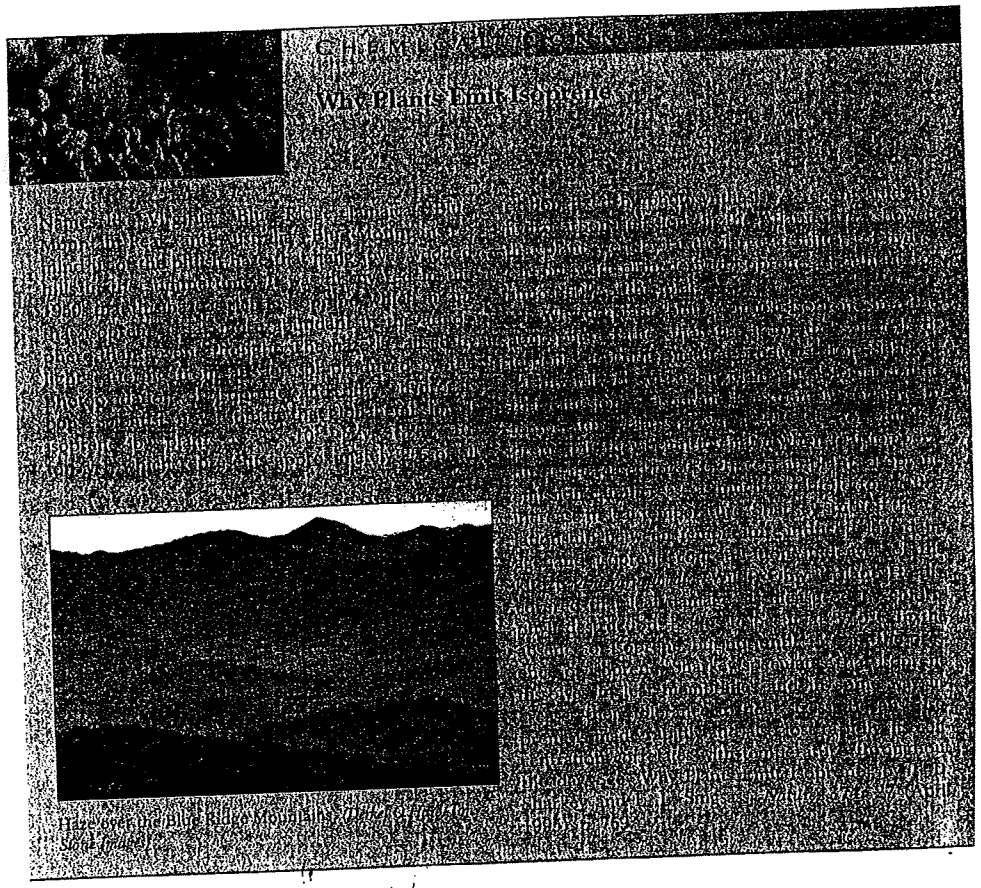


5.3 PHYSICAL PROPERTIES

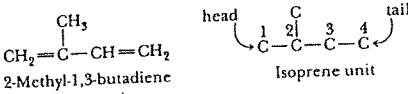
Alkenes and alkynes are nonpolar compounds, and the only attractive forces between their molecules are dispersion forces. Therefore, their physical properties are similar to those of alkanes (Section 3.8) with the same carbon skeletons. Those that are liquid at room temperature have densities less than 1.0 g/mL (they are less dense than water). They are insoluble in water but soluble in one another, in other nonpolar organic liquids, and in ethanol.

5.4 NATURALLY OCCURRING ALKENES — THE TERPENES

A terpene is a compound whose carbon skeleton can be divided into two or more units that are identical with the carbon skeleton of isoprene. Carbon 1 of an isoprene unit is called the head, and carbon 4 is called the tail. Terpenes are formed by stringing together the tail of one isoprene unit to the head of another.



Silk worms spinning cocoons on a loom, silk farm, Japan. *(Paul Chesley/Tony Stone Worldwide)*



2-Methyl-1,3-butadiene (Isoprene)

Isoprene unit

Terpenes are among the most widely distributed compounds in the biologic world, and a study of their structure provides a glimpse of the wondrous diversi

Terpene A compound whose carbon skeleton can be divided into two or more units identical with the carbon skeleton of isoprene.

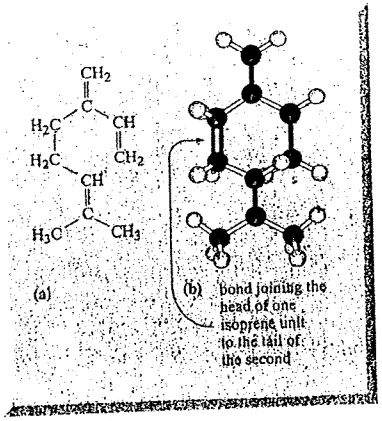


Figure 5.2
Myrcene. (a) The structural formula of myrcene and (b) a ball-and-stick model divided to show two isoprene units joined by a carbon-carbon bond between the head of one unit and the tail of the other.

that nature can generate from a simple carbon skeleton. Terpenes also illustrate an important principle of the molecular logic of living systems, namely that in building large molecules, small subunits are strung together enzymatically by an iterative process and then chemically modified by precise enzyme-catalyzed reactions. Chemists use the same principles in the laboratory, but our methods do not have the precision and selectivity of the enzyme-catalyzed reactions of cellular systems.

Probably the terpenes most familiar to you, at least by odor, are components of the so-called essential oils obtained by steam distillation or ether extraction of various parts of plants. Essential oils contain the relatively low-molecular-weight substances that are, in large part, responsible for characteristic plant fragrances. Many essential oils, particularly those from flowers, are used in perfumes.

One example of a terpene obtained from an essential oil is myrcene, $C_{10}H_{16}$, a component of bayberry wax and oils of bay and verbena. Myrcene is a triene with a parent chain of eight carbon atoms and two one-carbon branches (Figure 5.2).

Head-to-tail linkages of isoprene units are vastly more common in nature than are the alternative head-to-head or tail-to-tail patterns. Figure 5.3 shows structural formulas of six more terpenes, all derived from two isoprene units. Geraniol and the aggregating pheromone of the bark beetle have the same isoprene skeleton as myrcene. In addition, each has an —OH (hydroxyl) group. In the last four terpenes of Figure 5.3, the carbon atoms present in myrcene, geraniol, and the bark beetle pheromone are cross-linked to give cyclic structures. To help you identify the points of cross linkage and ring formation, the carbon atoms of the geraniol skeleton are numbered 1 through 8. This numbering pattern is used in the remaining terpenes to show points of cross-linking.

California laurel, *Umbellularia californica*, one source of myrcene. *(© Don Suzio)*

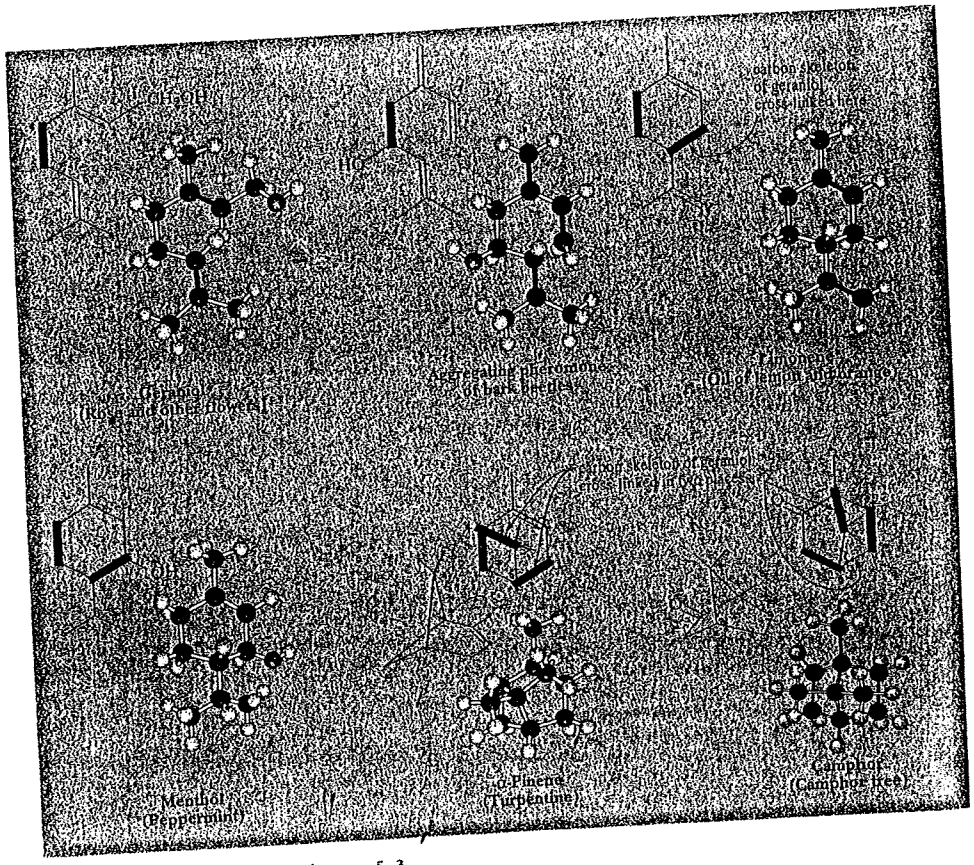


Figure 5.3
Six terpenes, each divisible into two isoprene units.

Shown in Figure 5.4 are structural formulas of three terpenes divisible into three isoprene units. For reference, the carbon atoms of the parent chain of farnesol are numbered 1 through 12. A bond between carbon atoms 1 and 6 of this skeleton gives the carbon skeleton of zingiberene. Try to discover for yourself what pattern of cross-linking gives the carbon skeleton of caryophyllene.

Vitamin A (Section 5.2G), a terpene of molecular formula $C_{20}H_{30}O$, consists of four isoprene units linked head-to-tail and cross-linked at one point to form a six-membered ring.

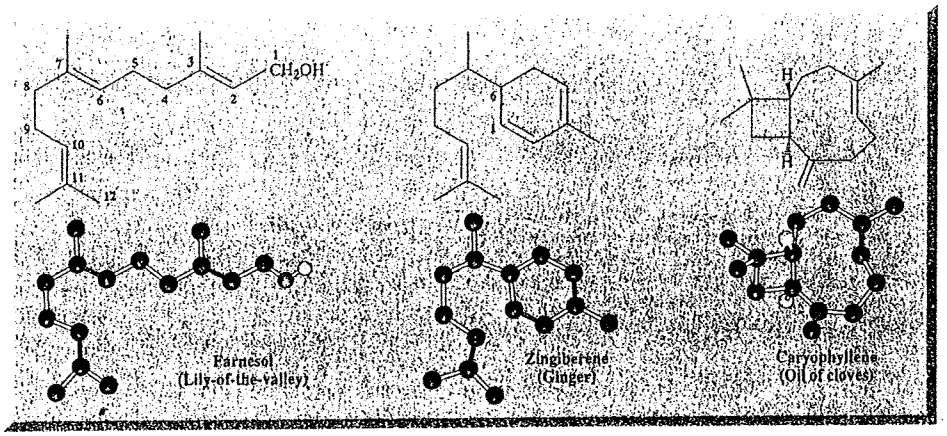


Figure 5.4
Three terpenes containing three isoprene units.

SUMMARY

An alkene is an unsaturated hydrocarbon that contains a carbon-carbon double bond. Alkenes have the general formula C_nH_{2n}. An **alkyne** is an unsaturated hydrocarbon that contains a carbon-carbon triple bond. Alkynes have the general formula C_nH_{2n-2}. According to the **orbital overlap model** (Section 5.1B), a carbon-carbon double bond consists of one sigma bond formed by the overlap of sp^2 hybrid orbitals and one pi bond formed by the overlap of parallel $2p$ atomic orbitals. It takes approximately 63 kcal/mol (264 kJ/mol) to break the pi bond in ethylene. A carbon-carbon triple bond consists of one sigma bond formed by the overlap of sp hybrid orbitals and two pi bonds formed by the overlap of pairs of parallel $2p$ orbitals.

The structural feature that makes **cis-trans isomerism** possible in alkenes is restricted rotation about the two carbons of the double bond (Section 5.1C). To date, *trans*-cyclooctene is the smallest trans cycloalkene that has been prepared in pure form and is stable at room temperature.

According to the IUPAC system (Section 5.2A), the presence of a **carbon-carbon double bond** is shown by changing the infix of the parent hydrocarbon from -an- to -en-. The names vinyl and allyl are commonly used to show the presence of $-CH=CH_2$ and $-CH_2CH=CH_2$ groups. The presence of a **carbon-carbon triple bond** is shown by changing the infix of the parent alkane from -an- to -yn-.

Whether the configuration of an alkene is cis or trans is determined by the orientation of the parent chain about the double bond (Section 5.2C). If atoms of the parent are on the same side of the double bond, the configuration of the alkene is cis; if they are on opposite sides, the configuration is trans. The configuration of a carbon-carbon double bond can also be specified by the **E,Z system** (Section 5.2C) using a set of priority rules. If the two groups of higher priority are on the same side of the double bond, the configuration of the alkene is **Z** (German: *zusammen*, together); if they are on opposite sides, it is **E** (German: entgegen, opposite).

For compounds containing two or more double bonds, the infix is changed to -adien-, -atrien-, and so on (Section 5.2F). Compounds containing several double bonds are called polyenes.

Because alkenes and alkynes are nonpolar compounds and the only interactions between their molecules are **dispersion forces**, their physical properties are similar to those of alkanes (Section 5.3).

The characteristic structural feature of a **terpene** (Section 5.4) is a carbon skeleton that can be divided into two or more **isoprene units**. Terpenes illustrate an important principle of the molecular logic of living systems, namely that in building large molecules, small subunits are strung together by an iterative process and then chemically modified by precise enzyme-catalyzed reactions.

TABLE 21.3 Average Values of Chemical Shifts of Representative Types of Hydrogens

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
$(CH_3)_4Si$	0 (by definition)	$RCOCH_3$	3.7–3.9
RCH_3	0.8–1.0	$RCOCH_2R$	4.1–4.7
RCH_2R	1.2–1.4	RCH_2I	3.1–3.3
R_3CH	1.4–1.7	RCH_2Br	3.4–3.6
$R_2C{=}CRCHR_2$	1.6–2.6	RCH_2Cl	3.6–3.8
$RC{\equiv}CH$	2.0–3.0	RCH_2F	4.4–4.5
$ArCH_3$	2.2–2.5	$ArOH$	4.5–4.7
$ArCH_2R$	2.3–2.8	$R_2C{=}CH_2$	4.6–5.0
ROH	0.5–6.0	$R_2C{=}CHR$	5.0–5.7
RCH_2OH	3.4–4.0	ArH	6.5–8.5
RCH_2OR	3.3–4.0	RCH	9.5–10.1
R_2NH	0.5–5.0	$RCOH$	10–13
$RCCH_3$	2.1–2.3		
$RCCH_2R$	2.2–2.6		

* Values are approximate. Other atoms within the molecule may cause the signal to appear outside these ranges.

Practice Problem 21.5

Following are two constitutional isomers of molecular formula $C_4H_8O_2$.

$CH_3CH_2OCCH_3$ (1) $CH_3CH_2COCH_3$ (2)

(a) Predict the number of signals in the ^{1}H-NMR spectrum of each isomer.
(b) Predict the ratio of areas of the signals in each spectrum.

21.9 SIGNAL SPLITTING AND THE (n + 1) RULE

We have now seen three kinds of information that can be derived from examination of a ^{1}H-NMR spectrum.

1. From the number of signals, we can determine the number of sets of equivalent hydrogens.
2. From integration of signal areas, we can determine the relative numbers of hydrogens giving rise to each signal.
3. From the chemical shift of each signal, we can derive information about the types of hydrogens in each set.

CHEMICAL CONNECTIONS

Magnetic Resonance Imaging

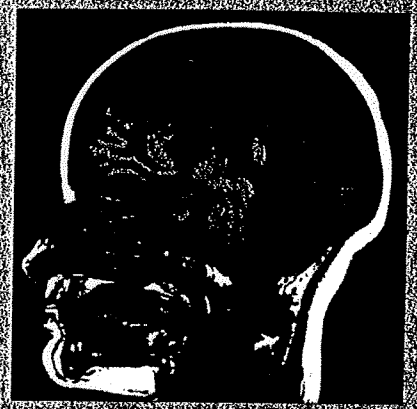
The NMR phenomenon was discovered and explained by physicists in the 1950s, and by the 1960s it had become an invaluable analytical tool for chemists. It was realized by the early 1970s that imaging of parts of the body using NMR could be a valuable addition to diagnostic medicine. Because the term "nuclear magnetic resonance" sounds to many people as if the technique might involve radioactive material, health care personnel call the technique "magnetic resonance imaging (MRI)."

The body contains several nuclei that in principle could be used for MRI. Of these, hydrogen, most of which comes from the hydrogens of water, triglycerides, and membrane phospholipids, gives the most useful signals. Phosphorus MRI is also used in diagnostic medicine.

Recall that in NMR spectroscopy, energy in the form of radio frequency radiation is absorbed by nuclei in the sample. The relaxation time is the characteristic time at which excited nuclei give up this energy and relax to their ground state.

In 1971, it was discovered that relaxation of water in certain cancerous tumors takes much longer than the relaxation of water in normal cells. Thus, it was reasoned if a relaxation image of a body could be obtained, it might be possible to identify tumors at an early stage. Subsequent work demonstrated that many tumors can be identified in this way. Another important application of MRI is in the examination of the brain and spinal cord. White and gray matter are easily distinguished by MRI, which is useful in the study of such diseases as multiple sclerosis. Magnetic resonance imaging and x-ray imaging are in many cases complementary. The hard, outer layer of bone is essentially invisible to MRI but shows up extremely well in x-ray images, whereas soft tissue is nearly transparent to x-rays but shows up in MRI.

The key to any medical imaging technique is to know which part of the body gives rise to which signal. In MRI, spatial information is encoded using magnetic field gradients. We know that a linear relationship exists between the frequency at which a nucleus resonates and the intensity of the magnetic field. In ^{1}H-NMR spectroscopy we use a homogeneous magnetic field, in which all equivalent hydrogens absorb at the same radio frequency and have the same chemical shift. In MRI, a patient is placed in a magnetic field gradient that can be varied from place to place. Nuclei in a weaker magnetic field gradient absorb at a lower frequency. Nuclei elsewhere, in a stronger magnetic field, absorb at a higher frequency. A gradient along a single axis images a plane. Two mutually perpendicular gradients image a line segment, and three mutually perpendicular gradients image a point. In practice, more complicated procedures are used to obtain magnetic resonance images, but they are all based on the idea of magnetic field gradients.



Computer-enhanced MRI of normal human brain with pituitary gland highlighted.

TABLE 21.4 ^{13}C-NMR Chemical Shifts

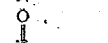
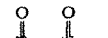
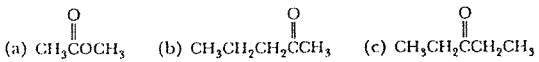
Type of Carbon	Chemical Shift (δ)	Type of Carbon	Chemical Shift (δ)
RCH_3	0–40		110–160
RCH_2R	15–55		
R_3CH	20–60		
RCH_2I	0–40		160–180
RCH_2Br	25–65		
RCH_2Cl	35–80		165–180
R_3COH	40–80		
R_3COR	40–80		175–185
$RC{\equiv}CR$	65–85		
$R_2C{=}CR_2$	100–150		180–210

Table 21.4 shows approximate chemical shifts for carbon-13 spectroscopy. Notice how much broader the range of chemical shifts is for ^{13}C-NMR spectroscopy than for ^{1}H-NMR spectroscopy. Whereas most chemical shifts for ^{1}H-NMR spectroscopy fall within a rather narrow range of 0–10 ppm, those for ^{13}C-NMR spectroscopy cover 0–220 ppm. Because of this expanded scale, it is very unusual to find any two nonequivalent carbons in the same molecule with identical chemical shifts. Most commonly, each different type of carbon within a molecule has a distinct signal clearly resolved from all other signals. Notice further that the chemical shift of carbonyl carbons is quite distinct from those of sp^3 hybridized carbons and of other types of sp^2 hybridized carbons. The presence or absence of a carbonyl carbon is quite easy to recognize in a ^{13}C-NMR spectrum.

A great advantage of ^{13}C-NMR spectroscopy is that it is generally possible to count the number of types of carbon atoms in a molecule. There is one caution here, however. Because of the particular manner in which spin-flipped ^{13}C nuclei return to their lower energy states, integration of signal heights is often unreliable, and it is generally not possible to determine the number of carbons of each type based on signal heights.

EXAMPLE 21.7

Predict the number of signals in a proton-decoupled ^{13}C-NMR spectrum of each compound.



(a) CH_3COCH_3 (b) $CH_3CH_2CH_2CCH_3$ (c) $CH_3CH_2CCH_2CH_3$

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CHEMISTRY

FIFTH EDITION

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HOUGHTON MIFFLIN COMPANY Boston New York

Next, we need to compute the pressure (force per unit of area)

$$\text{Pressure due to "average" particle} = \frac{\overline{\text{force}}_{\text{TOTAL}}}{\text{area}_{\text{TOTAL}}}$$

$$= \frac{\dfrac{2m\overline{u^2}}{L}}{6L^2} = \frac{m\overline{u^2}}{3L^3}$$

The 6 sides of the cube; Area of each side

Since the volume V of the cube is equal to L^3, we can write

$$\text{Pressure} = P = \frac{m\overline{u^2}}{3V}$$

So far we have considered the pressure on the walls due to a single, "average" particle. Of course, we want the pressure due to the entire gas sample. The number of particles in a given gas sample can be expressed as follows:

$$\text{Number of gas particles} = nN_A$$

where n is the number of moles and N_A is Avogadro's number.

The total pressure on the box due to n moles of a gas is therefore

$$P = nN_A\frac{m\overline{u^2}}{3V}$$

Next we want to express the pressure in terms of the kinetic energy of the gas molecules. Kinetic energy (the energy due to motion) is given by $\frac{1}{2}mu^2$, where m is the mass and u the velocity. Since we are using the average of the velocity squared ($\overline{u^2}$), and since $m\overline{u^2} = 2(\frac{1}{2}m\overline{u^2})$, we have

$$P = \left(\frac{2}{3}\right)\frac{nN_A(\frac{1}{2}m\overline{u^2})}{V}$$

$$\frac{PV}{n} = \left(\frac{2}{3}\right)N_A(\tfrac{1}{2}m\overline{u^2})$$

Thus, based on the postulates of the kinetic molecular model, we have been able to derive an equation that has the same form as the ideal gas equation,

$$\frac{PV}{n} = RT$$

This agreement between experiment and theory supports the validity of the assumptions made in the kinetic molecular model about the behavior of gas particles, at least for the limiting case of an ideal gas.

Appendix Three Spectral Analysis

Although volumetric and gravimetric analyses are still very commonly used, spectroscopy is the technique most often used for modern chemical analysis. *Spectroscopy* is the study of electromagnetic radiation emitted or absorbed by a given chemical species. Since the quantity of radiation absorbed or emitted can be related

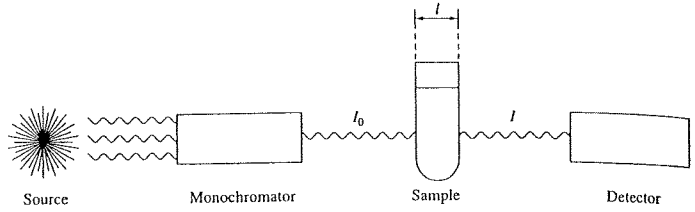

Figure A.6

A schematic diagram of a simple spectrophotometer. The source emits all wavelengths of visible light, which are dispersed using a prism or grating and then focused, one wavelength at a time, onto the sample. The detector compares the intensity of the incident light (I_0) to the intensity of the light after it has passed through the sample (I).

to the quantity of the absorbing or emitting species present, this technique can be used for quantitative analysis. There are many spectroscopic techniques, since electromagnetic radiation spans a wide range of energies to include X rays, ultraviolet, infrared, and visible light, and microwaves, to name a few of its familiar forms. However, we will consider here only one procedure, which is based on the absorption of visible light.

If a liquid is colored, it is because some component of the liquid absorbs visible light. In a solution the greater the concentration of the light-absorbing substance, the more light is absorbed, and the more intense the color of the solution.

The quantity of light absorbed by a substance can be measured by a *spectrophotometer,* shown schematically in Fig. A.6. This instrument consists of a source that emits all wavelengths of light in the visible region (wavelengths of ~400 to 700 nm); a monochromator, which selects a given wavelength of light; a sample holder for the solution being measured; and a detector, which compares the intensity of incident light I_0 to the intensity of light after it has passed through the sample I. The ratio I/I_0, called the *transmittance,* is a measure of the fraction of light that passes through the sample. The amount of light absorbed is given by the *absorbance* A, where

$$A = -\log\frac{I}{I_0}$$

The absorbance can be expressed by the *Beer–Lambert law:*

$$A = \epsilon lc$$

where ϵ is the molar absorptivity or the molar extinction coefficient (in L/mol · cm), l is the distance the light travels through the solution (in cm), and c is the concentration of the absorbing species (in mol/L). The Beer–Lambert law is the basis for using spectroscopy in quantitative analysis. If ϵ and l are known, measuring A for a solution allows us to calculate the concentration of the absorbing species in the solution.

Suppose we have a pink solution containing an unknown concentration of $Co^{2+}(aq)$ ions. A sample of this solution is placed in a spectrophotometer, and the absorbance is measured at a wavelength where ϵ for $Co^{2+}(aq)$ is known to be

12 L/mol · cm. The absorbance A is found to be 0.60. The width of the sample tube is 1.0 cm. We want to determine the concentration of $Co^{2+}(aq)$ in the solution. This problem can be solved by a straightforward application of the Beer–Lambert law,

$$A = \epsilon l c$$

where

$$A = 0.60$$

$$\epsilon = \frac{12\ \text{L}}{\text{mol} \cdot \text{cm}}$$

$$l = \text{light path} = 1.0\ \text{cm}$$

Solving for the concentration gives

$$c = \frac{A}{\epsilon l} = \frac{0.60}{\left(12\ \frac{\text{L}}{\text{mol} \cdot \text{cm}}\right)(1.0\ \text{cm})} = 5.0 \times 10^{-2}\ \text{mol/L}$$

To obtain the unknown concentration of an absorbing species from the measured absorbance, we must know the product ϵl, since

$$c = \frac{A}{\epsilon l}$$

We can obtain the product ϵl by measuring the absorbance of a solution of *known* concentration, since

$$\epsilon l = \frac{A}{c}$$

(A: measured using a spectrophotometer; c: known from making up the solution)

However, a more accurate value of the product ϵl can be obtained by plotting A versus c for a series of solutions. Note that the equation $A = \epsilon l c$ gives a straight line with slope ϵl when A is plotted against c.

For example, consider the following typical spectroscopic analysis. A sample of steel from a bicycle frame is to be analyzed to determine its manganese content. The procedure involves weighing out a sample of the steel, dissolving it in strong acid, treating the resulting solution with a very strong oxidizing agent to convert all the manganese to permanganate ion (MnO_4^-), and then using spectroscopy to determine the concentration of the intensely purple MnO_4^- ions in the solution. To do this, however, the value of ϵl for MnO_4^- must be determined at an appropriate wavelength. The absorbance values for four solutions with known MnO_4^- concentrations were measured to give the following data:

Solution	*Concentration of MnO_4^- (mol/L)*	*Absorbance*
1	7.00×10^{-5}	0.175
2	1.00×10^{-4}	0.250
3	2.00×10^{-4}	0.500
4	3.50×10^{-4}	0.875

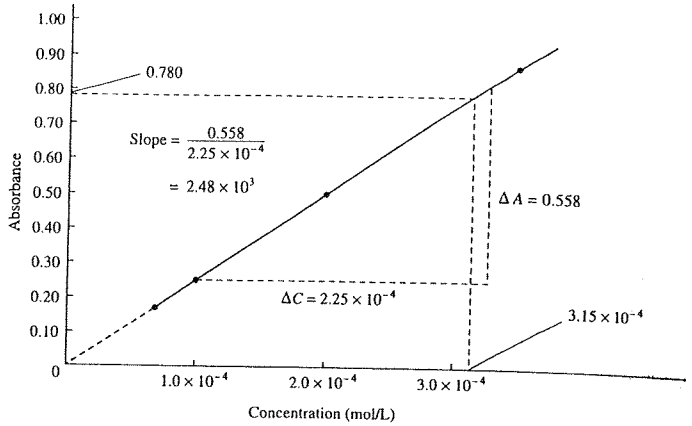

Figure A.7
A plot of absorbance versus concentration of MnO_4^- in a series of solutions of known concentration.

A plot of absorbance versus concentration for the solutions of known concentration is shown in Fig. A.7. The slope of this line (change in A/change in c) is 2.48×10^3 L/mol. This quantity represents the product ϵl.

A sample of the steel weighing 0.1523 g was dissolved and the unknown amount of manganese was converted to MnO_4^- ions. Water was then added to give a solution with a final volume of 100.0 mL. A portion of this solution was placed in a spectrophotometer, and its absorbance was found to be 0.780. Using these data, we want to calculate the percent manganese in the steel. The MnO_4^- ions from the manganese in the dissolved steel sample show an absorbance of 0.780. Using the Beer–Lambert law, we calculate the concentration of MnO_4^- in this solution:

$$c = \frac{A}{\epsilon l} = \frac{0.780}{2.48 \times 10^3\ \text{L/mol}} = 3.15 \times 10^{-4}\ \text{mol/L}$$

There is a more direct way for finding c. Using a graph such as that in Fig. A.7 (often called a *Beer's law plot*), we can read the concentration that corresponds to $A = 0.780$. This interpolation is shown by dashed lines on the graph. By this method, $c = 3.15 \times 10^{-4}$ mol/L, which agrees with the value obtained above.

Recall that the original 0.1523-g steel sample was dissolved, the manganese was converted to permanganate, and the volume was adjusted to 100.0 mL. We now know that the $[MnO_4^-]$ in that solution is 3.15×10^{-4} *M*. Using this concentration, we can calculate the total number of moles of MnO_4^- in that solution:

$$\text{mol of } MnO_4^- = 100.0\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times 3.15 \times 10^{-4}\ \frac{\text{mol}}{\text{L}}$$

$$= 3.15 \times 10^{-5}\ \text{mol}$$

Since each mole of manganese in the original steel sample yields a mole of MnO_4^-, that is,

$$1\ \text{mol of Mn} \xrightarrow{\text{Oxidation}} 1\ \text{mol of } MnO_4^-$$

the original steel sample must have contained 3.15×10^{-5} mol of manganese. The mass of manganese present in the sample is

$$3.15 \times 10^{-5} \text{ mol of Mn} \times \frac{54.938 \text{ g of Mn}}{1 \text{ mol of Mn}} = 1.73 \times 10^{-3} \text{ g of Mn}$$

Since the steel sample weighed 0.1523 g, the present manganese in the steel is

$$\frac{1.73 \times 10^{-3} \text{ g of Mn}}{1.523 \times 10^{-1} \text{ g of sample}} \times 100 = 1.14\%$$

This example illustrates a typical use of spectroscopy in quantitative analysis. The steps commonly involved are as follows:

1. Preparation of a calibration plot (a Beer's law plot) by measuring the absorbance values of a series of solutions with known concentrations.
2. Measurement of the absorbance of the solution of unknown concentration.
3. Use of the calibration plot to determine the unknown concentration.

Appendix Four Selected Thermodynamic Data

Note: All values are assumed precise to at least ±1.

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Aluminum			
$Al(s)$	0	0	28
$Al_2O_2(s)$	−1676	−1582	51
$Al(OH)_3(s)$	−1277		
$AlCl_3(s)$	−704	−629	111
Barium			
$Ba(s)$	0	0	67
$BaCO_3(s)$	−1219	−1139	112
$BaO(s)$	−582	−552	70
$Ba(OH)_2(s)$	−946		
$BaSO_4(s)$	−1465	−1353	132
Beryllium			
$Be(s)$	0	0	10
$BeO(s)$	−599	−569	14
$Be(OH)_2(s)$	−904	−815	47
Bromine			
$Br_2(l)$	0	0	152
$Br_2(g)$	31	3	245
$Br_2(aq)$	−3	4	130
$Br^-(aq)$	−121	−104	82
$HBr(g)$	−36	−53	199
Cadmium			
$Cd(s)$	0	0	52
$CdO(s)$	−258	−228	55
$Cd(OH)_2(s)$	−561	−474	96
$CdS(s)$	−162	−156	65
$CdSO_4(s)$	−935	−823	123

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Calcium			
$Ca(s)$	0	0	41
$CaC_2(s)$	−63	−68	70
$CaCO_3(s)$	−1207	−1129	93
$CaO(s)$	−635	−604	40
$Ca(OH)_2(s)$	−987	−899	83
$Ca_3(PO_4)_2(s)$	−4126	−3890	241
$CaSO_4(s)$	−1433	−1320	107
$CaSiO_3(s)$	−1630	−1550	84
Carbon			
$C(s)$ (graphite)	0	0	6
$C(s)$ (diamond)	2	3	2
$CO(g)$	−110.5	−137	198
$CO_2(g)$	−393.5	−394	214
$CH_4(g)$	−75	−51	186
$CH_3OH(g)$	−201	−163	240
$CH_3OH(l)$	−239	−166	127
$H_2CO(g)$	−116	−110	219
$HCOOH(g)$	−363	−351	249
$HCN(g)$	135.1	125	202
$C_2H_2(g)$	227	209	201
$C_2H_4(g)$	52	68	219
$CH_3CHO(g)$	−166	−129	250
$C_2H_5OH(l)$	−278	−175	161
$C_2H_6(g)$	−84.7	−32.9	229.5
$C_3H_6(g)$	20.9	62.7	266.9
$C_3H_8(g)$	−104	−24	270

(continued)

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Royal Society of Chemistry Paperbacks

Basic Principles of COLLOID SCIENCE

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ROYAL SOCIETY OF CHEMISTRY

Contents

principles that underlie many colloid problems can be seen as extensions to such systems of the fundamental concepts of physical chemistry. One important objective of this book is to emphasise the close link between colloid science and physical chemistry and to show how a broad understanding can be built up on a few relatively simple physico-chemical ideas. We shall not only seek common features revealed by experimental study but also, of much greater significance, try to identify the fundamental concepts that link together many apparently unconnected aspects of the subject.

DEFINITION OF COLLOIDS

In setting out to define the scope of colloid science, it should first be said that any attempt to lay down too rigid a scheme of definitions and nomenclature is likely to be unnecessarily restrictive. Rather than try at the outset to develop a formal definition, it is preferable to describe examples of systems to which the term 'colloidal' is now applied.*

An essential part of any study of physics and chemistry involves first the recognition of three states of matter – solid, liquid, and gas – and a general discussion of the transformations – melting, sublimation, and evaporation – between them. Pure substances are considered, and then attention passes to solutions which are homogeneous mixtures of chemical species dispersed on a molecular scale. What remained largely unrecognised until about a century and a half ago was that there is an intermediate class of materials lying between bulk and molecularly dispersed systems, in which, although one component is finely dispersed in another, the degree of subdivision does not approach that in simple molecular mixtures. Systems of this kind, *colloids*, have special properties which are of great practical importance, and they were appropriately described by Ostwald as lying in the World of Neglected Dimensions. They consist of a *dispersed phase* (or *discontinuous phase*) distributed uniformly in a finely divided state in a *dispersion medium* (or *continuous phase*).

As familiar examples of colloidal systems we cite the following: fogs, mists, and smokes (dispersions of fine liquid droplets or solid particles in a gas – *aerosols*); milk (a dispersion of fine droplets of

* The etymology of the term colloidal (glue-like) introduced by Thomas Graham is now largely irrelevant.

fat in an aqueous phase – *emulsions*); paints, muds, and slurries (dispersions of fine solid particles in a liquid medium – *sols* or *colloidal suspensions*); jellies (dispersions of macromolecules in liquid – *gels*); opal and ruby stained glass (dispersions, respectively, of solid silica particles in a solid matrix or of gold particles in glass – *solid dispersions*). So-called (and miscalled) *photographic emulsions* are dispersions of finely divided silver halide crystallites in a gel – in a sense they are a colloid within a colloid. In *association colloids* molecules of soap or other surface-active substances are associated together to form small aggregates (*micelles*) in water. The aggregates formed by certain substances may adopt an ordered structure and form *liquid crystals*. Many biological structures are colloidal in nature. For example, blood is a dispersion of corpuscles in serum, and bone is essentially a dispersion of a calcium phosphate embedded in collagen.

In the above examples, which may be called *simple colloids*, a clear distinction can be made between the disperse phase and the dispersion medium. However, in *network colloids* this is hardly possible since both phases consist of interpenetrating networks, the elements of each being of colloidal dimensions. Porous solids, in which gas and solid networks interpenetrate, two-phase glasses (opal glasses), and many gels are examples of this category.

Furthermore, there are other instances (*multiple colloids*) that may involve the co-existence of three phases of which two (and sometimes three) phases are finely divided. One example is a porous solid partially filled with condensed vapour, when both the liquid and vapour phases within the pores are present in a finely divided form; a similar situation arises when oil and water co-exist in the pores of an oil-bearing rock, also in frost heaving when water and ice co-exist in a porous medium. *Multiple emulsions* consist for example of finely divided droplets of an aqueous phase contained within oil droplets, which themselves are dispersed in an aqueous medium.

Some of the more important types of colloidal systems outlined above are summarised in Table 1.1. For simplicity we shall limit ourselves in this book to a discussion of simple colloids, although the ideas developed can be extended and applied to more complex systems.

The fundamental question which has to be answered is 'What do we mean by "finely divided"?' It turns out, for reasons which will soon be apparent, that systems usually exhibit properties of a specifically 'colloidal character' (which we shall explain in more

Table 1.1 *Some typical colloidal systems.*

Examples	*Class*	*Nature of the disperse phase*	*dispersion medium*
Disperse systems			
Fog, mist, tobacco smoke, 'aerosol' sprays	Liquid aerosol or aerosol of liquid particles [a]	Liquid	Gas
Industrial smokes	Solid aerosol or aerosol of solid particles [a]	Solid	Gas
Milk, butter, mayonnaise, asphalt, pharmaceutical creams	Emulsions	Liquid	Liquid
Inorganic colloids (gold, silver iodide, sulphur, metallic hydroxides, *etc.*), paints [b]	Sols or colloidal suspensions	Solid	Liquid
Clay slurries, toothpaste, muds, polymer latices	When very concentrated called a paste	Solid	Liquid
Opal, pearl, stained glass, pigmented plastics	Solid suspension or dispersion	Solid	Solid
Froths, foams	Foam [c]	Gas	Liquid
Meerschaum, expanded plastics	Solid foam	Gas	Solid
Microporous oxides, 'silica gel', porous glass, microporous carbons, zeolites	Xerogels[d]		
Macromolecular colloids			
Jellies, glue	Gels	Macro-molecules	Solvent
Association colloids			
Soap/water, detergent/water, dye solutions	—	Micelles	Solvent

Table 1.1 *(cont.)*

Examples	*Class*	*Nature of the disperse phase*	*dispersion medium*
Biocolloids			
Blood		Corpuscles	Serum
Bone		Hydroxy-apatite	Collagen
Muscle, cell membranes		Protein structures, thin films of lethecin, *etc.*	
Three-phase colloidal systems (multiple colloids)			
		Coexisting phases	
Oil-bearing rock	Porous rock	Oil	Water
Capillary condensed vapours	Porous solid	Liquid	Vapour
Frost heaving	Porous rock or soil	Ice	Water
Mineral flotation	Mineral	Water	Air bubbles or oil droplets
Double emulsions	Oil	Aqueous phase	Water

[a] Preferred nomenclature according to IUPAC recommendations. [b] Many modern paints are more complex, containing both dispersed pigment and emulsion droplets. [c] In a foam it is usually the thickness of the film of dispersion medium which is of colloidal dimensions, although the dispersed phase may also be finely divided. [d] In some cases both phases are continuous, forming interpenetrating networks both of which have colloidal dimensions.

detail in later chapters) when the dimensions of the dispersed phase lie in the range 1—1000 nm, *i.e.* between 10 Å and 1 μm.*

These limits are not rigid, for in some special cases (*e.g.* emulsions and some slurries) particles of larger size are present. Moreover, it is not necessary for all three dimensions to lie below 1 μm, since colloidal behaviour is observed in systems containing fibres in which only two dimensions are in the colloid range. In other systems, such as clays and thin films, only one dimension is in the colloid range. This is illustrated schematically in Figures 1.1 and 1.2, while Figure 1.3 shows electron microscope photographs of colloidal particles of several types.

* These dimensions are below the limits of resolution of simple optical microscopes so that direct imaging and measurement of the sizes of colloidal particles only became possible with the development of electron microscopes.

represents the attractive free energy $\Delta G^{att}/2A$ and becomes increasingly negative as the surfaces approach.

REPULSIVE FORCES: THE TOTAL FREE-ENERGY CURVE

If the medium between the two surfaces is no longer a pure liquid, but is one of certain types of solution to be discussed later, then new phenomena may arise leading to a repulsive force between the surfaces. If such a repulsive force exists, then work must be done to reduce the distance between them. This is shown in Figure 2.7: the free energy arising from repulsion increases as the separation decreases.

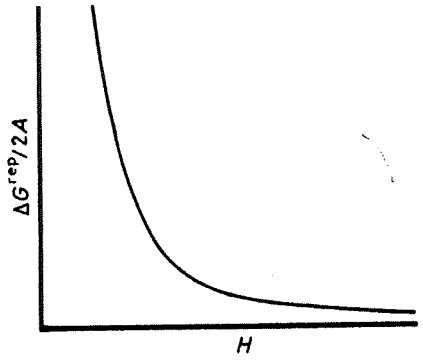


Figure 2.7 *Influence of repulsive forces on the free energy of interaction of surfaces as a function of separation, taking the energy at infinite separation as the energy zero. Work has to be done on the system to bring the surfaces together.*

It is usually assumed that the contributions to the total free energy from attractive and repulsive forces are additive, so that depending on the range and relative strengths of these two contributions a variety of total free-energy curves may result. Some typical shapes are shown in Figure 2.8. We shall leave until the next chapter a discussion of the origins of the various forces leading to surface free-energy curves such as those in Figure 2.8. Before doing so we will consider how the stability of a colloid is related to the shape of such curves. It is their contribution to the total free energy of a dispersion that is usually the most important.*

COLLOID STABILITY

From what has been said earlier, it will be clear that a colloidal dispersion represents a state of higher free energy than that corresponding to the material in bulk (Figure 2.4); passage to a state of lower free energy will therefore tend to occur spontaneously unless there is a substantial energy barrier preventing the elimination of the colloidal state. In the presence of such a barrier the system will be *metastable* and may remain in that state for a very long time.** On the other hand, if conditions are adjusted so that the energy barrier becomes negligibly small, or disappears altogether [Figure 2.8(b) and (c)], then the colloid becomes *unstable*. Thus the whole question of the preparation and stability of colloidal systems is closely tied up with the factors that give rise to free-energy barriers of adequate height to prevent the breakdown of the colloidal state. Conversely the problems of the destruction of colloids depend on our ability to change conditions so that such energy barriers are reduced or eliminated.

In the case of colloidal dispersions the energy necessary to carry a system over the energy barrier comes from the Brownian motion of the particles (see Chapter 6) which results from the random bombardment of the surface of the particles by molecules of the medium. It turns out that the average translational energy of colloidal particles undergoing Brownian motion is of the order of $(3/2)kT$ per particle, where k is Boltzmann's constant, equal to 1.38×10^{-23} J molecule^{-1} K^{-1}, and T is the absolute temperature. At 300 K two particles bring into a collision an energy of the order of 10^{-20} J. However, there is a finite probability that at a given moment a particle may have a larger or smaller energy. The chances of a collision involving a total energy of several times kT (say $10kT$) become very small so that, provided the free-energy barrier is sufficiently high, compared with kT, the dispersion will remain indefinitely in a metastable state: it is said to be

* The entropy change associated with subdivision or aggregation cannot always be ignored and is responsible for a number of special phenomena (see Chapters 9 and 11).

** Some of Faraday's original gold sols are still in existence at the Royal Institution in London.

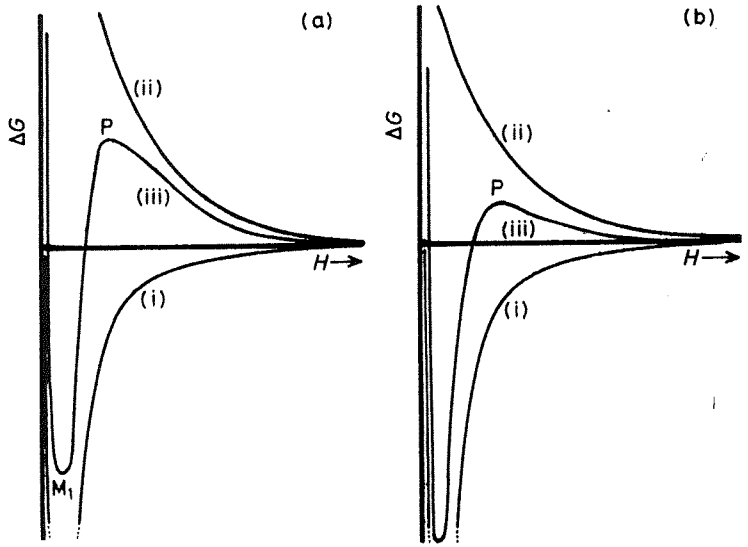
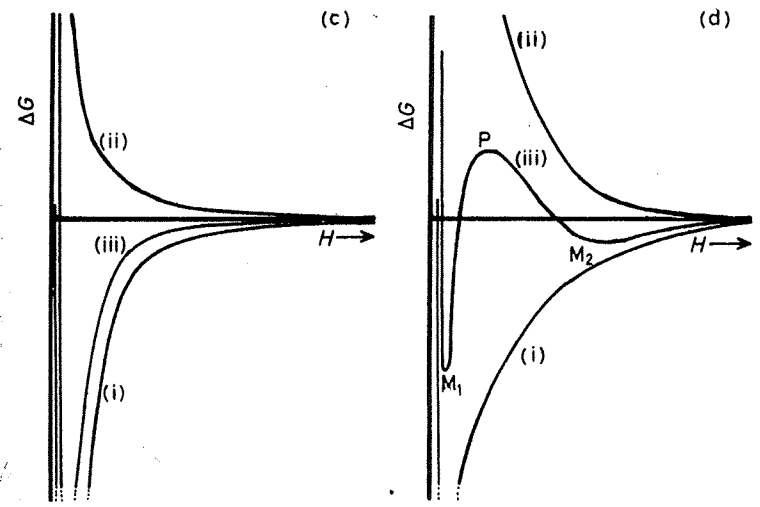


Figure 2.8 *Some possible forms of the total-interaction free energy* (iii) *resulting from a combination of attractive* (i) *and repulsive* (ii) *contributions:* (a) *states of separation and contact separated by a high energy barrier (*primary maximum, P*) arising from strong repulsive interaction,* (b) *lowering of the energy barrier by reduction of the repulsive interactions or a decrease in their range, the system being able to pass over into the* primary minimum, M_1, *if the primary maximum is lowered to a few kT,* (c) *elimination of the energy barrier, the system being able to pass over into the* primary minimum, M_1, *without any activation energy,* (d) *it is sometimes found that a shallow minimum exists (*secondary minimum, M_2*) before the primary maximum is reached. In these diagrams account is also taken of the short-range repulsive forces when the surfaces are almost in contact (Born repulsion). Figures 2.4 and 2.6 refer to 'hard' interactions where on contact the repulsive force becomes infinite.*

colloidally stable.

Instability will ensue if the ratio of the barrier height to kT is reduced to say 1—2. This may arise in various ways. In principle, if the absolute height remained constant, then instability could be induced by an increase in temperature, but this is a relatively small effect. In practice the barrier height is found to be a sensitive function of several factors including the composition of the medium, temperature, and pressure. Instability and flocculation are, therefore, more often caused by the reduction in the height of the barrier resulting from a change in one or more of these factors.

A situation peculiar to colloidal systems is that in which the free-energy curve has the form of Figure 2.8(d). Here aggregation is prevented by a high energy barrier, but preceding this is a relatively shallow minimum – called a *secondary minimum* to distinguish it from the deep *primary minimum*. If the depth of the



secondary minimum is of the order of a few kT, then small relatively weakly bound aggregates (*flocs*) can form. These have a limited lifetime, and a kinetic equilibrium may be set up between single particles and flocs, which is often described as *weak flocculation* or *secondary minimum flocculation*. An important feature of such a situation is that, although the flocs are sufficiently stable not to be completely dissociated by Brownian motion, they may disintegrate under externally applied hydrodynamic forces, such as vigorous stirring. Some practical implications of this phenomenon will be discussed in Chapter 14.

In the following chapters we shall first seek to understand the origin of free-energy curves of the various types illustrated in Figure 2.8 and then apply these ideas to a discussion of the formation and stability of some typical systems.

So far we have limited our attention to one particular kind of colloid, namely particulate dispersions. In these the driving force for aggregation or dispersion is the gradient of the free-energy

surface charge [Figure 3.3(e)]. In this case the p.z.c. can be reached by reducing the pH, the added H^+ ions combining with the negative charges on the surface to form OH groups.

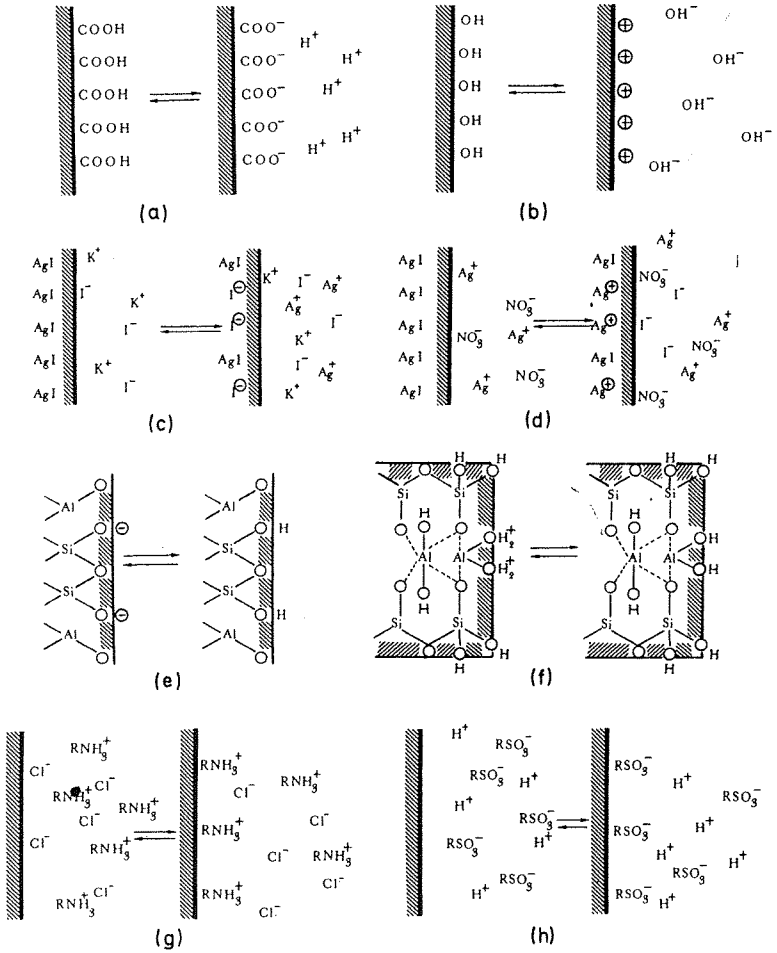


Figure 3.3 *Origin of surface charges by:* (a) *ionisation of acid groups to give a negatively charged surface,* (b) *ionisation of basic groups to give a positively charged surface,* (c) *differential solution of silver ions from a AgI surface,* (d) *differential solution of iodide ions from a AgI surface,* (e) *isomorphous substitution in a clay surface to give a negatively charged surface,* (f) *breaking a clay crystal to give a positively charged edge,* (g) *specific adsorption of a cationic surfactant,* (h) *specific adsorption of an anionic surfactant.*

(iv) *Charged crystal surfaces.* It may happen that, when a crystal is broken, surfaces with different properties are exposed. Thus in some clays (*e.g.* kaolinite), when a platelet is broken, the exposed edges contain AlOH groups which take up H^+ ions to give a positively charged edge [Figure 3.3(f)]. This may coexist with negatively charged basal surfaces, leading to special properties (see Chapter 13). In this case there will be no single p.z.c., but each type of surface will have its own value.

(v) *Specific ion adsorption.* Surfactant ions may be specifically adsorbed, leading, in the case of cationic surfactants, to a positively charged surface [Figure 3.3(g)] and, in the case of anionic surfactants, to a negatively charged surface [Figure 3.3(h)].

To examine the way in which these charges affect the properties of colloids, it is first necessary to say a little about fundamental electrostatic theory.

The fundamental law of electrostatics – Coulomb's law – expresses the inverse square law of force between two electric charges q_1 and q_2 separated by a distance d in a vacuum in the form:

$$\mathcal{F} = q_1 q_2/(4\pi\varepsilon_0 d^2), \tag{3.15}$$

where ε_0 is the permittivity of free space (vacuum). If q_1 and q_2 have the same sign, the force is a repulsion; if they are of opposite sign, the force is an attraction.*

In the presence of a material medium surrounding both charges, the force is reduced by a factor $\varepsilon_r = \varepsilon/\varepsilon_0$, the *relative permittivity* (or *dielectric constant*) of the medium. The work done in bringing two charges together from infinite separation to a distance d in a medium of permittivity ε is therefore given by

$$\Delta G^{el} = \Delta W = -\int_{\infty}^{d} \mathcal{F}\mathrm{d}h = q_1 q_2/(4\pi\varepsilon d) \tag{3.16}$$

and measures the electrical free energy of the system relative to that at infinite separation.

The charge q_1 may be thought of as producing an *electric field* at a point d, such that the work needed to bring a *unit charge* to this point is $q_1/(4\pi\varepsilon d)$; this is called the *electrical potential* at d due to

* This is the form taken in the S.I. system of units. The original form (in e.s.u. units) may be more familiar to some readers: $\mathcal{F} = q_1 q_2/d^2$. Note the sign convention on page 28.

Fundamentals of Organic Chemistry

Fourth Edition

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Cornell University

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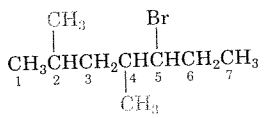
7.1 Naming Alkyl Halides

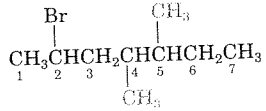
Alkyl halides are named in the same way as alkanes (Section 2.3), by considering the halogen as a substituent on the parent alkane chain. There are three steps:

Step 1 Find the longest chain, and name it as the parent. If a multiple bond is present, the parent chain must contain it.

Step 2 Number the carbons of the parent chain beginning at the end nearer the first substituent, regardless of whether it is alkyl or halo. Assign each substituent a number according to its position on the chain. If there are substituents the same distance from both ends, begin numbering at the end nearer the substituent with alphabetical priority.

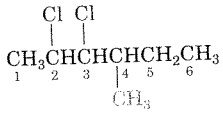


5-Bromo-2,4-dimethylheptane



2-Bromo-4,5-dimethylheptane

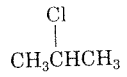
Step 3 Write the name, listing all substituents in alphabetical order and using one of the prefixes *di-*, *tri-*, and so forth if more than one of the same substituent is present.



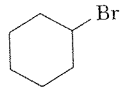
2,3-Dichloro-4-methylhexane

In addition to their systematic names, many simple alkyl halides are also named by identifying first the alkyl group and then the halogen. For example, CH_3I can be called either iodomethane or methyl iodide.

Iodomethane (or methyl iodide)



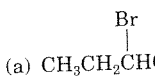
2-Chloropropane (or isopropyl chloride)



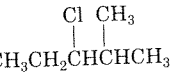
Bromocyclohexane (or cyclohexyl bromide)

PROBLEM

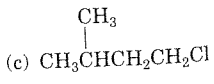
7.1 Give the IUPAC names of the following alkyl halides:



(a)



(b)



(c)

implies, the initiation step starts the reaction by producing reactive radicals. In the chlorination reaction, for instance, the relatively weak Cl–Cl bond is broken by irradiation with ultraviolet light to give two chlorine radicals, Cl·.

Once an initiation step has occurred and a small number of radicals have been produced, the reaction continues in a self-sustaining cycle of two propagation steps. In the first propagation step, Cl· abstracts an H atom from methane to produce HCl and a methyl radical (·CH_3). In the second propagation step, the methyl radical abstracts a Cl atom from Cl_2 to yield chloromethane and a new chlorine radical, which then cycles back into the first propagation step, making the overall process a *chain reaction*.

Occasionally, two radicals might collide and combine to form a stable product. When this happens, the propagation cycle is interrupted and the chain reaction is terminated. The overall mechanism of methane chlorination is shown in Figure 7.1.

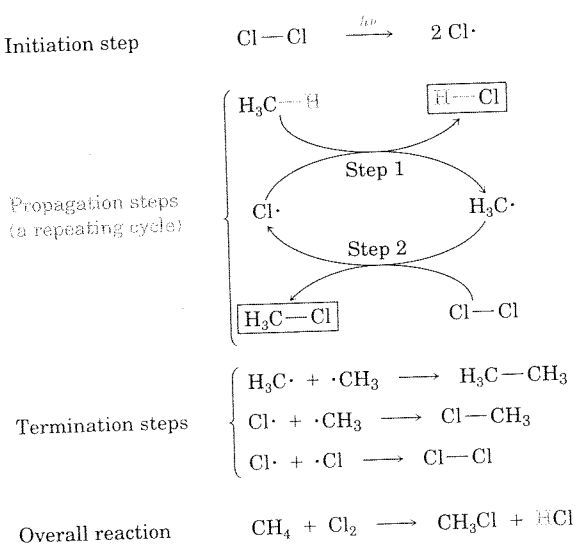


Figure 7.1 Mechanism of the radical chlorination of methane. Three kinds of steps are required: *initiation, propagation,* and *termination.*

Though interesting from a mechanistic point of view, alkane chlorination is a poor method for preparing most alkyl chlorides because mixtures of products usually result. Chlorination of methane does not stop cleanly at the monochlorinated stage, but continues on, giving a mixture of dichloro, trichloro, and even tetrachloro products that must be separated:

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$
$$\xrightarrow{Cl_2} CH_2Cl_2 + HCl$$
$$\xrightarrow{Cl_2} CHCl_3 + HCl$$
$$\xrightarrow{Cl_2} CCl_4 + HCl$$

The situation is even worse for chlorination of alkanes that have more than one kind of hydrogen. Chlorination of butane, for instance, gives two monochlorinated products as well as several dichlorobutanes, trichlorobutanes, and so on. Of the monochloro product, 30% is 1-chlorobutane and 70% is 2-chlorobutane:

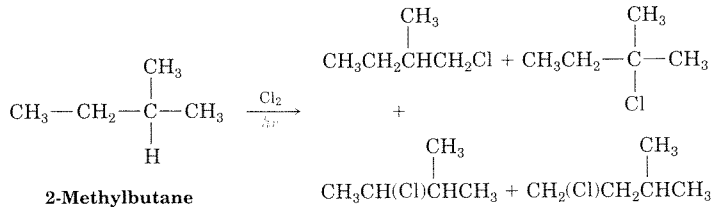
$$CH_3CH_2CH_2CH_3 + Cl_2 \xrightarrow{h\nu} \underbrace{CH_3CH_2CH_2CH_2Cl}_{\text{1-Chlorobutane}} + \underbrace{CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3}_{\text{2-Chlorobutane}} + \text{Dichloro-, trichloro-, tetrachloro-, and so on}$$

Butane — 30:70

PRACTICE PROBLEM 7.1

Draw all the monochloro products you might get from radical chlorination of 2-methylbutane.

Solution Draw the structure of the starting material and begin systematically replacing each kind of hydrogen by chlorine. In this example, there are four possibilities.



PROBLEM

7.3 Draw and name all monochloro products you might obtain from radical chlorination of 3-methylpentane. Which, if any, are chiral?

PROBLEM

7.4 Radical chlorination of pentane is a poor way to prepare 1-chloropentane, but radical chlorination of 2,2-dimethylpropane is a good way to prepare 1-chloro-2,2-dimethylpropane. Explain.

Organic Chemistry

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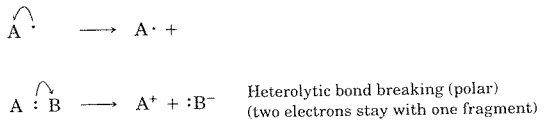
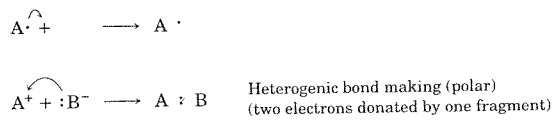
two-electron bond can break: A bond can break in an electronically *symmetrical* way so that one electron remains with each product fragment, or a bond can break in an electronically *unsymmetrical* way so that both bonding electrons remain with one product fragment, leaving the other fragment with a vacant orbital. The symmetrical cleavage is said to be **homolytic**, and the unsymmetrical cleavage is said to be **heterolytic**. We'll develop this point in more detail later, but you might notice now that the movement of *one* electron in a homolytic process is indicated using a half-headed, or "fishhook," arrow (↶), whereas the movement of *two* electrons in a heterolytic process is indicated using a full-headed curved arrow (↷).



Just as there are two ways in which a bond can break, there are two ways in which a covalent two-electron bond can form: A bond can form in an electronically symmetrical **homogenic** way when one electron is donated to the new bond by each reactant, or a bond can form in an electronically unsymmetrical **heterogenic** way when both bonding electrons are donated to the new bond by one reactant.



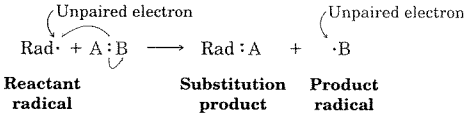
Processes that involve symmetrical bond breaking and bond making are called **radical reactions**. A **radical** (sometimes called a "free radical") is a neutral chemical species that contains an odd number of electrons and thus has a single, unpaired electron in one of its orbitals. Processes that involve unsymmetrical bond breaking and bond making are called **polar reactions**. Polar reactions involve species that have an even number of electrons and thus have only electron pairs in their orbitals. Polar processes are the more common reaction type in organic chemistry, and a large part of this book is devoted to their description.

In addition to polar and radical reactions, there is a third, less commonly encountered process called a *pericyclic reaction*. Rather than explain pericyclic reactions now, though, we'll study them in more detail in Chapter 30.

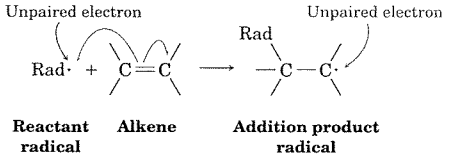
5.3 Radical Reactions and How They Occur

Radical reactions are not as common as polar reactions, but they're nevertheless important in organic chemistry, particularly in some industrial processes. Let's see how they occur.

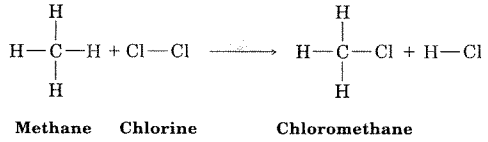
Radicals are highly reactive because they contain an atom with an odd number of electrons (usually seven) in its valence shell, rather than a stable noble-gas octet. A radical can achieve a valence-shell octet in several ways. For example, a radical might abstract an atom from another molecule, leaving behind a new radical. The net result is a radical *substitution* reaction:



Alternatively, a reactant radical might add to an alkene, taking one electron from the alkene double bond and yielding a new radical. The net result is a radical *addition* reaction:



Let's look at a specific example of a radical reaction—the chlorination of methane—to see its characteristics. A more detailed discussion of this radical substitution reaction is given in Chapter 10. For the present, it's only necessary to know that methane chlorination is a multistep process.

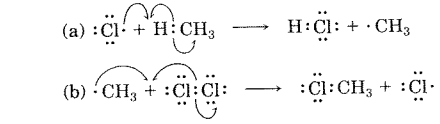


Radical substitution reactions normally require three kinds of steps: *initiation*, *propagation*, and *termination*.

STEP 1 **Initiation** The initiation step starts off the reaction by producing a small number of reactive radicals. In the present case, the relatively weak Cl–Cl bond is homolytically broken by irradiation with ultraviolet light. Two reactive chlorine radicals are produced:

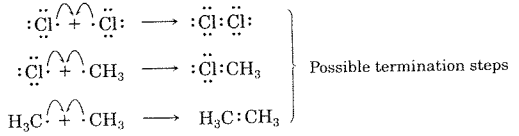
STEP 2 **Propagation** Once a few chlorine radicals have been produced, propagation steps take place. When a reactive chlorine radical collides with a methane molecule, it abstracts a hydrogen atom to produce HCl and a

methyl radical ($\cdot CH_3$). This methyl radical reacts further with Cl_2 in a second propagation step to give the product chloromethane and a new chlorine radical ($Cl\cdot$), which cycles back into the first propagation step. Once the sequence has been initiated, it becomes a self-sustaining cycle of repeating steps (a) and (b), making the overall process a **chain reaction**.



(c) Repeat steps (a) and (b) over and over.

STEP 3 **Termination** Occasionally, two radicals might collide and combine to form a stable product. When this happens, the reaction cycle is broken and the chain is ended. Such termination steps occur infrequently, however, because the concentration of radicals in the reaction at any given moment is very small. Thus, the likelihood that two radicals will collide is also small.



Possible termination steps

The radical substitution reaction just discussed is only one of several different processes that radicals can undergo. The fundamental principle behind all radical reactions is the same, however: *All bonds are broken and formed by reaction of species that have an odd number of electrons.*

Problem 5.2 Alkane chlorination is not a generally useful reaction because most alkanes have several different kinds of hydrogens, causing mixtures of chlorinated products to result. Draw and name all monochloro substitution products you might obtain by reaction of 2-methylpentane with Cl_2.

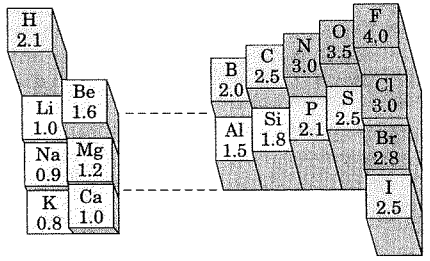
Problem 5.3 Radical chlorination of pentane is a poor way to prepare 1-chloropentane, $CH_3CH_2CH_2CH_2CH_2Cl$, but radical chlorination of neopentane, $(CH_3)_4C$, is a good way to prepare neopentyl chloride, $(CH_3)_3CCH_2Cl$. Explain.

5.4 Polar Reactions and How They Occur

Polar reactions occur because of the attraction between positive and negative charges on different functional groups in molecules. To see how these reactions take place, we first need to recall the discussion of polar covalent bonds in Section 2.1 and then we need to look more deeply into the effects of bond polarity on organic molecules.

Most organic molecules are electrically neutral; they have no net charge, either positive or negative. We saw in Section 2.1, however, that certain bonds within a molecule, particularly the bonds in functional groups, are polar. Bond polarity is a consequence of an unsymmetrical electron distribution in a bond and is due to the difference in electronegativity of the bonded atoms. Figure 5.1, which repeats some of the information in Figure 2.2 for convenience, gives the electronegativities of some commonly encountered elements.

FIGURE 5.1 ▼
Electronegativity of some common elements.

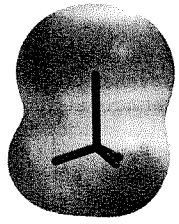


Elements such as oxygen, nitrogen, fluorine, chlorine, and bromine are more electronegative than carbon. Thus, a carbon atom bonded to one of these electronegative atoms has a partial positive charge ($\delta+$). Conversely, metals are less electronegative than carbon, so a carbon atom bonded to a metal has a partial negative charge ($\delta-$). Electrostatic potential maps of chloromethane and methyllithium illustrate these charge distributions, showing that the carbon atom in chloromethane is electron-poor (blue) while the carbon in methyllithium is electron-rich (red).

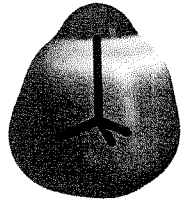
Y = O, N, Cl, Br

M = A metal

chloromethane, methyllithium



CH_3Cl



CH_3Li