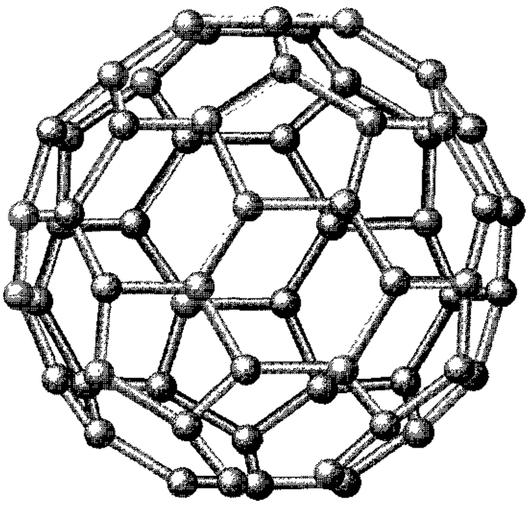
CHAPTER

8

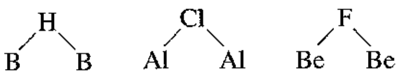
Chemistry of the Main Group Elements



This chapter presents some of the most significant physical and chemical data on each of the main groups of elements (also known as the representative elements), treating hydrogen first and continuing in sequence through Groups 1, 2, and 13 through 18 (Groups IA through VIIIA, in common American notation).

The 20 industrial chemicals produced in greatest amounts in the United States are main group elements or compounds (Table 8-1), and eight of the top ten may be classified as "inorganic"; numerous other compounds of these elements are of great commercial importance.

A discussion of main group chemistry provides a useful context in which to introduce a variety of topics not covered previously in this text. These topics may be particularly characteristic of main group chemistry but may be applicable to the chemistry of other elements as well. For example, many examples are known in which atoms form bridges between other atoms. Main group examples include



In this chapter, we will discuss in some detail one important type of bridge, the hydrogens that form bridges between boron atoms in boranes. A similar approach can be used to describe bridges by other atoms and by groups such as CO (CO bridges between transition metal atoms will be discussed in Chapter 13).

This chapter also provides examples in which modern chemistry has developed in ways surprisingly different from previously held ideas. Examples include compounds in which carbon is bonded to more than four atoms, the synthesis of alkali metal anions, and the now fairly extensive chemistry of noble gas elements. The past two decades have also seen the remarkable development of the fullerenes, previously unknown clusters of carbon atoms. Much of the information in this chapter is included for the sake of handy reference; for more details, the interested reader should consult the references listed at the end of this chapter. The bonding and structures of main group compounds (Chapters 3

TABLE 8-1
Top 20 Industrial Chemicals Produced in the United States, 2001

Rank	*Chemical*	*Production* ($\times 10^9$ *kg*)
1	Sodium chloride, NaCl	45.1
2	Sulfuric acid, H_2SO_4	36.3
3	Phosphate rock, MPO_4	34.2
4	Nitrogen, N_2	29.4
5	Ethylene, $H_2C{=}CH_2$	22.5
6	Oxygen, O_2	21.6
7	Lime, CaO	18.7
8	Propylene, $H_2C{=}CH{-}CH_3$	13.2
9	Ammonia, NH_3	11.8
10	Chlorine, Cl_2	10.9
11	Phosphoric acid, H_3PO_4	10.5
12	Sodium carbonate, Na_2CO_3	10.3
13	Sodium hydroxide, NaOH	9.7
14	Dichloroethane, $H_2ClC{-}CH_2Cl$	9.4
15	Sulfur, S_8	9.2
16	Nitric acid, HNO_3	7.1
17	Ammonium nitrate, NH_4NO_3	6.4
18	Benzene, C_6H_6	6.4
19	Urea, $(NH_2)_2C{=}O$	6.4
20	Ethylbenzene ($C_2H_5C_6H_5$)	4.7

SOURCE: *Chem. Eng. News*, **2002**, *80*, 60.

and 5) and acid-base reactions involving these compounds (Chapter 6) have already been discussed in this text.

8-1 GENERAL TRENDS IN MAIN GROUP CHEMISTRY

8-1-1 PHYSICAL PROPERTIES

The main group elements complete their electron configurations using *s* and *p* electrons. The total number of such electrons in the outermost shell is conveniently given by the traditional American group numbers in the periodic table. It is also the last digit in the group numbers recommended by the IUPAC (Groups 1, 2, and 13 through 18).[1] These elements range from the most metallic to the most nonmetallic, with elements of intermediate properties, the semimetals (also known as metalloids), in between. On the far left, the alkali metals and alkaline earths exhibit the expected metallic characteristics of luster, high ability to conduct heat and electricity, and malleability. The distinction between metals and nonmetals is best illustrated by their difference in conductance. In Figure 8-1, electrical resistivities (inversely proportional to conductivity) of the solid main group elements are plotted.[2] At the far left are the alkali metals, having low resistivities (high conductances); at the far right are the nonmetals. Metals contain loosely bound valence electrons that are relatively free to move and thereby conduct current. In most cases, nonmetals contain much more localized lone electron pairs and covalently bonded pairs that are less mobile. An exception, as we will see, is graphite, a form of carbon that has a much greater ability to conduct than most nonmetals because of delocalized electron pairs.

[1] G. J. Leigh, ed., *Nomenclature of Inorganic Chemistry, Recommendations 1990*, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, Oxford, pp. 41–43.

[2] The electrical resistivity shown for carbon is for the diamond allotrope. Graphite, another allotrope of carbon, has a resistivity between that of metals and semiconductors.

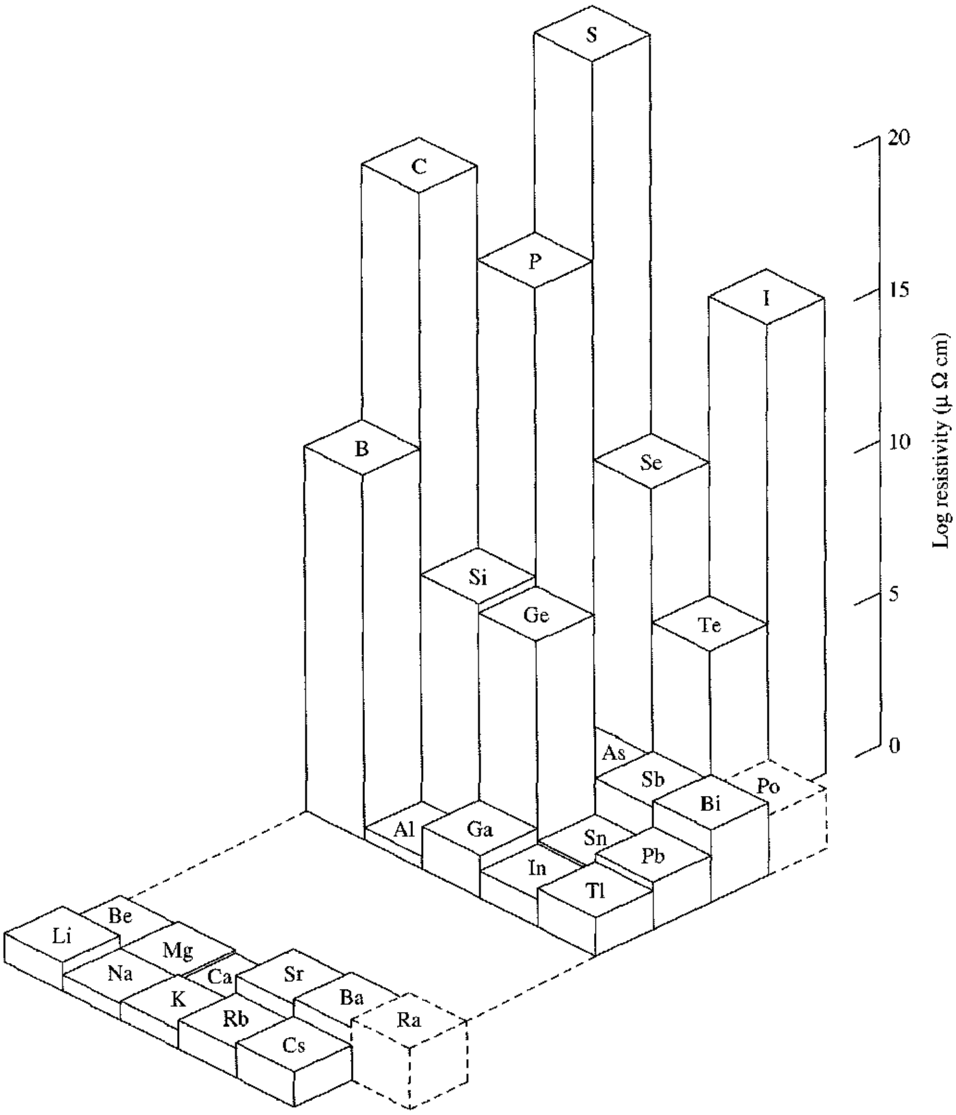


FIGURE 8-1 Electrical Resistivities of the Main Group Elements. Dashed lines indicate estimated values. (Data from J. Emsley, *The Elements*, Oxford University Press, New York, 1989.)

Elements along a rough diagonal from boron to polonium are intermediate in behavior, in some cases having both metallic and nonmetallic allotropes (elemental forms); these elements are designated as **metalloids** or **semimetals**. As described in Chapter 7, some elements, such as silicon and germanium, are capable of having their conductivity finely tuned by the addition of small amounts of impurities and are consequently of enormous importance in the manufacture of semiconductors in the computer industry.

Some of the columns of main group elements have long been designated by common names (e.g., the halogens); names for others have been suggested, and some have been used more frequently in recent years:

Group	*Common Name*	*Group*	*Common Name*
1(I)	Alkali metals	15(V)	Pnicogens
2(II)	Alkaline earths	16(VI)	Chalcogens
13(III)	Triel elements	17(VII)	Halogens
14(IV)	Tetrel elements	18(VIII)	Noble gases

8-1-2 ELECTRONEGATIVITY

Electronegativity, shown in Figure 8-2, also provides a guide to the chemical behavior of the main group elements. The extremely high electronegativity of the nonmetal fluorine and the noble gases helium and neon are evident, with a steady decline in electronegativity toward the left and the bottom of the periodic table. The semimetals form a diagonal of intermediate electronegativity. Definitions of electronegativity have been given in Chapter 3 (Section 3-2-3) and tabulated values for the elements are given in Table 3-3 and Appendix B-4.

Hydrogen, although usually classified with Group 1 (IA), is quite dissimilar from the alkali metals in its electronegativity, as well as in many other properties, both chemical and physical. Hydrogen's chemistry is distinctive from all the groups, so this element will be discussed separately in this chapter.

The noble gases have higher ionization energies than the halogens, and calculations have suggested that the electronegativities of the noble gases may match or even exceed those of the halogens.[3] The noble gas atoms are somewhat smaller than the neighboring halogen atoms (e.g., Ne is smaller than F) as a consequence of a greater effective nuclear charge. This charge, which attracts noble gas electrons strongly toward the nucleus, is also likely to exert a strong attraction on electrons of neighboring atoms; hence, high electronegativities predicted for the noble gases are reasonable. Estimated values of these electronegativities are included in Figure 8-2 and Appendix B-4.

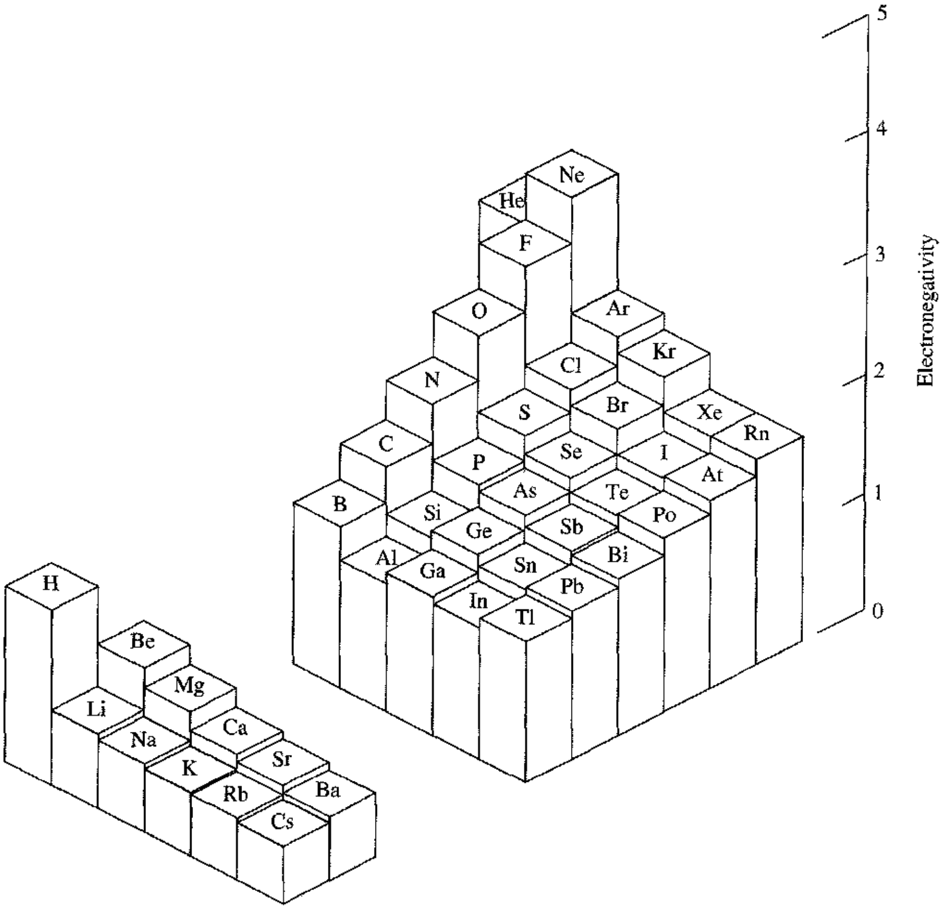


FIGURE 8-2 Electronegativities of the Main Group Elements. (Data from J. B. Mann, T. L. Meek, and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, *122*, 2780.)

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[3] L. C. Allen and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **1980**, *42*, 1523; T. L. Meek, *J. Chem. Educ.*, **1995**, *72*, 17.

8-1-3 IONIZATION ENERGY

Ionization energies of the main group elements exhibit trends similar to those of electronegativity, as shown in Figure 8-3. There are some subtle differences, however.

As discussed in Section 2-3-1, although a general increase in ionization energy occurs toward the upper right-hand corner of the periodic table, two of the Group 13 (IIIA) elements have lower ionization energies than the preceding Group 2 (IIA) elements, and several Group 16 (VIA) elements have lower ionization energies than the preceding Group 15 (VA) elements. For example, the ionization energy of boron is lower than that of beryllium, and the ionization energy of oxygen is lower than that of nitrogen (see also Figure 2-13). Be and N have electron subshells that are completely filled ($2s^2$ for Be) or half-filled ($2p^3$ for N). The next atoms (B and O) have an additional electron that is lost with comparative ease. In boron, the outermost electron, a $2p$, has significantly higher energy (higher quantum number l) than the filled $1s$ and $2s$ orbitals and is thus more easily lost than a $2s$ electron of Be. In oxygen, the fourth $2p$ electron must pair with another $2p$ electron; occupation of this orbital by two electrons is accompanied by an increase in electron-electron repulsions that facilitates loss of an electron. Additional examples of this phenomenon can be seen in Figures 8-3 and 2-13 (tabulated values of ionization energies are included in Appendix B-2).

8-1-4 CHEMICAL PROPERTIES

Efforts to find similarities in the chemistry of the main group elements began well before the formulation of the modern periodic table. The strongest parallels are within each group: the alkali metals most strongly resemble other alkali metals, halogens resemble other halogens, and so on. In addition, certain similarities have been recognized

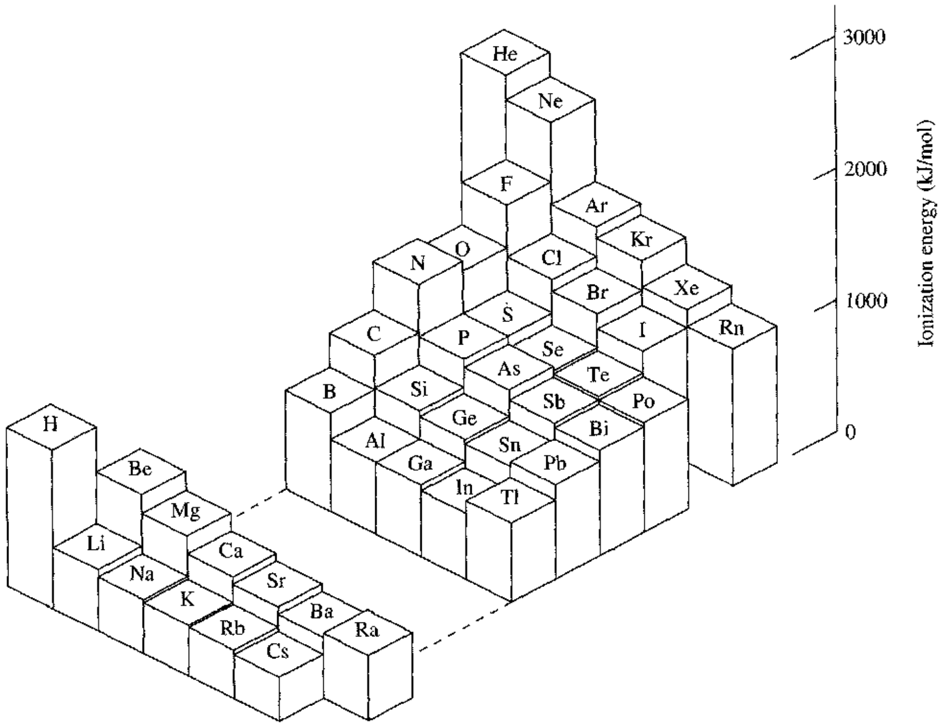

FIGURE 8-3 Ionization Energies of the Main Group Elements. (Data from C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra*, National Standard Reference Data Series, U. S. National Bureau of Standards, NSRDS-NBS 34, Washington, DC, 1970.)

between some elements along diagonals (upper left to lower right) in the periodic table. One example is that of electronegativities. As can be seen from Figure 8-2, electronegativities along diagonals are similar; for example, values along the diagonal from B to Te are in the range 1.9 to 2.2. Other "diagonal" similarities include the unusually low solubilities of LiF and MgF_2 (a consequence of the small sizes of Li^+ and Mg^{2+}, which lead to high lattice energies in these ionic compounds), similarities in solubilities of carbonates and hydroxides of Be and Al, and the formation of complex three-dimensional structures based on SiO_4 and BO_4 tetrahedra. These parallels are interesting but somewhat limited in scope; they can often be explained on the basis of similarities in sizes and electronic structures of the compounds in question.

The main group elements show the "first-row anomaly" (counting the elements Li through Ne as the first row). Properties of elements in this row are frequently significantly different from properties of other elements in the same group. For example, consider the following: F_2 has a much lower bond energy than expected by extrapolation of the bond energies of Cl_2, Br_2, and I_2; HF is a weak acid in aqueous solution, whereas HCl, HBr, and HI are all strong acids; multiple bonds between carbon atoms are much more common than between other elements in Group 14 (IVA); and hydrogen bonding is much stronger for compounds of F, O, and N than for compounds of other elements in their groups. No single explanation accounts for all the differences between elements in this row and other elements. However, in many cases, the distinctive chemistry of the first-row elements is related to the small atomic sizes and the related high electronegativities of these elements.

Oxidation-reduction reactions

Oxidation-reduction reactions of inorganic species can be described in many different ways. For example, hydrogen exhibits oxidation states of −1, 0, and +1. In acidic aqueous solution, these oxidation states occur in the half-reactions

$$2\,H^+ + 2\,e^- \longrightarrow H_2 \qquad \mathscr{E}^\circ = 0\text{ V} \tag{1}$$

$$H_2 + 2\,e^- \longrightarrow 2\,H^- \qquad \mathscr{E}^\circ = -2.25\text{ V} \tag{2}$$

These oxidation states and their matching reduction potentials are shown in a Latimer diagram[4] as

$$\begin{array}{cccccc} +1 & & 0 & & -1 & \longleftarrow \text{Oxidation states} \\ H^+ & \xrightarrow{0} & H_2 & \xrightarrow{-2.25} & H^- & \end{array}$$

In basic solution, the half-reactions for hydrogen are

$$H_2O + e^- \longrightarrow OH^- + \tfrac{1}{2}H_2 \qquad \mathscr{E}^\circ = -0.828\text{ V} \tag{3}$$

$$H_2 + 2\,e^- \longrightarrow 2\,H^- \qquad \mathscr{E}^\circ = -2.25\text{ V} \tag{4}$$

The matching Latimer diagram is

$$\begin{array}{ccccc} +1 & & 0 & & -1 \\ H_2O & \xrightarrow{-0.828} & H_2 & \xrightarrow{-2.25} & H^- \end{array}$$

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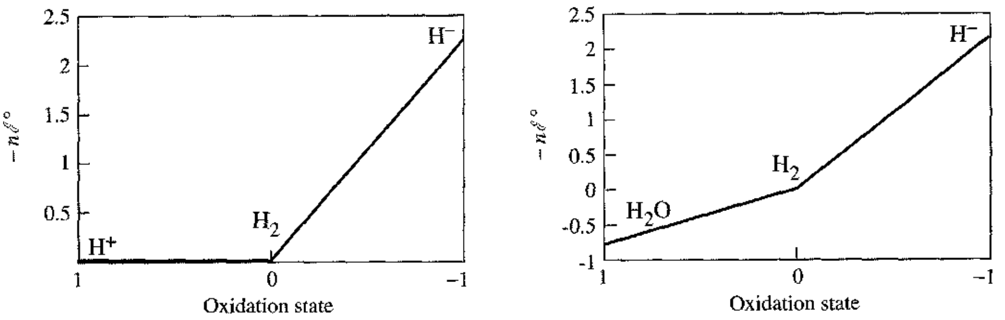
[4] W. M. Latimer, *Oxidation Potentials*, Prentice Hall, Englewood Cliffs, NJ, 1952.



(a) (b)

FIGURE 8-4 Frost Diagrams for Hydrogen. (a) Acidic solution. (b) Basic solution.

The half-reaction $2\,H^+ + 2\,e^- \longrightarrow H_2$ is used as the standard for all electrode potentials in acid solutions; all the others shown are less favorable, as shown by the negative potentials.

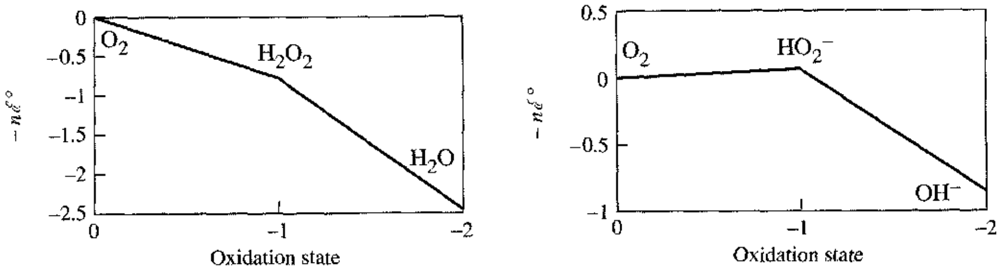
Another way to describe the same reactions is with Frost diagrams, as shown in Figure 8-4, in which $-n\mathscr{E}^\circ$ (proportional to the free energy change, $\Delta G^\circ = -n\mathscr{F}\mathscr{E}^\circ$, where n is the oxidation state) is plotted against the oxidation state in the same order as in Latimer diagrams. In these graphs, the element has a value of zero on both scales, and the species with the lowest potential (lowest free energy) is the most stable. Similar diagrams for oxygen show that the most stable form in either acid or base is water or hydroxide ion.

The Latimer diagrams for oxygen are

$$\begin{array}{ccccccl} 0 & & -1 & & -2 & & \\ O_2 & \xrightarrow{0.695} & H_2O_2 & \xrightarrow{1.763} & H_2O & & \text{in acid} \\ 0 & & -1 & & -2 & & \\ O_2 & \xrightarrow{-0.0649} & HO_2^- & \xrightarrow{0.867} & OH^- & & \text{in base} \end{array}$$

and the Frost diagrams are given in Figure 8-5. Species such as HO_2, OH, and $O_2\cdot$ are omitted from these diagrams for simplicity. They are needed when dealing with free radical reactions, but not with ordinary solution chemistry.

Latimer diagrams for many elements are in Appendix B-7.



(a) (b)

FIGURE 8-5 Frost Diagrams for Oxygen. (a) Acidic solution. (b) Basic solution.

8-2 HYDROGEN

The most appropriate position of hydrogen in the periodic table has been a matter of some dispute among chemists. Its electron configuration, $1s^1$, is similar to the valence electron configurations of the alkali metals (ns^1); hence, hydrogen is most commonly listed in the periodic table at the top of Group 1 (IA). However, it has little chemical similarity to the alkali metals. Hydrogen is also one electron short of a noble gas configuration and could conceivably be classified with the halogens. Although hydrogen has some similarities with the halogens—for example, in forming a diatomic molecule and an ion of 1− charge—these similarities are limited. A third possibility is to place hydrogen in Group 14 (IVA) above carbon: both elements have half-filled valence electron shells, are of similar electronegativity, and usually form covalent rather than ionic bonds. We prefer not to attempt to fit hydrogen into any particular group in the periodic table because it is a unique element in many ways and deserves separate consideration.

Hydrogen is by far the most abundant element in the universe (and on the sun) and, primarily in its compounds, is the third most abundant element in the Earth's crust. The element occurs as three isotopes: ordinary hydrogen or protium, ^{1}H; deuterium, ^{2}H or D; and tritium, ^{3}H or T. Both ^{1}H and ^{2}H have stable nuclei; ^{3}H undergoes β decay

$$^3_1\text{H} \longrightarrow {}^3_2\text{He} + {}^{\;0}_{-1}\text{e}$$

and has a half-life of 12.35 years. Naturally occurring hydrogen is 99.985% ^{1}H and essentially all the remainder is ^{2}H; only traces of the radioactive ^{3}H are found on earth. Deuterium compounds are used extensively as solvents for nuclear magnetic resonance (NMR) spectroscopy and in kinetic studies on reactions involving bonds to hydrogen (deuterium isotope effects). Tritium is produced in nuclear reactors by bombardment of ^{6}Li nuclei with neutrons:

$$^6_3\text{Li} + {}^1_0\text{n} \longrightarrow {}^4_2\text{He} + {}^3_1\text{H}$$

It has many applications as a tracer, for example, to study the movement of ground waters, and to study the *ab*sorption of hydrogen by metals and the *ad*sorption of hydrogen on metal surfaces. Many deuterated and tritiated compounds have been synthesized and studied. Some of the important physical properties of the isotopes of hydrogen are listed in Table 8-2.

TABLE 8-2
Properties of Hydrogen, Deuterium, and Tritium

			Properties of Molecules, X_2			
Isotope	*Abundance (%)*	*Atomic Mass*	*Melting Point (K)*	*Boiling Point (K)*	*Critical Temperature (K)*[a]	*Enthalpy of Dissociation*
Protium (^{1}H), H	99.985	1.007825	13.957	20.30	33.19	435.88
Deuterium (^{2}H), D	0.015	2.014102	18.73	23.67	38.35	443.35
Tritium (^{3}H), T	$\sim 10^{-16}$	3.016049	20.62	25.04	40.6 (calc)	446.9

SOURCES: Abundance and atomic mass data from I. Mills, T. Cuitoš, K. Homann, N. Kallay, and K. Kuchitsu, eds., *Quantities, Units, and Symbols in Physical Chemistry*, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, Oxford, 1988. Other data are from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984.

NOTE: [a]The highest temperature at which a gas can be condensed to a liquid.

8-2-1 CHEMICAL PROPERTIES

Hydrogen can gain an electron to achieve a noble gas configuration in forming the hydride ion, H^-. Many metals, such as the alkali metals and alkaline earths, form hydrides that are essentially ionic and contain discrete H^- ions. The hydride ion is a powerful reducing agent ($\mathscr{E}^\circ = 2.25$ V for $2\,H^- \longrightarrow H_2 + 2\,e^-$); it reacts, for example, with water and other protic solvents to generate H_2:

$$2\,H^- + H_2O \longrightarrow H_2 + 2\,OH^-$$

In many other cases, bonding to hydrogen atoms is essentially covalent—for example, in compounds with carbon and the other nonmetals. Hydride ions may also act as ligands in bonding to metals, with as many as nine hydrogens on a single metal, as in $ReH_9{}^{2-}$. Many complex hydrides, such as $BH_4{}^-$ and $AlH_4{}^-$, serve as important reagents in organic and inorganic synthesis. Although such complexes may be described formally as hydrides, their bonding is essentially covalent.

Lithium aluminum hydride can be prepared by the treatment of lithium hydride with a solution of aluminum chloride in ether:[5]

$$4\,LiH + AlCl_3 \longrightarrow LiAlH_4 + 3\,LiCl$$

$LiAlH_4$ is a versatile reducing agent for many organic compounds, such as ketones, aldehydes, nitriles, and nitro compounds. This ion also has many applications in inorganic synthesis. Examples of the inorganic conversions effected by $LiAlH_4$ include

$$SiCl_4 \longrightarrow SiH_4$$
$$BCl_3 \longrightarrow B_2H_6$$
$$NO \longrightarrow HON{=}NOH$$

Reference to the "hydrogen ion," H^+, is also common. However, in the presence of solvent, the extremely small size of the proton (radius approximately 1.5×10^{-3} pm) requires that it be associated with solvent molecules or other dissolved species. In aqueous solution, a more correct description is $H_3O^+(aq)$, although larger species such as $H_9O_4{}^+$ are also likely. Another important characteristic of H^+ that is a consequence of its small size is its ability to form hydrogen bonds.

The ready combustibility of hydrogen, together with the lack of potentially polluting byproducts, has led to the proposal to use hydrogen as a fuel. For example, as a potential fuel for automobiles, H_2 can provide a greater amount of energy per unit mass than gasoline without producing such environmentally damaging byproducts as carbon monoxide, sulfur dioxide, and unburned hydrocarbons. A challenge for chemists is to develop practical thermal or photochemical processes for generating hydrogen from its most abundant source, water.

Small amounts of H_2 can be generated in the laboratory by reacting "active" metals such as zinc, magnesium, or aluminum with acid:

$$Zn(s) + 2\,H^+(aq) \longrightarrow H_2(g) + Zn^{2+}(s)$$

Commercially, H_2 is frequently prepared by "cracking" petroleum hydrocarbons with solid catalysts, also forming alkenes:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

or by steam reforming of natural gas, typically using a nickel catalyst:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

Molecular hydrogen is also an important reagent, especially in the industrial hydrogenation of unsaturated organic molecules. Examples of such processes involving transition metal catalysts are discussed in Chapter 14.

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[5] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **1947**, *69*, 1199.

8-3

GROUP 1 (IA): THE ALKALI METALS

Alkali metal salts, in particular sodium chloride, have been known and used since antiquity. In early times, long before the chemistry of these compounds was understood, salt was used in the preservation and flavoring of food and even as a medium of exchange. However, because of the difficulty of reducing the alkali metal ions, the elements were not isolated until comparatively recently, well after many other elements. Two of the alkali metals, sodium and potassium, are essential for human life; their careful regulation is often important in treating a variety of medical conditions.

8-3-1 THE ELEMENTS

Potassium and sodium were first isolated within a few days of each other in 1807 by Humphry Davy as products of the electrolysis of molten KOH and NaOH. In 1817, J. A. Arfvedson, a young chemist working with J. J. Berzelius, recognized similarities between the solubilities of compounds of lithium and those of sodium and potassium. The following year, Davy also became the first to isolate lithium, this time by electrolysis of molten Li_2O. Cesium and rubidium were discovered with the help of the spectroscope in 1860 and 1861, respectively; they were named after the colors of the most prominent emission lines (Latin, *caesius*, sky blue, *rubidus*, deep red). Francium was not identified until 1939 as a short-lived radioactive isotope from the nuclear decay of actinium.

The alkali metals are silvery (except for cesium, which has a golden appearance), highly reactive solids having low melting points. They are ordinarily stored under nonreactive oil to prevent air oxidation, and are soft enough to be easily cut with a knife or spatula. Their melting points decrease with increasing atomic number because metallic bonding between the atoms becomes weaker with increasing atomic size. Physical properties of the alkali metals are summarized in Table 8-3.

TABLE 8-3
Properties of the Group 1(IA) Elements: The Alkali Metals

Element	*Ionization Energy (kJ mol⁻¹)*	*Electron Affinity (kJ mol⁻¹)*	*Melting Point (°C)*	*Boiling Point (°C)*	*Electronegativity*	$\mathscr{E}^\circ$ $(M^+ \longrightarrow M)$ $(V)^a$
Li	520	60	180.5	1347	0.912	−3.04
Na	496	53	97.8	881	0.869	−2.71
K	419	48	63.2	766	0.734	−2.92
Rb	403	47	39.0	688	0.706	−2.92
Cs	376	46	28.5	705	0.659	−2.92
Fr	$400^{b,c}$	$60^{b,d}$	27		0.7^b	-2.9^d

Sources: Ionization energies cited in this chapter are from C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra*, National Standard Reference Data Series, U.S. National Bureau of Standards, NSRDS-NBS 34, Washington, DC, 1970, unless noted otherwise. Electron affinity values listed in this chapter are from H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **1985**, *14*, 731. Standard electrode potentials listed in this chapter are from A. J. Bard, R. Parsons, and J. Jordan, eds., *Standard Potentials in Aqueous Solutions*, Marcel Dekker (for IUPAC), New York, 1985. Electronegativities cited in this chapter are from J. B. Mann, T. L. Meek, and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, *122*, 2780, Table 2. Other data are from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, except where noted.

Notes: [a] Aqueous solution, 25° C.

[b] Approximate value.

[c] J. Emsley, *The Elements*, Oxford University Press, New York, 1989.

[d] S. G. Bratsch, *J. Chem. Educ.*, **1988**, *65*, 34.

8-3-2 CHEMICAL PROPERTIES

The alkali metals are very similar in their chemical properties, which are governed in large part by the ease with which they can lose one electron (the alkali metals have the lowest ionization energies of all the elements) and thereby achieve a noble gas configuration. All are highly reactive metals and are excellent reducing agents. The metals react vigorously with water to form hydrogen; for example,

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

This reaction is highly exothermic, and the hydrogen formed may ignite in air, sometimes explosively if a large quantity of sodium is used. Consequently, special precautions must be taken to prevent these metals from coming into contact with water when they are stored.

Alkali metals react with oxygen to form oxides, peroxides, and superoxides, depending on the metal. Combustion in air yields the following products:[6]

Principal Combustion Product (Minor Product)

Alkali Metal	*Oxide*	*Peroxide*	*Superoxide*
Li	Li_2O	(Li_2O_2)	
Na	(Na_2O)	Na_2O_2	
K			KO_2
Rb			RbO_2
Cs			CsO_2

Alkali metals dissolve in liquid ammonia and other donor solvents, such as aliphatic amines (NR_3, in which R = alkyl) and $OP(NMe_2)_3$ (hexamethylphosphoramide), to give blue solutions believed to contain solvated electrons:

$$Na + x\,NH_3 \longrightarrow Na^+ + e(NH_3)_x^-$$

Because of these solvated electrons, dilute solutions of alkali metals in ammonia conduct electricity far better than completely dissociated ionic compounds in aqueous solutions. As the concentration of the alkali metals is increased, the conductivity first declines, then increases. At sufficiently high concentration, the solution acquires a bronze metallic luster and a conductivity comparable to a molten metal. Dilute solutions are paramagnetic, with approximately one unpaired electron per metal atom (corresponding to one solvated electron per metal atom); this paramagnetism decreases at higher concentrations. One interesting aspect of these solutions is that they are less dense than liquid ammonia itself. The solvated electrons may be viewed as creating cavities for themselves (estimated radius of approximately 300 pm) in the solvent, thus increasing the volume significantly. The blue color, corresponding to a broad absorption band near 1500 nm that tails into the visible range, is attributed to the solvated electron (alkali metal ions are colorless). At higher concentrations these solutions have a coppery color and contain alkali metal anions, M^-.

Not surprisingly, solutions of alkali metals in liquid ammonia are excellent reducing agents. Examples of reductions that can be effected by these solutions:

$$RC{\equiv}CH + e^- \longrightarrow RC{\equiv}C^- + \tfrac{1}{2}H_2$$

$$NH_4^+ + e^- \longrightarrow NH_3 + \tfrac{1}{2}H_2$$

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[6] Additional information on the peroxide, superoxide, and other oxygen-containing ions is provided in Table 8-12.

$$S_8 + 2\,e^- \longrightarrow S_8^{2-}$$

$$Fe(CO)_5 + 2\,e^- \longrightarrow [Fe(CO)_4]^{2-} + CO$$

The solutions of alkali metals are unstable and undergo slow decomposition to form amides:

$$M + NH_3 \longrightarrow MNH_2 + \tfrac{1}{2}H_2$$

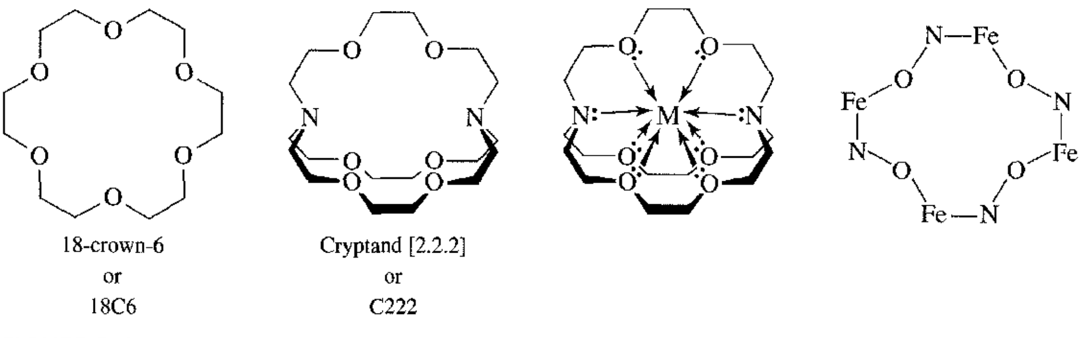
Other metals—especially the alkaline earths Ca, Sr, and Ba and the lanthanides Eu and Yb (both of which can form 2+ ions)—can also dissolve in liquid ammonia to give the solvated electron; however, the alkali metals undergo this reaction more efficiently and have been used far more extensively for synthetic purposes.

Alkali metal atoms have very low ionization energies and readily lose their outermost (ns^1) electron to form their common ions of 1+ charge. These ions can form complexes with a variety of Lewis bases (ligands, to be discussed more fully in Chapters 9 through 14). Of particular interest are cyclic Lewis bases that have several donor atoms that can surround, or trap, cations. Examples of such molecules are shown in Figure 8-6. The first of these is one of a large group of cyclic ethers, commonly known as "crown" ethers, which donate electron density to metals through their oxygen atoms. The second, one of a family of cryptands (or cryptates), can be even more effective as a cage with eight donor atoms surrounding a central metal. Metallacrowns, which incorporate metals into the crown structure, have also been developed.[7] An example of the framework structure of an iron-containing metallacrown is also shown in Figure 8-6. The importance of these structures is shown by the fact that D. J. Cram, C. J. Pedersen, and J.-M. Lehn won the Nobel Prize in Chemistry in 1987 for work with these compounds.[8]

As might be expected, the ability of a cryptand to trap an alkali metal cation depends on the sizes of both the cage and the metal ion: the better the match between these sizes, the more effectively the ion can be trapped. This effect is shown graphically for the alkali metal ions in Figure 8-7.

The largest of the alkali metal cations, Cs^+, is trapped most effectively by the largest cryptand ([3.2.2]), and the smallest, Li^+, by the smallest cryptand ([2.1.1]).[9] Other correlations can easily be seen in Figure 8-6. Cryptands have played an important role in the study of a characteristic of the alkali metals that was not recognized until rather recently, a capacity to form negatively charged ions.

Although the alkali metals are known primarily for their formation of unipositive ions, numerous examples of alkali metal anions (alkalides) have been reported since 1974.



18-crown-6
or
18C6

Cryptand [2.2.2]
or
C222

FIGURE 8-6 A Crown Ether, a Cryptand, a Metal Ion Encased in a Cryptand, and a Metallacrown.

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[7] V. L. Pecoraro, A. J. Stemmler, B. R. Gibney, J. J. Bodwin, H. Wang, J. W. Kampf, and A. Barwinski, "Metallacrowns: A New Class of Molecular Recognition Agents," in *Progr. Inorg. Chem.*, **1997**, *45*, 83–177.

[8] Their Nobel Prize lectures: D. J. Cram, *Angew. Chem.*, **1988**, *100*, 1041; C. J. Pedersen, *Angew Chem.*, **1988**, *100*, 1053; J.-M. Lehn, *Angew. Chem.*, **1988**, *100*, 91.

[9] The numbers indicate the number of oxygen atoms in each bridge between the nitrogens. Thus, cryptand [2.2.2] has one bridge with three oxygens and two bridges with two oxygens, as shown in Figure 8-7.

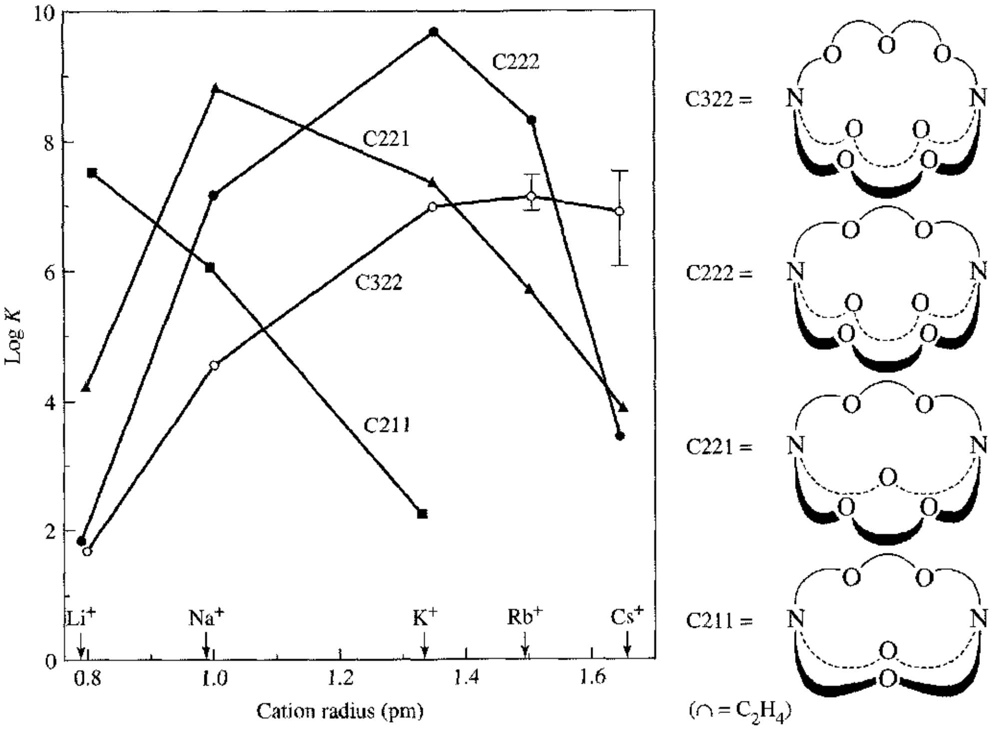

FIGURE 8-7 Formation Constants of Alkali Metal Cryptands. (From J. L. Dye, *Progr. Inorg. Chem.*, **1984** *32*, 337. © 1984, John Wiley & Sons. Reproduced by permission of John Wiley & Sons, Inc.)

The first of these was the sodide ion, Na^-, formed from the reaction of sodium with the cryptand $N\{(C_2H_4O)_2C_2H_4\}_3N$ in the presence of ethylamine:

$$\underset{\text{cryptand[2.2.2]}}{2\,Na + N\{(C_2H_4O)_2C_2H_4\}_3N} \longrightarrow \underset{[Na(\text{cryptand}[2.2.2])]^+}{[Na\,N\{(C_2H_4O)_2C_2H_4\}_3N]^+} + Na^-$$

In this complex, the Na^- occupies a site sufficiently remote from the coordinating N and O atoms of the cryptand that it can be viewed as a separate entity; it is formed as the result of disproportionation of Na into Na^+ (surrounded by the cryptand) plus Na^-. Alkalide ions are also known for the other members of Group 1 (IA) and for other metals, especially those for which a 1− charge gives rise to an s^2d^{10} electron configuration. As might be expected, alkalide ions are powerful reducing agents. This means that the cryptand or other cyclic group must be highly resistant to reduction to avoid being reduced by the alkalide ion. Even if such groups are carefully chosen, most alkalides are rather unstable and subject to irreversible decomposition.

The crystal structure of the crown ether sandwich electride $Cs^+(15C5)_2e^-$ in Figure 8-8(a) shows both the coordination of two 15C5 rings to each Cs^+ ion and the cavity occupied by the electron e^-.[10]

Among the intriguing developments in alkalide chemistry has been the recent synthesis of "inverse sodium hydride," which contains a sodide ion, Na^-, and an H^+ ion encapsulated in 3^6 adamanzane.[11] The H^+ in this structure is strongly coordinated by four nitrogen atoms in the adamanzane ligand, shown in Figure 8-8(b).

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[10] J. L. Dye, *Inorg. Chem.*, **1997**, *36*, 3816.

[11] M. Y. Redko, M. Vlassa, J. E. Jackson, A. W. Misiolek, R. H. Huang, and J. L. Dye, *J. Am. Chem. Soc.*, **2002**, *124*, 5928.

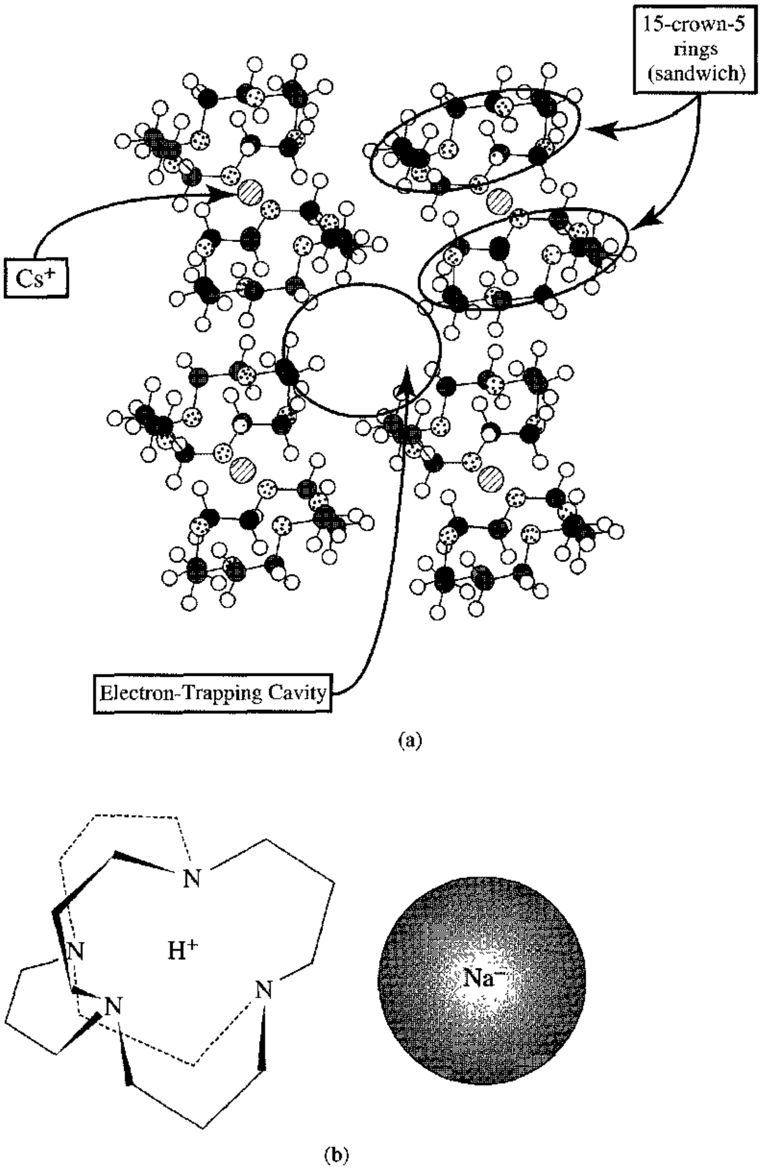


FIGURE 8-8 (a) Cs$^+$(15C5)$_2$e$^-$, a crown ether electride. (Reproduced with permission from J. L. Dye, *Inorg. Chem.*, **1997**, *36*, 3816.) (b) Na$^-$H$^+$ 3^6 adamanzane complex. (Reproduced with permission from M. Y. Redko, M. Vlassa, J. E. Jackson, A. W. Misiolek, R. H. Huang, and J. L. Dye, *J. Am. Chem. Soc.*, **2002**, *124*, 5928.)

8-4 GROUP 2 (IIA): THE ALKALINE EARTHS

8-4-1 THE ELEMENTS

Compounds of magnesium and calcium have been used since antiquity. For example, the ancient Romans used mortars containing lime (CaO) mixed with sand, and the ancient Egyptians used gypsum ($CaSO_4 \cdot 2\,H_2O$) in the plasters used to decorate their tombs. These two alkaline earths are among the most abundant elements in the Earth's crust (calcium is fifth and magnesium sixth by mass) and occur in a wide variety of minerals. Strontium and barium are less abundant; like magnesium and calcium, they commonly occur as sulfates and carbonates in their mineral deposits. Beryllium is fifth in abundance of the alkaline earths and is obtained primarily from the mineral beryl ($Be_3Al_2(SiO_3)_6$). All isotopes of radium are radioactive (longest lived isotope is ^{226}Ra, half-life of 1600 years); it was first isolated by Pierre and Marie Curie from the uranium ore pitchblende in 1898. Selected physical properties of the alkaline earths are given in Table 8-4.

TABLE 8-4
Properties of the Group 2 (IIA) Elements: The Alkaline Earths

Element	*Ionization Energy (kJ mol^{-1})*	*Electron Affinity (kJ mol^{-1})^b*	*Melting Point (°C)*	*Boiling Point (°C)*	*Electro-negativity*	$\mathscr{E}°$ ($M^{2+} + 2e^- \longrightarrow M$) *(V)^a*
Be	899	−50	1287	2500^b	1.576	−1.97
Mg	738	−40	649	1105	1.293	−2.36
Ca	590	−30	839	1494	1.034	−2.84
Sr	549	−30	768	1381	0.963	−2.89
Ba	503	−30	727	1850^b	0.881	−2.92
Ra	509	−30	700^b	1700^b	0.9^b	−2.92

SOURCE: See Table 8-3.
NOTES: [a]Aqueous solution, 25° C.
[b]Approximate values.

Atoms of the Group 2 (IIA) elements are smaller than the neighboring Group 1 (IA) elements as a consequence of the greater nuclear charge of the former. The observed result of this decrease in size is that the Group 2 elements are more dense and have higher ionization energies than the Group 1 elements. They also have higher melting and boiling points and higher enthalpies of fusion and vaporization, as can be seen from Tables 8-3 and 8-4. Beryllium, the lightest of the alkaline earth metals, is widely used in alloys with copper, nickel, and other metals. When added in small amounts to copper, for example, beryllium increases the strength of the metal dramatically and improves the corrosion resistance while preserving high conductivity and other desirable properties. Emeralds and aquamarine are obtained from two types of beryl, the mineral source of beryllium; the vivid green and blue colors of these stones are the result of small amounts of chromium and other impurities. Magnesium, with its alloys, is used widely as a strong, but very light, construction material; its density is less than one fourth that of steel. The other alkaline earth metals are used occasionally, but in much smaller amounts, in alloys. Radium has been used in the treatment of cancerous tumors, but its use has largely been superseded by other radioisotopes.

8-4-2 CHEMICAL PROPERTIES

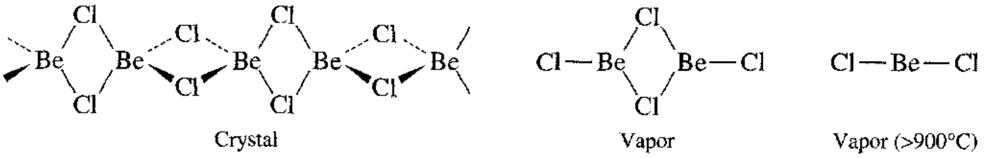
The elements in Group 2 (IIA), with the exception of beryllium, have very similar chemical properties, with much of their chemistry governed by their tendency to lose two electrons to achieve a noble gas electron configuration. In general, therefore, elements in this group are good reducing agents. Although not as violently reactive toward water as the alkali metals, the alkaline earths react readily with acids to generate hydrogen:

$$Mg + 2\,H^+ \longrightarrow Mg^{2+} + H_2$$

The reducing ability of these elements increases with atomic number. As a consequence, calcium and the heavier alkaline earths react directly with water in a reaction that can conveniently generate small quantities of hydrogen:

$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2$$

Beryllium is distinctly different from the other alkaline earths in its chemical properties. The smallest of the alkaline earths, it participates primarily in covalent rather than ionic bonding. Although the ion $[Be(H_2O)_4]^{2+}$ is known, free Be^{2+} ions are



Crystal

Vapor

Vapor (>900°C)

FIGURE 8-9 Structure of $BeCl_2$.

rarely, if ever, encountered. Beryllium and its compounds are extremely toxic, and special precautions are required in their handling. As discussed in Section 3-1-4, although beryllium halides of formula BeX_2 may be monomeric and linear in the gas phase at high temperature, in the crystal the molecules polymerize to form halogen-bridged chains, with tetrahedral coordination around beryllium, as shown in Figure 8-9. Beryllium hydride, BeH_2, is also polymeric in the solid, with bridging hydrogens. The three-center bonding involved in bridging by halogens, hydrogen, and other atoms and groups is also commonly encountered in the chemistry of the Group 13 (IIIA) elements and will be discussed more fully with those elements in Section 8-5.

Among the most chemically useful magnesium compounds are the Grignard reagents, of general formula RMgX (X = alkyl or aryl). These reagents are complex in their structure and function, consisting of a variety of species in solution linked by equilibria such as those shown in Figure 8-10. The relative positions of these equilibria, and hence the concentrations of the various species, are affected by the nature of the R group and the halogen, the solvent, and the temperature. Grignard reagents are versatile and can be used to synthesize a vast range of organic compounds, including alcohols, aldehydes, ketones, carboxylic acids, esters, thiols, and amines. Details of these syntheses are presented in many organic chemistry texts.[12]

Chlorophylls contain magnesium coordinated by chlorin groups. These compounds, essential in photosynthesis, will be discussed in Chapter 16.

Portland cement, a complex mixture of calcium silicates, aluminates, and ferrates, is one of the world's most important construction materials, with annual worldwide production in excess of 10^{12} kg. When mixed with water and sand, it changes by slow hydration to concrete. Water and hydroxide link the other components into larger crystals with great strength.

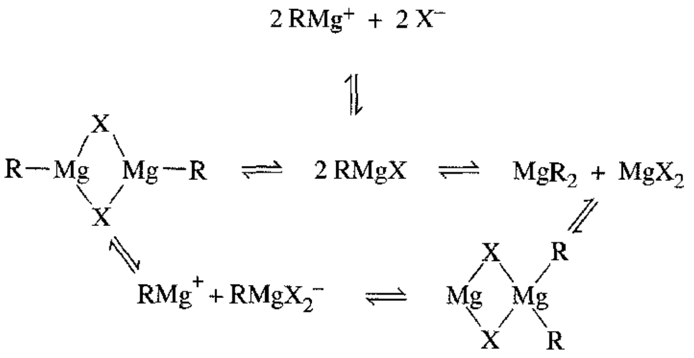


FIGURE 8-10 Grignard Reagent Equilibria.

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[12] The development of these reagents since their original discovery by Victor Grignard in 1900 has been reviewed. See *Bull. Soc. Chim. France*, **1972**, 2127–2186.

8-5 GROUP 13 (IIIA)

8-5-1 THE ELEMENTS

Elements in this group include one nonmetal, boron, and four elements that are primarily metallic in their properties. Physical properties of these elements are shown in Table 8-5.

TABLE 8-5
Properties of the Group 13 (IIIA) Elements

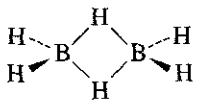
Element	*Ionization Energy (kJ mol^{-1})*	*Electron Affinity (kJ mol^{-1})*	*Melting Point (°C)*	*Boiling Point (°C)*	*Electro-negativity*
B	801	27	2180	3650^a	2.051
Al	578	43	660	2467	1.613
Ga	579	30^a	29.8	2403	1.756
In	558	30^a	157	2080	1.656
Tl	589	20^a	304	1457	1.789

SOURCE: See Table 8-3.
NOTE: ^{a}Approximate values.

Boron

Boron's chemistry is so different from that of the other elements in this group that it deserves separate discussion. Chemically, boron is a nonmetal; in its tendency to form covalent bonds, it shares more similarities with carbon and silicon than with aluminum and the other Group 13 elements. Like carbon, boron forms many hydrides; like silicon, it forms oxygen-containing minerals with complex structures (borates). Compounds of boron have been used since ancient times in the preparation of glazes and borosilicate glasses, but the element itself has proven extremely difficult to purify. The pure element has a wide diversity of allotropes (different forms of the pure element), many of which are based on the icosahedral B_{12} unit.

In the boron hydrides, called boranes, hydrogen often serves as a bridge between boron atoms, a function rarely performed by hydrogen in carbon chemistry. How is it possible for hydrogen to serve as a bridge? One way to address this question is to consider the bonding in diborane, B_2H_6:



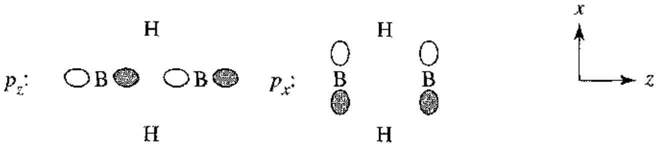
Diborane

Diborane has 12 valence electrons. By the Lewis approach to bonding, eight of these electrons are involved in bonding to the terminal hydrogens. Thus, four electrons remain to account for bonding in the bridges. This type of bonding, involving three atoms and two bonding electrons per bridge, is described as three-center, two-electron bonding.[13] To understand how this type of bonding is possible, we need to consider the orbital interactions in this molecule.

Diborane has D_{2h} symmetry. Focusing on the boron atoms and the bridging hydrogens, we can use the approach of Chapter 5 to sketch the group orbitals and determine their matching irreducible representations, as shown in Figure 8-11. The possible interactions between the boron group orbitals and the group orbitals of the bridging hydrogens can be determined by matching the labels of the irreducible representations. For example, one group orbital in each set has B_{3u} symmetry. This involves the hydrogen

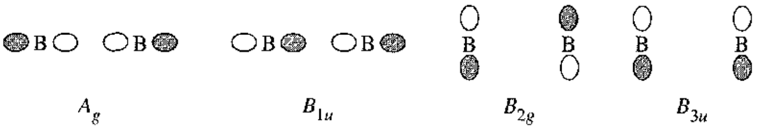
[13] W. N. Lipscomb, *Boron Hydrides*, W. A. Benjamin, New York, 1963.

Reducible representation for *p* orbitals involved in bonding with bridging hydrogens:

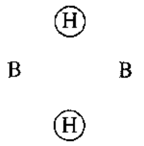


	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma(p_z)$	2	2	0	0	0	0	2	2	$= A_g + B_{1u}$
$\Gamma(p_x)$	2	-2	0	0	0	0	2	-2	$= B_{2g} + B_{3u}$

The irreducible representations have the following symmetries:



Reducible representation for 1*s* orbitals of bridging hydrogens:



	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma(1s)$	2	0	0	2	0	2	2	0

This reduces to $A_g + B_{3u}$, which have the following symmetries:

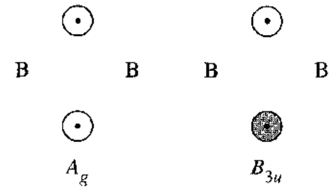


FIGURE 8-11 Group Orbitals of Diborane.

group orbital with lobes of opposite sign and one of the boron group orbitals derived from p_x atomic orbitals. The results, shown in Figure 8-12, are two molecular orbitals of b_{3u} symmetry, one bonding and one antibonding. The bonding orbital, with lobes on the top and bottom spanning the B—H—B bridges, is one of the orbitals chiefly responsible for the stability of the bridges.

The other hydrogen group orbital has A_g symmetry. Two boron group orbitals have A_g symmetry: one is derived from p_z orbitals and one is derived from *s* orbitals. All three group orbitals have similar energy. The result of the A_g interactions is the formation of three molecular orbitals, one strongly bonding, one weakly bonding, and one antibonding.[14] (The other boron group orbitals, with B_{1u} and B_{2g} symmetry, do not participate in interactions with the bridging hydrogens.) These interactions are summarized in Figure 8-13.[15] In contrast to the simple model (two three-center, two-electron bonds), three bonding orbitals play a significant role in joining the boron atoms through the hydride bridges, two of a_g symmetry and one of b_{3u} symmetry. The shapes of these orbitals are shown in Figure 8-14.

[14] One of the group orbitals on the terminal hydrogens also has A_g symmetry. The interaction of this group orbital with the other orbitals of A_g symmetry influences the energy and shape of the a_g molecular orbitals, shown in Figure 8-12, and generates a fourth, antibonding a_g molecular orbital (not shown in the figure).

[15] This figure does not show interactions with terminal hydrogens. One terminal atom group orbital has B_{1u} symmetry and therefore interacts with the B_{1u} group orbitals of boron, resulting in molecular orbitals that are no longer nonbonding.

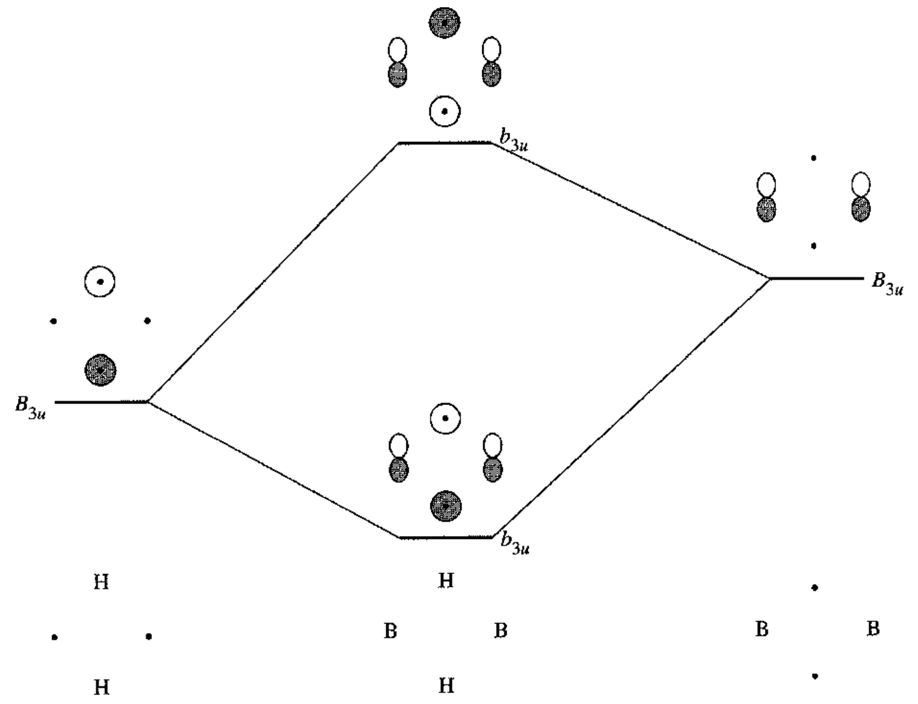


FIGURE 8-12 B_{3u} Orbital Interactions in Diborane.

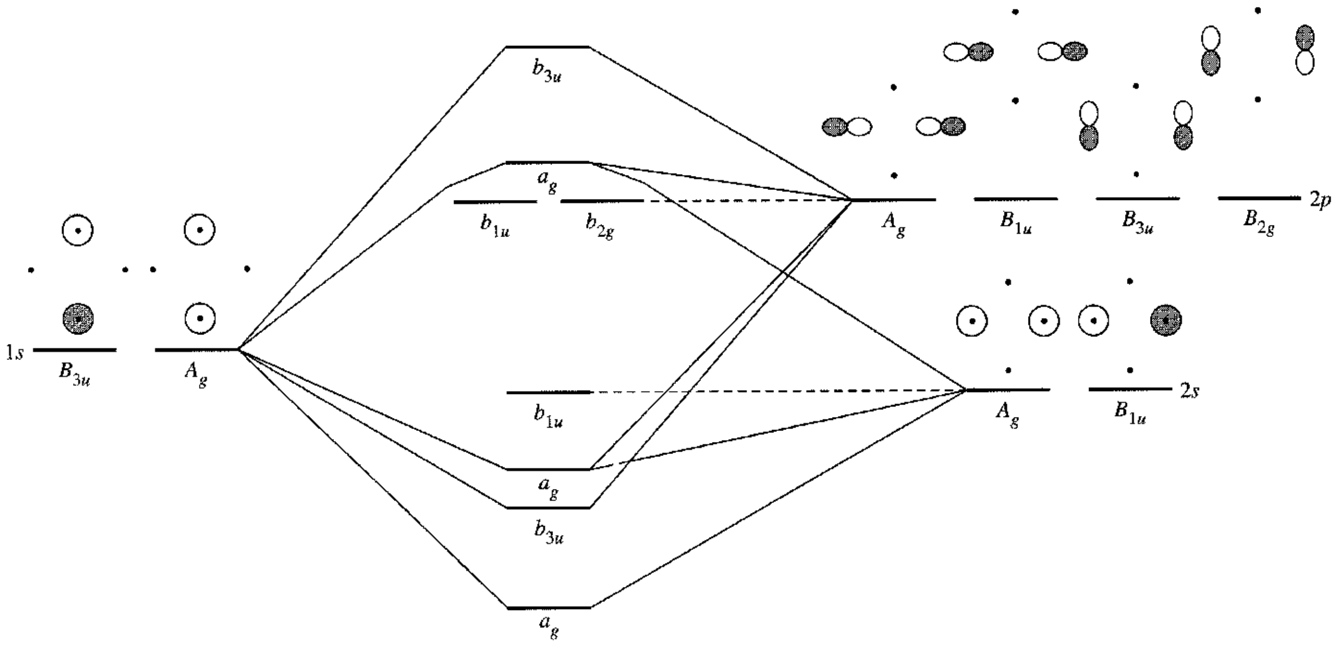
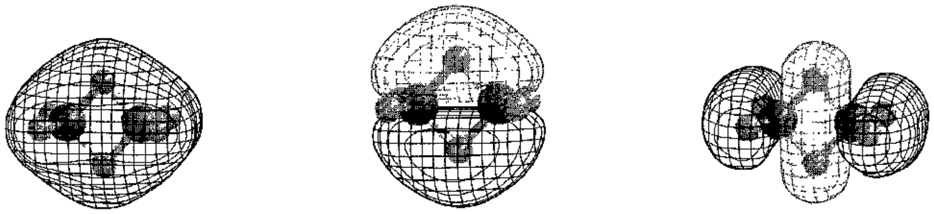
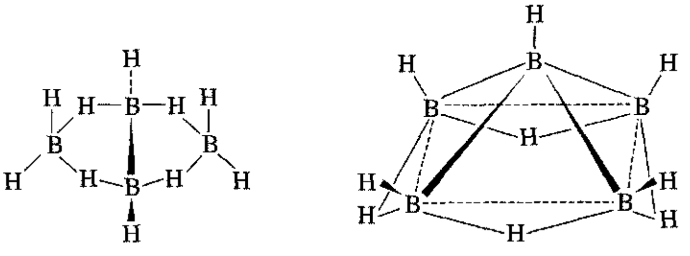


FIGURE 8-13 Bridging Orbital Interactions in Diborane.



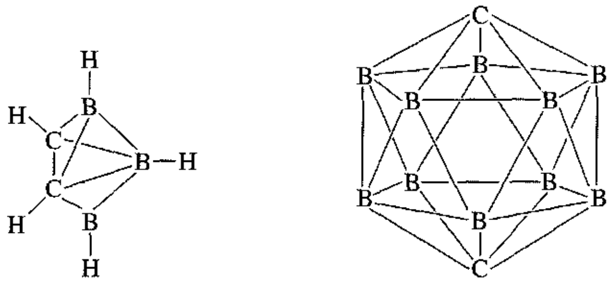
a_g (lowest energy) b_{3u} a_g

FIGURE 8-14 Bonding Orbitals Involved in Hydrogen Bridges in Diborane.



B_4H_{10} B_5H_9

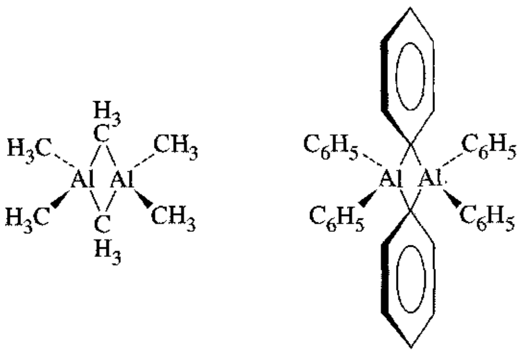
Boranes



$C_2B_3H_5$

para-$C_2B_{10}H_{12}$ (one H on each C and B)

Carboranes



Bridged Aluminum Compounds

FIGURE 8-15 Boranes, Carboranes, and Bridged Aluminum Compounds.

Similar bridging hydrogen atoms occur in many other boranes, as well as in carboranes, which contain both boron and carbon atoms arranged in clusters. In addition, bridging hydrogens and alkyl groups are frequently encountered in aluminum chemistry. A few examples of these compounds are shown in Figure 8-15.

The boranes, carboranes, and related compounds are also of interest in the field of cluster chemistry, the chemistry of compounds containing metal-metal bonds. The bonding in these compounds will be discussed and compared with the bonding in transition metal cluster compounds in Chapter 15.

Boron has two stable isotopes, ^{11}B (80.4% abundance) and ^{10}B (19.6%). ^{10}B has a very high neutron absorption cross section (it is a good absorber of neutrons). This property has been developed for use in the treatment of cancerous tumors in a process called boron neutron capture therapy (BNCT).[16] Boron-containing compounds having a

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[16] M. F. Hawthorne, *Angew. Chem., Int. Ed.*, **1993**, *32*, 950.

strong preference for attraction to tumor sites, rather than healthy sites, can be irradiated with beams of neutrons. The subsequent nuclear decay emits high-energy particles, ${}^{7}_{3}\mathrm{Li}$ and ${}^{4}_{2}\mathrm{He}$ (alpha particles), which can kill the adjacent cancerous tissue:

$$
\begin{aligned}
{}^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} &\longrightarrow {}^{11}_{5}\mathrm{B} \\
{}^{11}_{5}\mathrm{B} &\longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He}
\end{aligned}
$$

The challenge to chemists has been to develop boron-containing reagents that can be selectively concentrated in cancerous tissue while avoiding healthy tissue. Various approaches to this task have been attempted.[17]

8-5-2 OTHER CHEMISTRY OF THE GROUP 13 (IIIA) ELEMENTS

Elements in this group, especially boron and aluminum, form three-coordinate Lewis acids capable of accepting an electron pair and increasing their coordination number. Some of the most commonly used Lewis acids are the boron trihalides, BX_3. These compounds are monomeric (unlike diborane, B_2H_6, and aluminum halides, Al_2X_6) and, as discussed in Section 3-1-4, are planar molecules having significant π bonding. In their Lewis acid role, they can accept an electron pair from a halide ion to form tetrahaloborate ions, BX_4^-. The Lewis acid behavior of these compounds has been discussed in Chapter 6.

Boron halides can also act as halide ion acceptors when they serve as catalysts—for example, in the Friedel-Crafts alkylation of aromatic hydrocarbons:

$$
\begin{array}{ll}
 & BF_3 + RX \longrightarrow R^+ + BF_3X^- \\
 & R^+ + PhH \longrightarrow H^+ + RPh \\
 & \underline{H^+ + BF_3X^- \longrightarrow HX + BF_3} \\
\text{Net:} & RX + PhH \longrightarrow RPh + HX
\end{array}
$$

The metallic nature of the elements in Group 13 (IIIA) increases as one descends in the group. Aluminum, gallium, indium, and thallium commonly form 3+ ions by loss of their valence p electron and both valence s electrons. Thallium also forms a 1+ ion by losing its p electron and retaining its two s electrons. This is the first case we have encountered of the **inert pair effect**, in which a metal has an oxidation state that is 2 less than the traditional American group number. For example, Pb is in Group IVA according to the traditional numbering system (Group 14 in IUPAC) and it has a 2+ ion as well as a 4+ ion. The effect is commonly ascribed to the stability of an electron configuration with entirely filled subshells: in the inert pair effect, a metal loses all the p electrons in its outermost subshell, leaving a filled s^2 subshell; the pair of s electrons seems relatively "inert" and is less easily removed. The actual reasons for this effect are considerably more complex than described here.[18]

Parallels between main group and organic chemistry can be instructive. One of the best known of these parallels is between the organic molecule benzene and the isoelectronic borazine (alias "inorganic benzene"), $B_3N_3H_6$. Some of the similarities in physical properties between these two are striking, as shown in Table 8-6.

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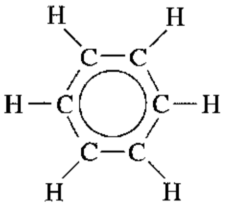
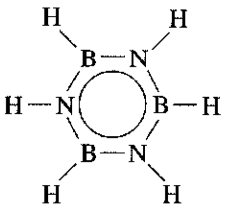
[17] See S. B. Kahl and J. Li, *Inorg. Chem.*, **1996**, *35*, 3878, and references therein.

[18] See, for example, N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, pp. 255–256.

TABLE 8-6
Benzene and Borazine





Property	*Benzene*	*Borazine*
Melting point (°C)	6	−57
Boiling point (°C)	80	55
Density (*l*) (g cm^{-3})[a]	0.81	0.81
Surface tension (*l*) (N m^{-1})[a]	0.0310	0.0311
Dipole moment	0	0
Internuclear distance in ring (pm)	142	144
Internuclear distance, bonds to H (pm)	C—H: 108	B—H: 120 N—H: 102

SOURCE: Data from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, p. 238.

NOTE: [a]At the melting point.

Despite these parallels, the chemistry of these two compounds is quite different. In borazine, the difference in electronegativity between boron (2.051) and nitrogen (3.066) adds considerable polarity to the B—N bonds and makes the molecule much more susceptible to attack by nucleophiles (at the more positive boron) and electrophiles (at the more negative nitrogen) than benzene.

Parallels between benzene and isoelectronic inorganic rings remain of interest. Some examples include reports on boraphosphabenzenes (containing B_3P_3 rings)[19] and $[(CH_3)AlN(2,6\text{-diisopropylphenyl})]_3$ containing an Al_3N_3 ring.[20]

Another interesting parallel between boron-nitrogen chemistry and carbon chemistry is offered by boron nitride, BN. Like carbon (Section 8-6), boron nitride exists in a diamond-like form and in a form similar to graphite. In the diamond-like (cubic) form, each nitrogen is coordinated tetrahedrally by four borons and each boron by four nitrogens. As in diamond, such coordination gives high rigidity to the structure and makes BN comparable to diamond in hardness. In the graphite-like hexagonal form, BN also occurs in extended fused ring systems. However, there is much less delocalization of π electrons in this form and, unlike graphite, hexagonal BN is a poor conductor. As in the case of diamond, the harder, more dense form (cubic) can be formed from the less dense form (hexagonal) under high pressures.

8-6
GROUP 14 (IVA)

8-6-1 THE ELEMENTS

Elements in this group range from a nonmetal, carbon, to the metals tin and lead, with the intervening elements showing semimetallic behavior. Carbon has been known from prehistory as the charcoal resulting from partial combustion of organic matter. In recorded history, diamonds have been prized as precious gems for thousands of years. Neither form of carbon, however, was recognized as a chemical element until late in the

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[19] H. V. R. Dias and P. P. Power, *Angew. Chem., Int. Ed.*, **1987**, *26*, 1270; *J. Am. Chem. Soc.*, **1989**, *111*, 144.

[20] K. M. Waggoner, H. Hope, and P. P. Power, *Angew. Chem., Int. Ed.*, **1988**, *27*, 1699.

18th century. Tools made of flint (primarily SiO_2) were used throughout the Stone Age. However, free silicon was not isolated until 1823, when J. J. Berzelius obtained it by reducing K_2SiF_6 with potassium. Tin and lead have also been known since ancient times. A major early use of tin was in combination with copper in the alloy bronze; weapons and tools containing bronze date back more than 5000 years. Lead was used by the ancient Egyptians in pottery glazes and by the Romans for plumbing and other purposes. In recent decades, the toxic effects of lead and lead compounds in the environment have gained increasing attention and have led to restrictions on the use of lead compounds—for example, in paint pigments and in gasoline additives, primarily tetraethyllead, $(C_2H_5)_4Pb$. Germanium was a "missing" element for a number of years. Mendeleev accurately predicted the properties of this then-unknown element in 1871 ("eka-silicon") but it was not discovered until 1886, by C. A. Winkler. Properties of the Group 14 (IVA) elements are summarized in Table 8-7.

TABLE 8-7
Properties of the Group 14 (IVA) Elements

Element	*Ionization Energy (kJ mol^{-1})*	*Electron Affinity (kJ mol^{-1})*	*Melting Point (°C)*	*Boiling Point (°C)*	*Electronegativity*
C	1086	122	4100	[a]	2.544
Si	786	134	1420	3280[b]	1.916
Ge	762	120	945	2850	1.994
Sn	709	120	232	2623	1.824
Pb	716	35	327	1751	1.854

SOURCE: See Table 8-3.
NOTES: [a] Sublimes.
[b] Approximate value.

Although carbon occurs primarily as the isotope ^{12}C (whose atomic mass serves as the basis of the modern system of atomic mass), two other isotopes, ^{13}C and ^{14}C, are important as well. ^{13}C, which has a natural abundance of 1.11%, has a nuclear spin of $\frac{1}{2}$, in contrast to ^{12}C, which has zero nuclear spin. This means that even though ^{13}C comprises only about 1 part in 90 of naturally occurring carbon, it can be used as the basis of NMR observations for the characterization of carbon-containing compounds. With the advent of Fourier transform technology, ^{13}C NMR spectrometry has become a valuable tool in both organic and inorganic chemistry. Uses of ^{13}C NMR in organometallic chemistry are described in Chapter 13.

^{14}C is formed in the atmosphere from nitrogen by thermal neutrons from the action of cosmic rays:

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

^{14}C is formed by this reaction in comparatively small amounts (approximately $1.2 \times 10^{-10}\%$ of atmospheric carbon); it is incorporated into plant and animal tissues by biological processes. When a plant or animal dies, the process of exchange of its carbon with the environment by respiration and other biological processes ceases, and the ^{14}C in its system is effectively trapped. However, ^{14}C decays by beta emission, with a half-life of 5730 years:

$$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e$$

Therefore, by measuring the remaining amount of ^{14}C, one can determine to what extent this isotope has decayed and, in turn, the time elapsed since death. Often called simply "radiocarbon dating," this procedure has been used to estimate the ages of many archeological samples, including Egyptian remains, charcoal from early campfires, and the Shroud of Turin.

EXAMPLE

What fraction of ^{14}C remains in a sample that is 50,000 years old?

This is 50,000/5730 = 8.73 half-lives. For first-order reactions (such as radioactive decay), the initial amount decreases by $\frac{1}{2}$ during each half-life, so the fraction remaining is $\left(\frac{1}{2}\right)^{8.73} = 2.36 \times 10^{-3}$.

EXERCISE 8-1

A sample of charcoal from an archeological site has a remaining fraction of ^{14}C of 3.5×10^{-2}. What is its age?

Until 1985, carbon was encountered primarily in two allotropes, diamond and graphite. The diamond structure is very rigid, with each atom surrounded tetrahedrally by four other atoms in a structure that has a cubic unit cell; as a result, diamond is extremely hard, the hardest of all naturally occurring substances. Graphite, on the other hand, consists of layers of fused six-membered rings of carbon atoms. The carbon atoms in these layers may be viewed as being sp^2 hybridized. The remaining, unhybridized p orbitals are perpendicular to the layers and participate in extensive π bonding, with π electron density delocalized over the layers. Because of the relatively weak interactions between the layers, the layers are free to slip with respect to each other, and π electrons are free to move within each layer, making graphite a good lubricant and electrical conductor. The structures of diamond and graphite are shown in Figure 8-16, and their important physical properties are given in Table 8-8.

TABLE 8-8
Physical Properties of Diamond and Graphite

Property	*Diamond*	*Graphite*
Density (g cm^{-3})	3.513	2.260
Electrical resistivity (Ωm)	10^{11}	1.375×10^{-5}
Standard molar entropy (J mol^{-1} K^{-1})	2.377	5.740
C_p at 25° C (J mol^{-1} K^{-1})	6.113	8.527
C—C distance (pm)	154.4	141.5 (within layer) 335.4 (between layers)

SOURCE: J. Elmsley, *The Elements*, Oxford University Press, New York, 1989, p. 44.

At room temperature, graphite is thermodynamically the more stable form. However, the density of diamond is much greater than that of graphite, and graphite can be converted to diamond at very high pressure (high temperature and molten metal catalysts are also used to facilitate this conversion). Since the first successful synthesis of diamonds from graphite in the mid-1950s, the manufacture of industrial diamonds has developed rapidly, and nearly half of all industrial diamonds are now produced synthetically.

A thin layer of hydrogen bonded to a diamond surface significantly reduces the coefficient of friction of the surface in comparison with a clean diamond surface, presumably because the clean surface provides sites for attachment of molecules—bonds that must be broken for surfaces to be able to slip with respect to each other.[21]

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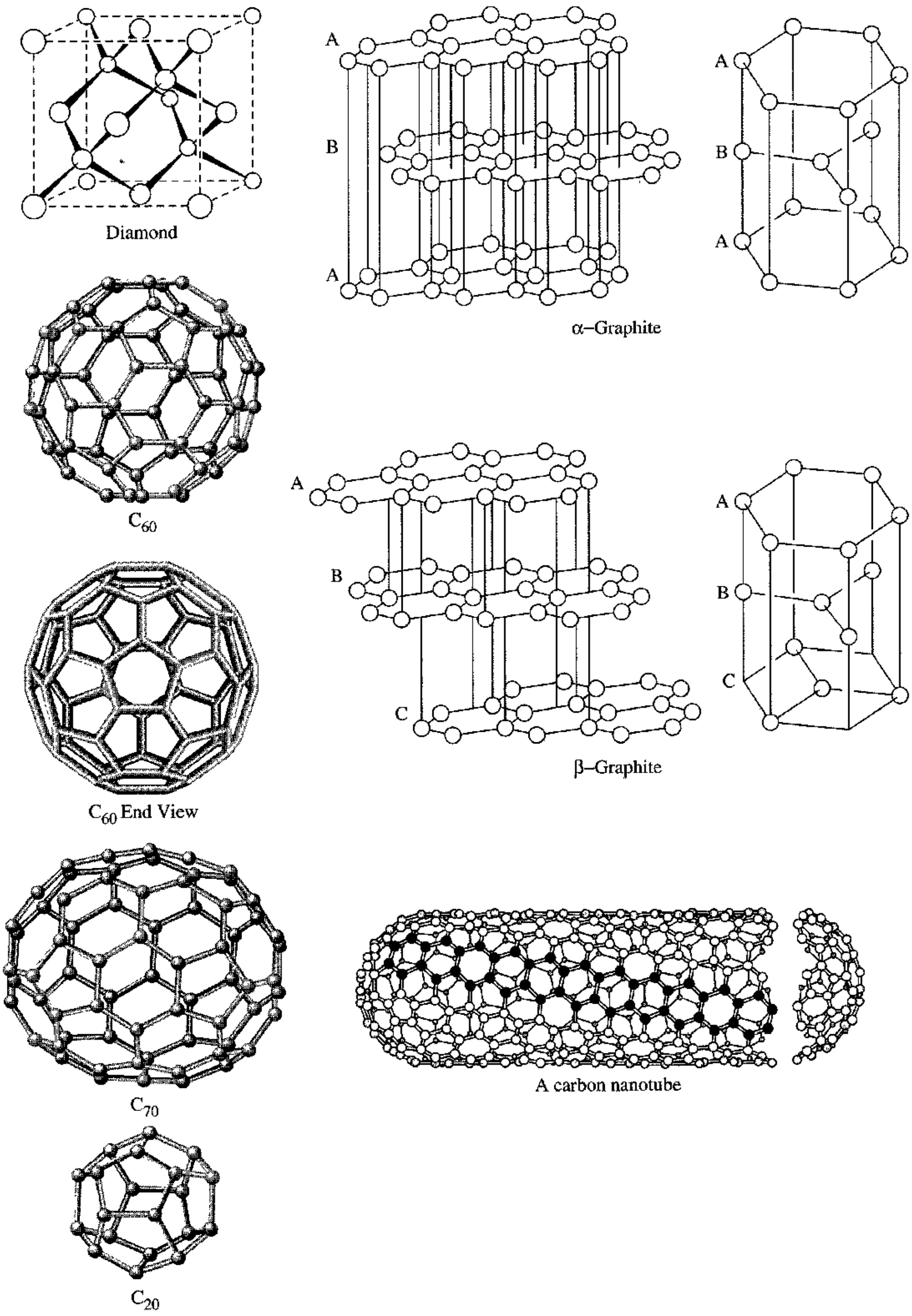
[21] R. J. A. van den Oetelaar and C. F. J. Flipse, *Surf. Sci.*, **1997**, *384*, L828.


Diamond

α–Graphite

C_{60}

β–Graphite

C_{60} End View

C_{70}

A carbon nanotube

C_{20}

FIGURE 8-16 Diamond, Graphite, and Fullerenes.

One of the most fascinating developments in modern chemistry has been the synthesis of buckminsterfullerene,[22] C_{60}, and the related "fullerenes," molecules having near-spherical shapes resembling geodesic domes. First reported by Kroto and colleagues[23] in 1985, C_{60}, C_{70}, C_{80}, and a variety of related species were soon synthesized; examples of their structures are shown in Figure 8-16. Subsequent work has been extensive, and many compounds of fullerenes containing groups attached to the outside of these large clusters have been synthesized. In addition, small atoms and molecules have been trapped inside fullerene cages. Remarkably, roughly 9 years after the first synthesis of fullerenes, natural deposits of these molecules were discovered at the impact sites of ancient meteorites.[24] The development of large-scale synthetic procedures for fullerenes has been a challenging undertaking, with most methods to date involving condensation of carbon in an inert atmosphere from laser or other high-energy vaporization of graphite or from controlled pyrolysis of aromatic hydrocarbons.[25]

The prototypical fullerene, C_{60}, consists of fused five- and six-membered carbon rings. Each 6-membered ring is surrounded, alternately, by hexagons and pentagons of carbons; each pentagon is fused to five hexagons. The consequence of this structural motif is that each hexagon is like the base of a bowl; the three pentagons fused to this ring, linked by hexagons, force the structure to curve (in contrast to graphite, in which each hexagon is fused to six surrounding hexagons in the same plane). This phenomenon, best seen by assembling a model of C_{60}, results in a domelike structure that eventually curves around on itself to give a structure resembling a sphere.[26] The shape resembles a soccer ball (the most common soccer ball has an identical arrangement of pentagons and hexagons on its surface); all 60 atoms are equivalent and give rise to a single ^{13}C NMR resonance.

Although all atoms in C_{60} are equivalent, the bonds are not. Two types of bonds occur (best viewed using a model), at the fusion of two six-membered rings and at the fusion of five- and six-membered rings. X-ray crystallographic studies on C_{60} complexes have shown that the C—C bond lengths at the fusion of two six-membered rings in these complexes are shorter, 135.5 pm, in comparison with the comparable distances at the fusion of five- and six-membered rings, 146.7 pm.[27] This indicates a greater degree of π bonding at the fusion of the six-membered rings.

Surrounding each six-membered ring with two pentagons (on opposite sides) and four hexagons (with each pentagon, as in C_{60}, fused to five hexagons) gives a slightly larger, somewhat prolate structure with 70 carbon atoms. C_{70} is often obtained as a byproduct of the synthesis of C_{60} and is among the most stable of the fullerenes. Unlike C_{60}, five different types of carbon are present in C_{70}, giving rise to five ^{13}C NMR resonances.[28]

Structural variations on fullerenes have evolved well beyond the individual clusters themselves. Examples include the following:

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[22] More familiarly known as "buckyball."

[23] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature (London)*, **1985**, *318*, 162.

[24] L. Becker, J. L. Bada, R. E. Winans, J. E. Hunt, T. E. Bunch, and B. M. French, *Science*, **1994**, *265*, 642; D. Heymann, L. P. F. Chibante, R. R. Brooks, W. S. Wolbach, and R. E. Smalley, *Science*, **1994**, *265*, 645.

[25] J. R. Bowser, *Adv. Inorg. Chem.*, **1994**, *36*, 61–62, and references therein.

[26] The structure of C_{60} has the same symmetry as an icosahedron.

[27] These distances were obtained for a twinned crystal of C_{60} at 110 K. (S. Liu, Y. Lu, M. M. Kappes, and J. A. Ibers, *Science*, **1991**, *254*, 408. Neutron diffraction data at 5 K give slightly different results: 139.1 pm at the fusion of the 6-membered rings and 145.5 pm at the fusion of 5- and 6-membered rings (W. I. F. David, R. M. Ibberson, J. C. Matthew, K. Pressides, T. J. Dannis, J. P. Hare, H. W. Kroto, R. Taylor, and D. C. M. Walton, *Nature*, **1991**, *353*, 147).

[28] R. Taylor, J. P. Hare, A. K. Abdul-Sada, and H. W. Kroto, *Chem. Commun (Cambridge)*, **1990**, 1423.

Nanotubes. If the ends of the nanotube shown in Figure 8-16 are uncapped, the result is a hollow tube of very small dimension. Such nanotubes have been synthesized both with single and multiple walls (multiple layers built up on the outside of the innermost tube). One of the most promising potential applications of such structures is in the electronics industry. Extensive work has been done to devise methods for constructing computer circuits that use carbon nanotubes, and the nanotubes have been cited as the leading candidate to replace silicon when the size limit on miniaturization of silicon chips has been reached.[29]

Megatubes. These tubes are larger in diameter than nanotubes and can be prepared with walls of different thicknesses. Potentially, these can be used for the transport of a variety of molecules of different sizes.[30]

Polymers. The rhombohedral polymer of C_{60} shown in Figure 8-17(a) has been reported to act as a ferromagnet at room temperature and above.[31] Linear chain polymers have also been reported.[32]

Nano "onions." These are spherical particles based on multiple carbon layers surrounding a C_{60} or other fullerene core. One proposed use is in lubricants.[33]

Other linked structures. These include fullerene rings,[34] linked "ball-and-chain" dimers,[35] and an increasing variety of other forms. Examples are shown in Figure 8-17.

The smallest known fullerene is C_{20} (Figure 8-16), synthesized by replacing the hydrogen atoms of dodecahedrane, $C_{20}H_{20}$, with bromines, followed by debromination.[36]

Additional forms of carbon, involving long $-C\equiv C-C\equiv C-C\equiv C-$ chains, have been identified in nature; they may also be prepared from graphite at high temperatures and pressures.

Silicon and germanium crystallize in the diamond structure. However, they have somewhat weaker covalent bonds than carbon as a consequence of less efficient orbital overlap. These weaker bonds result in lower melting points for silicon (1420°C for Si and 945°C for Ge, compared with 4100°C for diamond) and greater chemical reactivity. Both silicon and germanium are semiconductors, described in Chapter 7.

On the other hand, tin has two allotropes, a diamond form (α) more stable below 13.2°C and a metallic form (β) more stable at higher temperatures.[37] Lead is entirely metallic and is among the most dense (and most poisonous) of the metals.

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[29] V. Derycke, R. Martel, J. Appenzeller, and P. Avouris, *Nano Lett.*, **2001**, *1*, 453.

[30] D. R. Mitchell, R. M. Brown, Jr., T. L. Spires, D. K. Romanovicz, and R. J. Lagow, *Inorg. Chem.*, **2001**, *40*, 2751.

[31] T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. A. Davydov, L. S. Kashevarova, and A. V. Rakhmanina, *Nature (London)*, **2001**, *413*, 716; *Chem. Eng. News*, **2001**, *79*, 10.

[32] H. Brumm, E. Peters, and M. Jansen, *Angew. Chem., Int. Ed.*, **2001**, *40*, 2069.

[33] N. Sano, H. Wang, M. Chhowalla, I. Alexandrou, and G. A. J. Amaratunga, *Nature (London)*, **2001**, *414*, 506.

[34] Y. Li, Y. Huang, S. Du, and R. Liu, *Chem. Phys. Lett.*, **2001**, *335*, 524.

[35] A. A. Shvartsburg, R. R. Hudgins, R. Gutierrez, G. Jungnickel, T. Frauenheim, K. A. Jackson, and M. F. Jarrold, *J. Phys. Chem. A*, **1999**, *103*, 5275.

[36] H. Prinzbach, A. Weller, P. Landenberger, F. Wahl, J. Wörth, L. T. Scott, M. Gelmont, D. Olevano, and B. Issendorff, *Nature (London)*, **2000**, *407*, 60.

[37] These forms are *not* similar to the α and β forms of graphite (Figure 8-16).

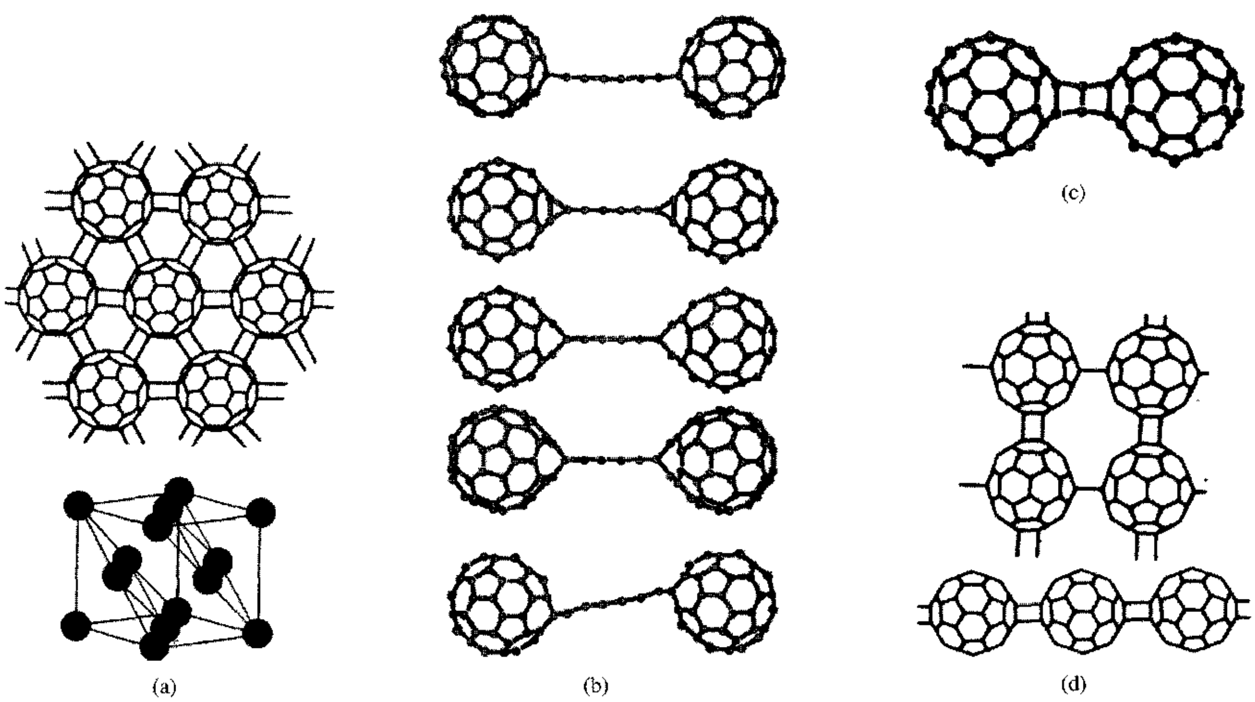

FIGURE 8-17 Polymers of C_{60}. (a) Rhombohedral polymer. (b) Ball-and-chain dimers. *Top to bottom*, *sp*, closed-66 sp^2, open-66 sp^2, open-56 sp^2, open-56 sp^2 in a distorted configuration. (c) Double [2 + 2] closed-66 isomer for C_{122}. (d) Other linked and linear chains. The 56 and 66 labels indicate that the bonds are to carbons common to five- and six-membered rings and to two six-membered rings, respectively. [(a) and (d) from M. Núñez-Tegueiro, L. Marques, J. L. Hodeau, O. Béthoux, and M. Perroux, *Phys. Rev. Lett.*, **1995**, *74*, 278; (b) and (c) from A. A. Shvartsburg, R. R. Hudgins, R. Gutierrez, G. Jungnickel, T. Frauenheim, K. A. Jackson, and M. F. Jarrold, *J. Phys. Chem. A*, **1999**, *103*, 5275. Reproduced with permission.]

8-6-2 COMPOUNDS

A common misconception is that carbon can, at most, be four-coordinate. Although carbon is bonded to four or fewer atoms in the vast majority of its compounds, many examples are now known in which carbon has coordination numbers of 5, 6, or higher. Five-coordinate carbon is actually rather common, with methyl and other groups frequently forming bridges between two metal atoms, as in $Al_2(CH_3)_6$ (see Figure 8-15). There is even considerable evidence for the five-coordinate ion CH_5^+.[38] Many organometallic cluster compounds contain carbon atoms surrounded by polyhedra of metal atoms. Such compounds, often designated carbide clusters, are discussed in Chapter 15. Examples of carbon atoms having coordination numbers of 5, 6, 7, and 8 are shown in Figure 8-18.

The two most familiar oxides of carbon, CO and CO_2, are colorless, odorless gases. Carbon monoxide is a rarity of sorts, a stable compound in which carbon formally has only three bonds. It is extremely toxic, forming a bright red complex with the iron in hemoglobin, which has a greater affinity for CO than for O_2. As described in Chapter 5, the highest occupied molecular orbital of CO is concentrated on carbon; this provides the molecule an opportunity to interact strongly with a variety of metal atoms, which in turn can donate electron density through their *d* orbitals to empty π^* orbitals (LUMOs) on CO. The details of such interactions will be described more fully in Chapter 13.

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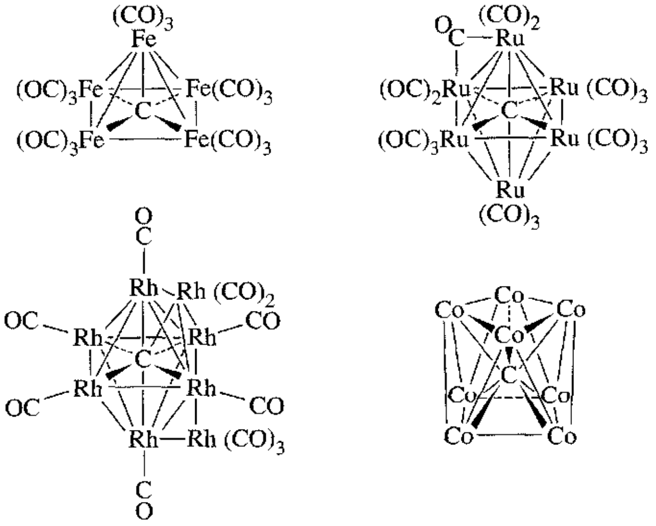
[38] G. A. Olah and G. Rasul, *Acc. Chem. Res.*, **1997**, *30*, 245.



$Rh_8C(CO)_{19}$
Not shown: Eight COs bridging edges of polyhedron

$[Co_8C(CO)_{18}]^{2-}$
COs not shown: One on each cobalt; ten bridging edges of polyhedron

FIGURE 8-18 High Coordination Numbers of Carbon.

Carbon dioxide is familiar as a component of the Earth's atmosphere (although only fifth in abundance, after nitrogen, oxygen, argon, and water vapor) and as the product of respiration, combustion, and other natural and industrial processes. It was the first gaseous component to be isolated from air, the "fixed air" isolated by Joseph Black in 1752. More recently, CO_2 has gained international attention because of its role in the "greenhouse" effect and the potential atmospheric warming and other climatic consequences of an increase in CO_2 abundance. Because of the energies of carbon dioxide's vibrational levels, it absorbs a significant amount of thermal energy and, hence, acts as a sort of atmospheric blanket. Since the beginning of the Industrial Revolution, the carbon dioxide concentration in the atmosphere has increased substantially, an increase that will continue indefinitely unless major policy changes are made by the industrialized nations. A start was made on policies for greenhouse gas reduction at an international conference in Kyoto, Japan, in 1997. The consequences of a continuing increase in atmospheric CO_2 are difficult to forecast; the dynamics of the atmosphere are extremely complex, and the interplay between atmospheric composition, human activity, the oceans, solar cycles, and other factors is not yet well understood.

Although only two forms of elemental carbon are common, carbon forms several anions, especially in combination with the most electropositive metals. In these compounds, called collectively the carbides, there is considerable covalent as well as ionic bonding, with the proportion of each depending on the metal. The best characterized carbide ions are shown here.

Ion	*Common Name*	*Systematic Name*	*Example*	*Major Hydrolysis Product*
C^{4-}	Carbide or methanide	Carbide	Al_4C_3	CH_4
C_2^{2-}	Acetylide	Dicarbide (2−)	CaC_2	$H—C≡C—H$
C_3^{4-}		Tricarbide (4−)	Mg_2C_3[a]	$H_3C—C≡C—H$

NOTE: [a]This is the only known compound containing the C_3^{4-} ion.

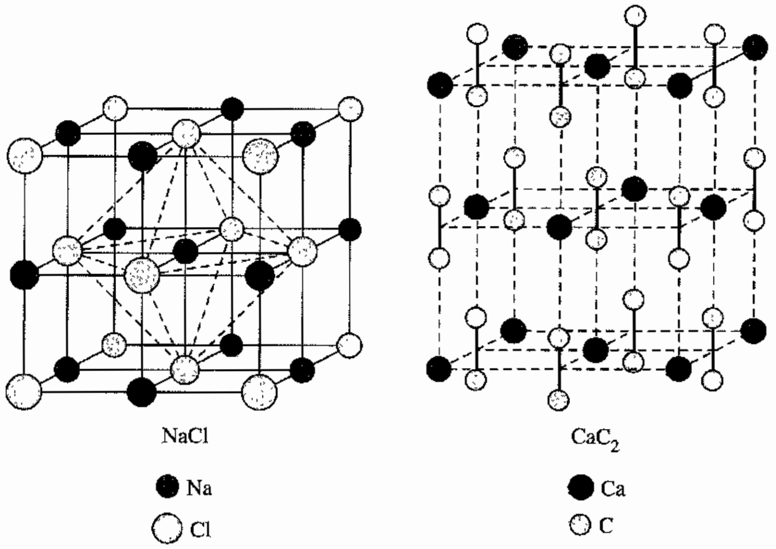


FIGURE 8-19 Crystal Structures of NaCl and CaC_2.

These carbides, as indicated, liberate organic molecules on reaction with water. For example,

$$Al_4C_3 + 12\,H_2O \longrightarrow 4\,Al(OH)_3 + 3\,CH_4$$

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + HC{\equiv}CH$$

Calcium carbide, CaC_2, is the most important of the metal carbides. Its crystal structure resembles that of NaCl, with parallel C_2^{2-} units, as shown in Figure 8-19. Before compressed gases were readily available, calcium carbide was commonly used as a source of acetylene for lighting and welding; carbide headlights were on early automobiles.

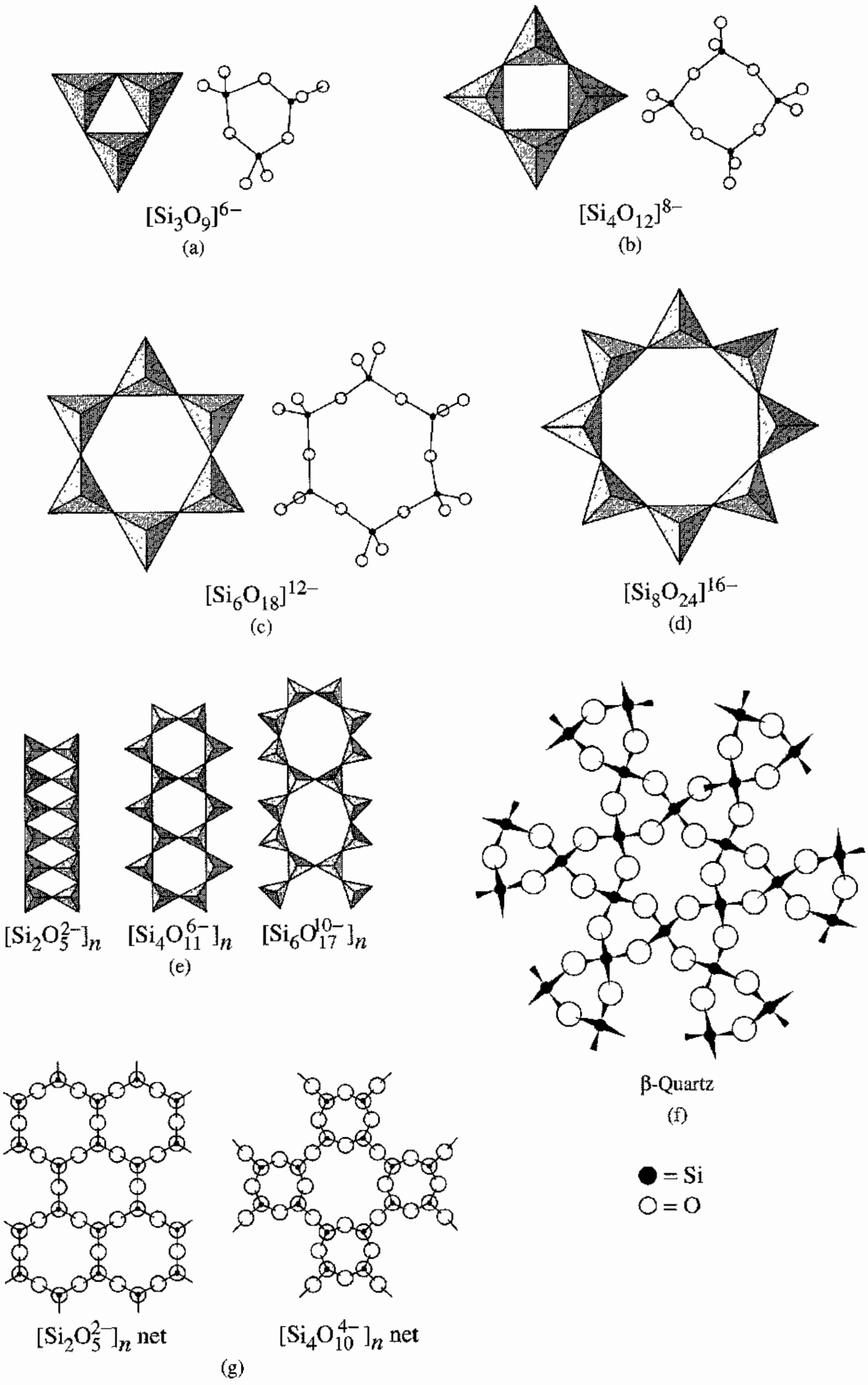
It may seem surprising that carbon, with its vast range of literally millions of compounds, is not the most abundant element in this group. By far the most abundant of Group 14 (IVA) elements on Earth is silicon, which comprises 27% of the Earth's crust (by mass) and is second in abundance (after oxygen); carbon is only 17th in abundance. Silicon, with its semimetallic properties, is of enormous importance in the semiconductor industry, with wide applications in such fields as computers and solar energy collection.

In nature, silicon occurs almost exclusively in combination with oxygen, with many minerals containing tetrahedral SiO_4 structural units. Silicon dioxide, SiO_2, occurs in a variety of forms in nature, the most common of which is α-quartz, a major constituent of sandstone and granite. SiO_2 is of major industrial importance as the major component of glass, in finely divided form as a chromatographic support (silica gel) and catalyst substrate, as a filtration aid (as diatomaceous earth, the remains of diatoms, tiny unicellular algae), and in many other applications.

The SiO_4 structural units occur in nature in silicates, compounds in which these units may be fused by sharing corners, edges, or faces in diverse ways. Examples of silicate structures are shown in Figure 8-20. The interested reader can find extensive discussions of these structures in the chemical literature.[39]

With carbon forming the basis for the colossal number of organic compounds, it is interesting to consider whether silicon or other members of this group can form the

[39] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, 1984, pp. 1009–1043.



$[Si_3O_9]^{6-}$
(a)

$[Si_4O_{12}]^{8-}$
(b)

$[Si_6O_{18}]^{12-}$
(c)

$[Si_8O_{24}]^{16-}$
(d)

$[Si_2O_5^{2-}]_n$ $[Si_4O_{11}^{6-}]_n$ $[Si_6O_{17}^{10-}]_n$
(e)

β-Quartz
(f)

$[Si_2O_5^{2-}]_n$ net $[Si_4O_{10}^{4-}]_n$ net
(g)

FIGURE 8-20 Examples of Silicate Structures. [Reproduced with permission. (a, b, c, d, e) from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, pp. 403, 405, © 1984; and (f, g) from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984, pp. 1006, 1024.]

foundation for an equally vast array of compounds. Unfortunately, such does not seem the case; the ability to catenate (form bonds with other atoms of the same element) is much lower for the other Group 14 (IVA) elements than for carbon, and the hydrides of these elements are also much less stable.

Silane, SiH_4, is stable and, like methane, tetrahedral. However, although silanes (of formula Si_nH_{n+2}) up to eight silicon atoms in length have been synthesized, their stability decreases markedly with chain length; Si_2H_6 (disilane) undergoes only very slow decomposition, but Si_8H_{18} decomposes rapidly. In recent years, a few compounds containing Si$=$Si bonds have been synthesized, but there is no promise of a chemistry of multiply bonded Si species comparable at all in diversity with the chemistry of unsaturated organic compounds. Germanes of formulas GeH_4 to Ge_5H_{12} have been made, as have SnH_4 (stannane), Sn_2H_6 and, possibly, PbH_4 (plumbane), but the chemistry in these cases is even more limited than of the silanes.

Why are the silanes and other analogous compounds less stable (more reactive) than the corresponding hydrocarbons? First, the Si—Si bond is slightly weaker than the C—C bond (approximate bond energies, 340 and 368 kJ mol^{-1}, respectively), and Si—H bonds are weaker than C—H bonds (393 versus 435 kJ mol^{-1}). Silicon is less electronegative (1.92) than hydrogen (2.30) and is, therefore, more susceptible to nucleophilic attack (in contrast to carbon, which is more electronegative [2.54] than hydrogen). Silicon atoms are also larger and therefore provide greater surface area for attack by nucleophiles. In addition, silicon atoms have low-lying *d* orbitals that can act as acceptors of electron pairs from nucleophiles. Similar arguments can be used to describe the high reactivity of germanes, stannanes, and plumbanes. Silanes are believed to decompose by elimination of $:SiH_2$ by way of a transition state having a bridging hydrogen, as shown in Figure 8-21. This reaction, incidentally, can be used to prepare silicon of extremely high purity.

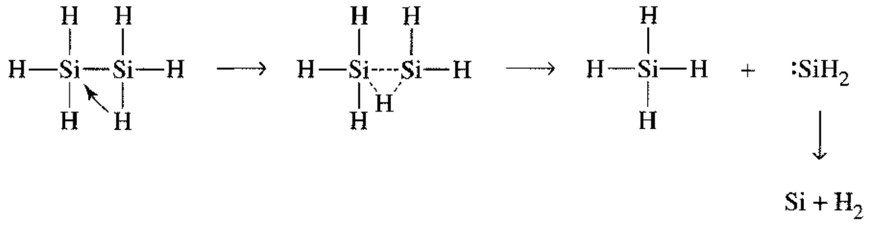


FIGURE 8-21 Decomposition of Silanes.

As mentioned, elemental silicon has the diamond structure. Silicon carbide, SiC, occurs in many crystalline forms, some based on the diamond structure and some on the wurtzite structure (see Figures 7-6 and 7-8(b)). It can be made from the elements at high temperature. Carborundum, one form of silicon carbide, is widely used as an abrasive, with a hardness nearly as great as diamond and a low chemical reactivity. SiC has now garnered interest as a high-temperature semiconductor.

The elements germanium, tin, and lead show increasing importance of the 2+ oxidation state, an example of the inert pair effect. For example, all three show two sets of halides, of formula MX_4 and MX_2. For germanium, the most stable halides have the formula GeX_4; for lead, it is PbX_2. For the dihalides, the metal exhibits a stereochemically active lone pair. This leads to bent geometry for the free molecules and to crystalline structures in which the lone pair is evident, as shown for $SnCl_2$ in Figure 8-22.

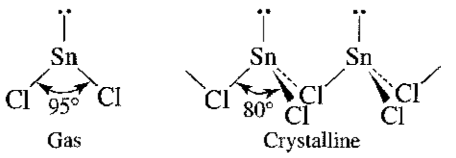


FIGURE 8-22 Structure of $SnCl_2$ in Gas and Crystalline Phases.

8-7
GROUP 15 (VA)

Nitrogen is the most abundant component of the Earth's atmosphere (78.1% by volume). However, the element was not successfully isolated from air until 1772, when Rutherford, Cavendish, and Scheele achieved the isolation nearly simultaneously by successively removing oxygen and carbon dioxide from air. Phosphorus was first isolated from urine by H. Brandt in 1669. Because the element glowed in the dark on exposure to air, it was named after the Greek *phos*, light, and *phoros*, bringing. Interestingly, the last three elements in Group 15 (VA)[40] had long been isolated by the time nitrogen and phosphorus were discovered. Their dates of discovery are lost in history, but all had been studied extensively, especially by alchemists, by the 15th century.

These elements again span the range from nonmetallic (nitrogen and phosphorus) to metallic (bismuth) behavior, with the elements in between (arsenic and antimony) having intermediate properties. Selected physical properties are given in Table 8-9.

TABLE 8-9
Properties of the Group 15 (VA) Elements

Element	*Ionization Energy (kJ mol^{-1})*	*Electron Affinity (kJ mol^{-1})*	*Melting Point (°C)*	*Boiling Point (°C)*	*Electro-negativity*
N	1402	−7	−210	−195.8	3.066
P	1012	72	44^a	280.5	2.053
As	947	78	^{b}	^{b}	2.211
Sb	834	103	631	1587	1.984
Bi	703	91	271	1564	2.01^c

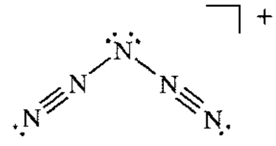
SOURCE: See Table 8-3.
NOTES: $^a\alpha$-P_4.
^{b}Sublimes at 615°.
^{c}Approximate value.

8-7-1 THE ELEMENTS

Nitrogen is a colorless diatomic gas. As discussed in Chapter 5, the dinitrogen molecule has a nitrogen-nitrogen triple bond of unusual stability. In large part, the stability of this bond is responsible for the low reactivity of this molecule (although it is by no means totally inert). Nitrogen is therefore suitable as an inert environment for many chemical studies of reactions that are either oxygen or moisture sensitive. Liquid nitrogen, at 77 K, is frequently used as a convenient, rather inexpensive coolant for studying low-temperature reactions, trapping of solvent vapors, and cooling superconducting magnets (actually, for preserving the liquid helium coolant, which boils at 4 K).

For more than a century, the only isolable chemical species containing nitrogen and no other elements were N_2 and the azide ion, N_3^-. Remarkably, in 1999, a third such species, N_5^+, was reported, a product of the following reaction:

$$N_2F^+[AsF_6]^- + HN_3 \longrightarrow N_5^+[AsF_6]^- + HF$$



$N_5^+[AsF_6]^-$ is not stable at room temperature but can be preserved for weeks at −78°C. The N_5^+ ion has a V-shaped structure, bent at the central nitrogen and linear at the neighboring atoms.[41] Furthermore, even though the ions C_2^{2-} and O_2^{2-} have been

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[40] Elements in this group are sometimes called the pnicogens or pnictogens.

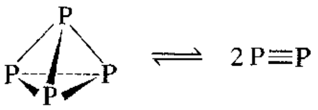
[41] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem., Int. Ed.*, **1999**, *38*, 2004; for more information on nitrogen-containing species, see T. M. Klapötke, *Angew. Chem., Int. Ed.*, **1999**, *38*, 2536.

known for many years, the N_2^{2-} ion was not characterized until recently.[42] In SrN_2, the bond distance in this ion is 122.4 pm, comparable to 120.7 pm in the isoelectronic O_2 molecule.

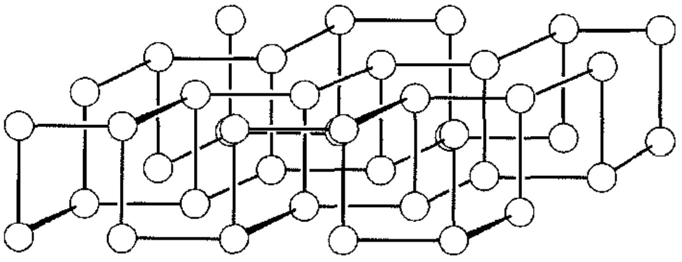
Phosphorus has many allotropes. The most common of these is white phosphorus, which exists in two modifications, α-P_4 (cubic) and β-P_4 (hexagonal). Condensation of phosphorus from the gas or liquid phases (both of which contain tetrahedral P_4 molecules) gives primarily the α form, which slowly converts to the β form at temperatures above −76.9°C. During slow air oxidation, α-P_4 emits a yellow-green light, an example of phosphorescence that has been known since antiquity (and is the source of the name of this element); to slow such oxidation, white phosphorus is commonly stored under water. White phosphorus was once used in matches; however, its extremely high toxicity has led to its replacement by other materials, especially P_4S_3 and red phosphorus, which are much less toxic.

Heating of white phosphorus in the absence of air gives red phosphorus, an amorphous material that exists in a variety of polymeric modifications. Still another allotrope, black phosphorus, is the most thermodynamically stable form; it can be obtained from white phosphorus by heating at very high pressures. Black phosphorus converts to other forms at still higher pressures. Examples of these structures are shown in Figure 8-23. The interested reader can find more detailed information on allotropes of phosphorus in other sources.[43]

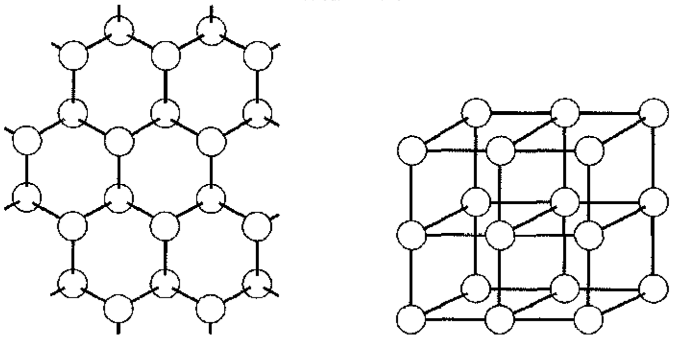
As mentioned, phosphorus exists as tetrahedral P_4 molecules in the liquid and gas phases. At very high temperatures, P_4 can dissociate into P_2:



At approximately 1800°C, this dissociation reaches 50%.



Orthorhombic



Rhombohedral

Cubic

FIGURE 8-23 Allotropes of Phosphorus. (Reproduced with permission from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, p. 558. © 1984, Pergamon Press PLC.)

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[42] G. Auffermann, Y. Prots, and R. Kniep, *Angew. Chem., Int. Ed.*, **2001**, *40*, 547.

[43] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, 1984, pp. 838–840, and references therein.

Arsenic, antimony, and bismuth also exhibit a variety of allotropes. The most stable allotrope of arsenic is the gray (α) form, which is similar to the rhombohedral form of phosphorus. In the vapor phase, arsenic, like phosphorus, exists as tetrahedral As_4. Antimony and bismuth also have similar α forms. These three elements have a somewhat metallic appearance but are brittle and are only moderately good conductors. Arsenic, for example, is the best conductor in this group but has an electrical resistivity nearly 20 times as great as copper.

Bismuth is the heaviest element to have a stable, nonradioactive nucleus; polonium and all heavier elements are radioactive.

Anions

Nitrogen exists in three anionic forms, N^{3-} (nitride), N_3^- (azide), and N^{2-}.[44] Nitrides of primarily ionic character are formed by lithium and the Group 2 (IIA) elements; many other nitrides having a greater degree of covalence are also known. In addition, N_3^- is a strong π-donor ligand toward transition metals (metal-ligand interactions will be described in Chapter 10). Stable compounds containing the linear N_3^- ion include those of the Groups 1 and 2 (IA and IIA) metals. However, some other azides are explosive. $Pb(N_3)_2$, for example, is shock sensitive and used as a primer for explosives.

Although phosphides, arsenides, and other Group 15 compounds are known with formulas that may suggest that they are ionic (e.g., Na_3P, Ca_3As_2), such compounds are generally lustrous and have good thermal and electrical conductivity, properties more consistent with metallic than with ionic bonding.

8-7-2 COMPOUNDS

Hydrides

In addition to ammonia, nitrogen forms the hydrides N_2H_4 (hydrazine), N_2H_2 (diazene or diimide), and HN_3 (hydrazoic acid). Structures of these compounds are shown in Figure 8-24.

The chemistry of ammonia and the ammonium ion is vast; ammonia is of immense industrial importance and is produced in larger molar quantities than any other chemical. More than 80% of the ammonia produced is used in fertilizers, with additional uses including the synthesis of explosives, the manufacture of synthetic fibers (such as rayon, nylon, and polyurethanes), and the synthesis of a wide variety of organic and inorganic compounds. As described in Chapter 6, liquid ammonia is used extensively as a nonaqueous ionizing solvent.

In nature, ammonia is produced by the action of nitrogen-fixing bacteria on atmospheric N_2 under very mild conditions (room temperature and 0.8 atm N_2 pressure). These bacteria contain nitrogenases, iron- and molybdenum-containing enzymes that catalyze the formation of NH_3. Industrially, NH_3 is synthesized from its elements by the Haber-Bosch process, which typically uses finely divided iron as catalyst:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

Even with a catalyst, this process is far more difficult than the nitrogenase-catalyzed route in bacteria; typically, temperatures above 380° C and pressures of approximately 200 atm are necessary. Fritz Haber won the 1918 Nobel Prize for this discovery and is

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[44] N_4^{4-} as a bridging ligand has also been reported by W. Massa, R. Kujanek, G. Baum, and K. Dehnicke, *Angew. Chem., Int. Ed.*, **1984**, *23*, 149.

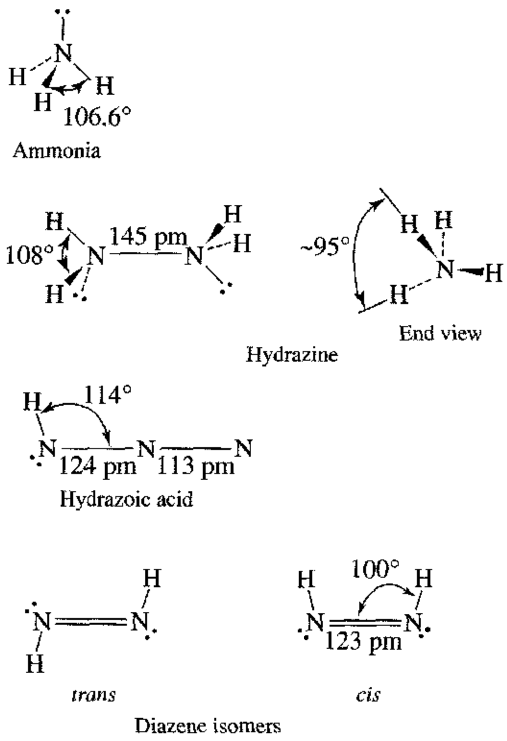


FIGURE 8-24 Nitrogen Hydrides. Some multiple bonds are not shown. (Bond angles and distances are from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984.)

credited both with making commercial fertilizers possible and for helping Germany in World War I to replace imported nitrates used in explosives.

The nitrogen for this process is obtained from fractional distillation of liquid air. Although originally obtained from electrolyis of water, H_2 is now obtained more economically from hydrocarbons (see p. 248).

Oxidation of hydrazine is highly exothermic:

$$N_2H_4 + O_2 \longrightarrow N_2 + 2\,H_2O \qquad \Delta H^\circ = -622 \text{ kJ mol}^{-1}$$

Advantage has been taken of this reaction in the major use of hydrazine and its methyl derivatives, in rocket fuels. Hydrazine is also a convenient and versatile reducing agent, capable of being oxidized by a wide variety of oxidizing agents, in acidic (as the protonated hydrazonium ion, $N_2H_5^+$) and basic solutions. It may be oxidized by one, two, or four electrons, depending on the oxidizing agent:

Oxidation Reaction	$\mathscr{E}^\circ$ *(Oxidation; V)*	*Examples of Oxidizing Agents*
$N_2H_5^+ \rightleftharpoons NH_4^+ + \frac{1}{2}N_2 + H^+ + e^-$	1.74	MnO_4^-, Ce^{4+}
$N_2H_5^+ \rightleftharpoons \frac{1}{2}NH_4^+ + \frac{1}{2}HN_3 + \frac{5}{2}H^+ + 2\,e^-$	−0.11	H_2O_2
$N_2H_5^+ \rightleftharpoons N_2 + 5\,H^+ + 4\,e^-$	0.23	I_2

Both the *cis* and *trans* isomers of diazene are known; they are unstable except at very low temperatures. The fluoro derivatives, N_2F_2, are more stable and have been characterized structurally. Both isomers of N_2F_2 show N—N distances consistent with double bonds (*cis*, 120.9 pm; *trans*, 122.4 pm).

Phosphine, PH_3, is a highly poisonous gas. Phosphine has significantly weaker intermolecular attractions than NH_3 in the solid state; consequently, its melting and boiling points are much lower than those of ammonia (−133.5°C and −87.5°C for PH_3 versus −77.8°C and −34.5°C for NH_3). Phosphine derivatives of formula PR_3 (phosphines; R = H, alkyl, or aryl) and $P(OR)_3$ (phosphites) are important ligands that form numerous coordination compounds. Examples of phosphine compounds will be discussed in Chapters 13 and 14. Arsines, AsR_3, and stibines, SbR_3, are also important ligands in coordination chemistry.

Nitrogen oxides and oxyions

Nitrogen oxides and ions containing nitrogen and oxygen are among the most frequently encountered species in inorganic chemistry. The most common of these are summarized in Table 8-10.

Nitrous oxide, N_2O, is commonly used as a mild dental anesthetic and propellant for aerosols; on atmospheric decomposition, it yields its innocuous parent gases and is therefore an environmentally acceptable substitute for chlorofluorocarbons. On the other hand, N_2O contributes to the greenhouse effect and is increasing in the atmosphere. Nitric oxide, NO, is an effective coordinating ligand; its function in this context is discussed in Chapter 13. It also has many biological functions, discussed in Chapter 16.

The gases N_2O_4 and NO_2 form an interesting pair. At ordinary temperatures and pressures, both exist in significant amounts in equilibrium:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta H^\circ = 57.20\ \text{kJ mol}^{-1}$$

Colorless, diamagnetic N_2O_4 has a weak N—N bond that can readily dissociate to give the brown, paramagnetic NO_2.

Nitric oxide is formed in the combustion of fossil fuels and is present in the exhausts of automobiles and power plants; it can also be formed from the action of lightning on atmospheric N_2 and O_2. In the atmosphere, NO is oxidized to NO_2. These gases, often collectively designated NO_x, contribute to the problem of acid rain, primarily because NO_2 reacts with atmospheric water to form nitric acid:

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

Nitrogen oxides are also believed to be instrumental in the destruction of the Earth's ozone layer, as will be discussed in the following section.

Nitric acid is of immense industrial importance, especially in the synthesis of ammonium nitrate and other chemicals. Ammonium nitrate is used primarily as a fertilizer. In addition, it is thermally unstable and undergoes violently exothermic decomposition at elevated temperature:

$$2\,NH_4NO_3 \longrightarrow 2\,N_2 + O_2 + 4\,H_2O$$

Because this reaction generates a large amount of gas in addition to being strongly exothermic, ammonium nitrate was recognized early as a potentially useful explosive. Its use in commercial explosives is now second in importance to its use as a fertilizer.

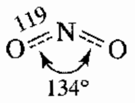
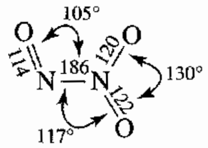
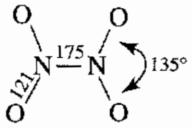
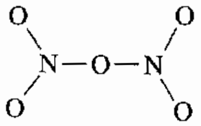
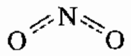
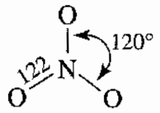
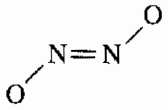
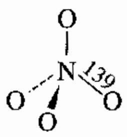
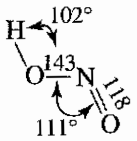
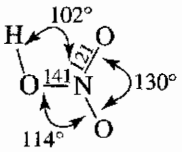
Nitric acid is also of interest as a nonaqueous solvent and undergoes the following autoionization:

$$2\,HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \rightleftharpoons H_2O + NO_2^+ + NO_3^-$$

Nitric acid is synthesized commercially via two nitrogen oxides. First, ammonia is reacted with oxygen using a platinum-rhodium gauze catalyst to form nitric oxide, NO:

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O$$

TABLE 8-10
Compounds and Ions Containing Nitrogen and Oxygen

Formula	*Name*	*Structure*[a]	*Notes*
N_2O	Nitrous oxide	$N{=}N{=}O$	mp = −90.9°C; bp = −88.5°C
NO	Nitric oxide	$\overset{115}{N\equiv O}$	mp = −163.6°C; bp = −151.8°C; bond order approximately 2.5; paramagnetic
NO_2	Nitrogen dioxide		Brown, paramagnetic gas; exists in equilibrium with N_2O_4; $2\,NO_2 \rightleftharpoons N_2O_4$
N_2O_3	Dinitrogen trioxide		mp = −100.1°C; dissociates above melting point: $N_2O_3 \rightleftharpoons NO + NO_2$
N_2O_4	Dinitrogen tetroxide		mp = −11.2°C; bp = −21.15°C; dissociates into $2\,NO_2$ [ΔH(dissociation) = 57 kJ/mol]
N_2O_5	Dinitrogen pentoxide		N—O—N bond may be bent; consists of $NO_2^+NO_3^-$ in the solid
NO^+	Nitrosonium or nitrosyl	$\overset{106}{N\equiv O}$	Isoelectronic with CO
NO_2^+	Nitronium or nitryl	$\overset{115}{O{=}N{=}O}$	Isoelectronic with CO_2
NO_2^-	Nitrite		N—O distance varies from 113 to 123 pm and bond angle varies from 116° to 132° depending on cation; versatile ligand (see Chapter 9)
NO_3^-	Nitrate		Forms compounds with nearly all metals; as ligand, has a variety of coordination modes
$N_2O_2^{2-}$	Hyponitrite		Useful reducing agent
NO_4^{3-}	Orthonitrate		Na and K salts known; decomposes in presence of H_2O and CO_2
HNO_2	Nitrous acid		Weak acid (pK_a = 3.3 at 25°C); disproportionates: $3\,HNO_2 \rightleftharpoons H_3O^+ + 2\,NO + NO_3^-$ in aqueous solution
HNO_3	Nitric acid		Strong acid in aqueous solution; concentrated aqueous solutions are strong oxidizing agents

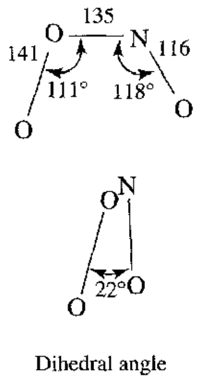


FIGURE 8-25 Peroxynitrite Structure.

The nitric oxide is then oxidized by air and water:

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

The first step, oxidation of NH_3, requires a catalyst that is specific for NO generation; otherwise, oxidation to form N_2 can occur:

$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O$$

An additional nitrogen oxyanion is peroxynitrite, $ONOO^-$, whose structure has recently been reported.[45] The structure of one conformation of $ONOO^-$ is shown in Figure 8-25; a twisted form with different bond angles and a different N—O distance is also found in the crystal. Peroxynitrite may play important roles in cellular defense against infection and in environmental water chemistry.[46]

Nitrogen has a rich redox chemistry in aqueous solution, as shown in the Latimer and Frost diagrams in the following example and in Figure 8-26. The Frost diagram in Figure 8-26 shows that the ammonium ion and elemental N_2 are the most stable nitrogen species in acidic solution, and hydroxylammonium ion, NH_3OH^+, and nitrate ion, NO_3^-, are the least stable.

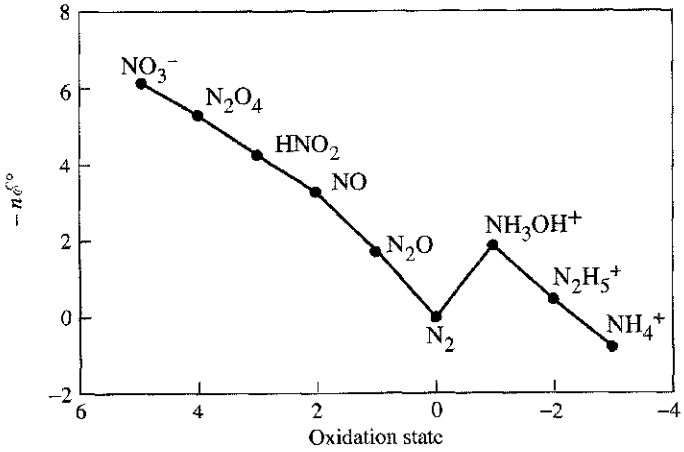


FIGURE 8-26 Frost Diagram for Nitrogen Compounds in Acid.

EXAMPLE

Combining half-reactions to find the potentials for other reactions depends on the fact that free energies are additive, but potentials may not be. If an oxidation reaction and a reduction reaction add to give a balanced reaction (no electrons in the final reaction), the potentials are additive. If the result is another half reaction, the potentials are not additive, and the $n\mathscr{E}°$ values (proportional to free energy, which is additive) must be used.

Part of the Latimer diagram for nitrogen in acidic solution is

$$\underbrace{\overset{+5}{NO_3^-}\ \overset{0.80}{\rule{2em}{0.4pt}}\ \overset{+4}{NO_2}\ \overset{1.07}{\rule{2em}{0.4pt}}\ \overset{+3}{HNO_2}}_{?}$$

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[45] M. Wörle, P. Latal, R. Kissner, R. Nesper, and W. H. Koppenol, *Chem. Res. Toxicol.*, **1999**, *12*, 305.

[46] O. V. Gerasimov and S. V. Lymar, *Inorg. Chem.*, **1999**, *38*, 4317; *Chem. Res. Toxicol.*, **1998**, *11*, 709.

To calculate $\mathscr{E}^\circ$ for the conversion of NO_3^- to HNO_2, it is necessary to find the change in free energy for each step:

$$\begin{array}{llll} & \mathscr{E}^\circ & \Delta G^\circ = -n\mathscr{F}\mathscr{E}^\circ & \\ NO_3^- + e^- \longrightarrow NO_2 & 0.80\text{ V} & -(1)(\mathscr{F})(0.80\text{ V}) & = -0.80\text{ V}\mathscr{F} \\ \underline{NO_2 + e^- \longrightarrow HNO_2} & 1.07\text{ V} & -(1)(\mathscr{F})(1.07\text{ V}) & = \underline{-1.07\text{ V}\mathscr{F}} \\ NO_3^- + 2\,e^- \longrightarrow HNO_2 & & -(2)\mathscr{F}\mathscr{E}^\circ & = -1.87\text{ V}\mathscr{F} \end{array}$$

$$\text{2 electrons transferred overall: } \mathscr{E}^\circ = \frac{-1.87\text{ V}\mathscr{F}}{-2\mathscr{F}} = 0.94\text{ V}$$

EXERCISE 8-2

Use the same approach to find the potential for the NO $\longrightarrow$ N_2O reaction, given the following:

$$NO \longrightarrow N_2 \quad \mathscr{E}^\circ = 1.68\text{ V}$$

$$N_2O \longrightarrow N_2 \quad \mathscr{E}^\circ = 1.77\text{ V}$$

EXERCISE 8-3

Show whether the decomposition of NH_4NO_3 can be a spontaneous reaction, based on the potentials given in Appendix B-7.

Among all the acids, phosphoric acid, H_3PO_4, is second only to sulfuric acid in industrial production. Two methods are commonly used. The first of these involves the combustion of molten phosphorus, sprayed into a mixture of air and steam in a stainless steel chamber. The P_4O_{10} formed initially is converted into H_3PO_4:

$$P_4 + 5\,O_2 \longrightarrow P_4O_{10}$$

$$P_4O_{10} + 6\,H_2O \longrightarrow 4\,H_3PO_4$$

Alternatively, phosphoric acid is made by treating phosphate minerals with sulfuric acid. For example,

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 \longrightarrow 2\,H_3PO_4 + 3\,CaSO_4$$

8-8
GROUP 16 (VIA)

8-8-1 THE ELEMENTS

The first two elements of this group, occasionally designated the "chalcogen" group, are familiar as O_2, the colorless gas that comprises about 21% of the earth's atmosphere, and sulfur, a yellow solid of typical nonmetallic properties. The third element in this group, selenium, is perhaps not as well known, but is important in the xerography process. A brilliant red formed by a combination of CdS and CdSe is used in colored glasses. Although elemental selenium is highly poisonous, trace amounts of the element are essential for life. Tellurium is of less commercial interest but is used in small amounts in metal alloys, tinting of glass, and catalysts in the rubber industry. All isotopes of polonium, a metal, are radioactive. The highly exothermic radioactive decay of this element has made it a useful power source for satellites.

Sulfur, which occurs as the free element in numerous natural deposits, has been known since prehistoric times; it is the "brimstone" of the Bible. It was of considerable interest to the alchemists and, following the development of gunpowder (a mixture of sulfur, KNO_3, and powdered charcoal) in the 13th century, to military leaders as well.

Although oxygen is widespread in the Earth's atmosphere and, combined with other elements, in the Earth's crust (which contains 46% oxygen by mass) and in bodies of water, the pure element was not isolated and characterized until the 1770s by C.W. Scheele and J. Priestley. Priestley's classic synthesis of oxygen by heating HgO with sunlight focused by a magnifying glass was a landmark in the history of experimental chemistry. Selenium (1817) and tellurium (1782) were soon discovered and, because of their chemical similarities, were named after the moon (Greek, *selene*) and earth (Latin, *tellus*). Polonium was discovered by Marie Curie in 1898; like radium, it was isolated in trace amounts from tons of uranium ore. Some important physical properties of these elements are summarized in Table 8-11.

TABLE 8-11
Properties of the Group 16 (VIA) Elements

Element	*Ionization Energy ($kJ\ mol^{-1}$)*	*Electron Affinity ($kJ\ mol^{-1}$)*	*Melting Point (°C)*	*Boiling Point (°C)*	*Electronegativity*
O	1314	141	−218.8	−183.0	3.610
S	1000	200	112.8	444.7	2.589
Se	941	195	217	685	2.424
Te	869	190	452	990	2.158
Po	812	180^a	250^a	962	2.19^a

SOURCE: See Table 8-3.
NOTE: ^{a}Approximate value.

Oxygen

Oxygen exists primarily in the diatomic form, O_2, but traces of ozone, O_3, are found in the upper atmosphere and in the vicinity of electrical discharges. O_2 is paramagnetic and O_3 is diamagnetic. As discussed in Chapter 5, the paramagnetism of O_2 is the consequence of two electrons with parallel spin occupying $\pi^*(2p)$ orbitals. In addition, the two known excited states of O_2 have π^* electrons of opposite spin and are higher in energy as a consequence of the effects of pairing energy and exchange energy (see Section 2-2-3):

	Relative Energy ($kJ\ mol^{-1}$)	
Excited states:	↑↓ ___	157.85
	↑ ___ ↓	94.72
Ground state:	↑ ___ ↑	0

The excited states of O_2 can be achieved when photons are absorbed in the liquid phase during molecular collisions; under these conditions, a single photon can simulteneously excite two colliding molecules. This absorption occurs in the visible region of the spectrum, at 631 and 474 nm, and gives rise to the blue color of the liquid.[47] The excited states are also important in many oxidation processes. Of course, O_2 is essential for respiration. The mechanism for oxygen transport to the cells via hemoglobin has received much attention and will be discussed briefly in Chapter 16.

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[47] E. A. Ogryzlo, *J. Chem. Educ.*, **1965**, *42*, 647.

Ozone absorbs ultraviolet radiation below 320 nm. It thus forms an indispensable shield in the upper atmosphere, protecting the Earth's surface from most of the potentially hazardous effects of such high-energy electromagnetic radiation. There is now increasing concern because atmospheric pollutants are depleting the ozone layer worldwide, with the most serious depletion over Antarctica as a result of seasonal variations in high-altitude air circulation. In the upper atmosphere, ozone is formed from O_2:

$$O_2 \xrightarrow{h\nu} 2\,O \qquad \lambda \leq 242 \text{ nm}$$
$$O + O_2 \longrightarrow O_3$$

Absorption of ultraviolet radiation by O_3 causes it to decompose to O_2. In the upper atmosphere, therefore, a steady-state concentration of ozone is achieved, a concentration ordinarily sufficient to provide significant ultraviolet protection of the Earth's surface. However, pollutants in the upper atmosphere such as nitrogen oxides (some of which occur in trace amounts naturally) from high-flying aircraft and chlorine atoms from photolytic decomposition of chlorofluorocarbons (from aerosols, refrigerants, and other sources) catalyze the decomposition of ozone. The overall processes governing the concentration of ozone in the atmosphere are extremely complex. The following reactions can be studied in the laboratory and are examples of the processes believed to be involved in the atmosphere:

$$\begin{array}{lrcl}
 & NO_2 + O_3 & \longrightarrow & NO_3 + O_2 \\
 & NO_3 & \longrightarrow & NO + O_2 \\
 & \underline{NO + O_3} & \underline{\longrightarrow} & \underline{NO_2 + O_2} \\
\text{Net:} & 2\,O_3 & \longrightarrow & 3\,O_2
\end{array}$$

$$\begin{array}{lrcll}
 & Cl + O_3 & \longrightarrow & ClO + O_2 & \text{Cl formed from photodecomposition} \\
 & \underline{ClO + O} & \underline{\longrightarrow} & \underline{Cl + O_2} & \text{of chlorofluorocarbons} \\
\text{Net:} & O_3 + O & \longrightarrow & 2\,O_2 &
\end{array}$$

Ozone is a more potent oxidizing agent than O_2; in acidic solution, it is exceeded only by fluorine among the elements as an oxidizing agent.

Several diatomic and triatomic oxygen ions are known and are summarized in Table 8-12.

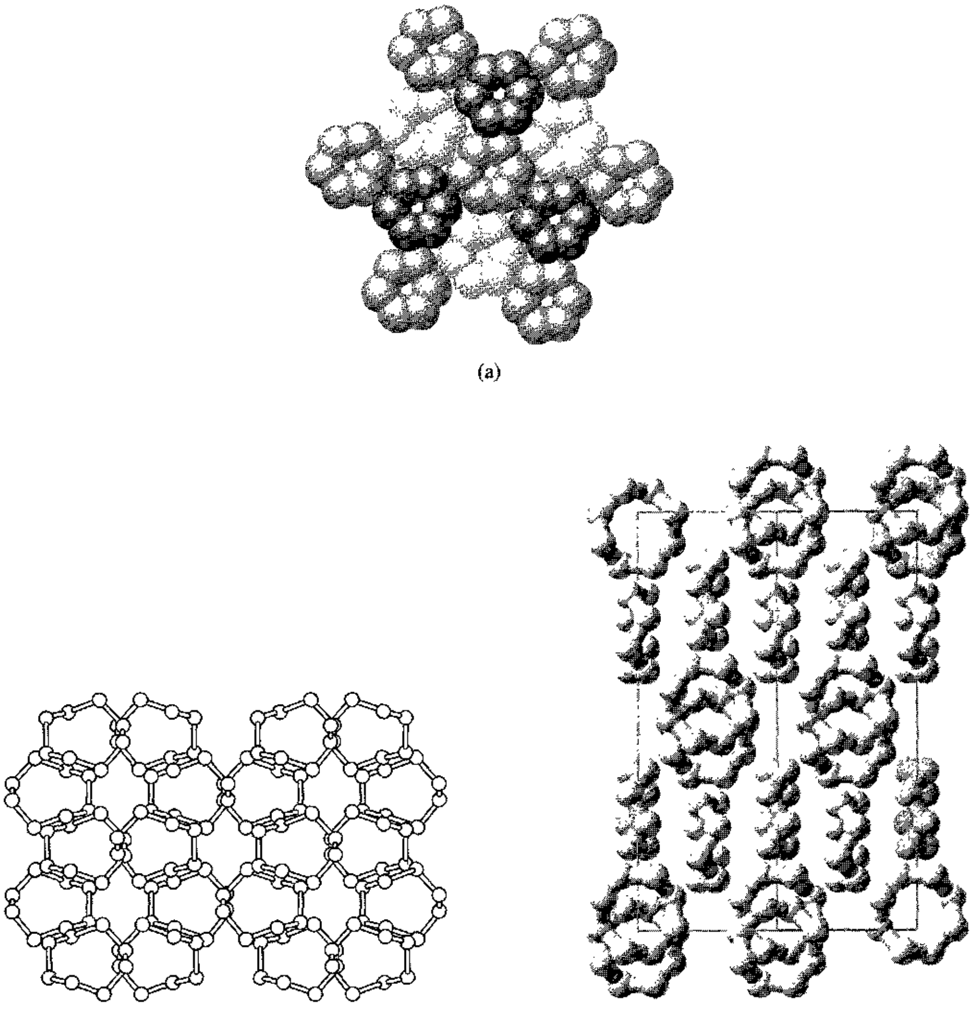
TABLE 8-12
Neutral and Ionic O_2 and O_3 Species

Formula	*Name*	*O—O Distance (pm)*	*Notes*
O_2^+	Dioxygenyl	112.3	Bond order 2.5
O_2	Dioxygen	120.7	Coordinates to transition metals; singlet O_2 (excited state) important in photochemical reactions; oxidizing agent
O_2^-	Superoxide	128	Moderate oxidizing agent; most stable compounds are KO_2, RbO_2, CsO_2
O_2^{2-}	Peroxide	149	Forms ionic compounds with alkali metals, Ca, Sr, Ba; strong oxidizing agent
O_3	Ozone	127.8	Bond angle 116.8°; strong oxidizing agent; absorbs in UV (below 320 nm)
O_3^-	Ozonide	134	Formed from reaction of O_3 with dry alkali metal hydroxides, decomposes to O_2^-

SOURCE: N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984.

Sulfur

More allotropes are known for sulfur than for any other element, with the most stable form at room temperature (orthorhombic, α-S_8) having eight sulfur atoms arranged in a puckered ring. Two of the most common sulfur allotropes are shown in Figure 8-27.[48]



(a)

(b) (c)

FIGURE 8-27 Allotropes of Sulfur. (a) S_6. (b) and (c) α-S_8, two different views. (a) and (b) reproduced with permission from M. Schmidt and W. Siebert, "Sulphur," in J. C. Bailar, Jr., H. C. Emeléus, R. Nyholm, and A. F. Trotman-Dickinson, eds., *Comprehensive Inorganic Chemistry*, vol. 2, Pergamon Press, Elmsford, NY, 1973, pp. 804, 806. © 1973, Pergamon Press PLC.)

Heating sulfur results in interesting changes in viscosity. At approximately 119° C, sulfur melts to give a yellow liquid, whose viscosity gradually decreases because of greater thermal motion until approximately 155° C (Figure 8-28). Further heating causes the viscosity to increase, dramatically so above 159° C, until the liquid pours very sluggishly. Above about 200° C, the viscosity again decreases, with the liquid eventually acquiring a reddish hue at higher temperatures.[49]

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[48] B. Meyer, *Chem. Rev.*, **1976**, *76*, 367.

[49] W. N. Tuller, ed., *The Sulphur Data Book*, McGraw-Hill, New York, 1954.

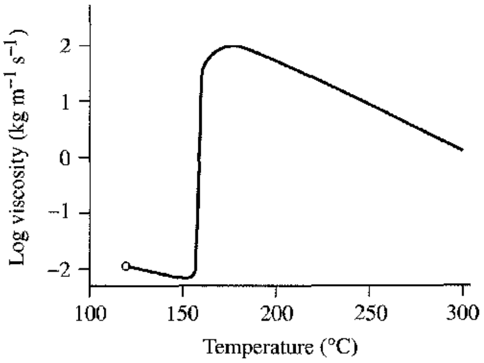
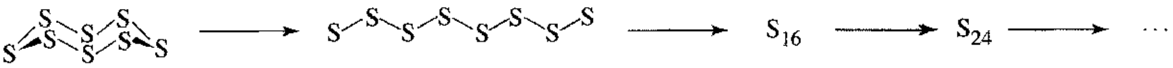


FIGURE 8-28 The Viscosity of Sulfur.

The explanation of these changes in viscosity involves the tendency of S—S bonds to break and to reform at high temperatures. Above 159° C, the S_8 rings begin to open; the resulting S_8 chains can react with other S_8 rings to open them and form S_{16} chains, S_{24} chains, and so on:



The longer the chains, the greater the viscosity (the more the chains can intertwine with each other). Large rings can also form, by the linking of ends of chains. Chains exceeding 200,000 sulfur atoms are formed at the temperature of maximum viscosity, near 180° C. At higher temperatures, thermal breaking of sulfur chains occurs more rapidly than propagation of chains, and the average chain length decreases, accompanied by a decrease in viscosity. At very high temperatures, brightly colored species such as S_3 increase in abundance and the liquid has a reddish coloration. When molten sulfur is poured into cold water, it forms a rubbery solid that can be molded readily. However, this form eventually converts to the yellow crystalline α form, the most thermodynamically stable allotrope, which consists again of the S_8 rings.

Sulfuric acid, produced in greater amounts than any other chemical, has been manufactured commercially for approximately 400 years. The modern process for producing H_2SO_4 begins with the synthesis of SO_2, either by combustion of sulfur or by roasting (heating in the presence of oxygen) of sulfide minerals:

$S + O_2 \longrightarrow SO_2$	Combustion of sulfur
$M_xS_y + O_2 \longrightarrow y\,SO_2 + M_xO_y$	Roasting of sulfide ore

SO_2 is then converted to SO_3 by the exothermic reaction

$$SO_2 + O_2 \longrightarrow SO_3$$

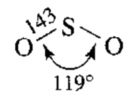
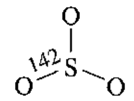
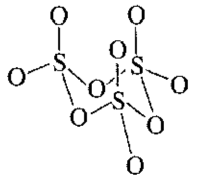
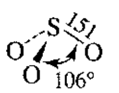
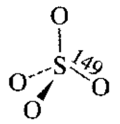
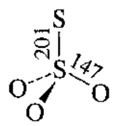
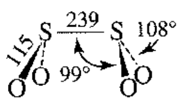
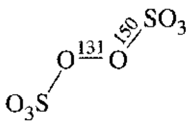
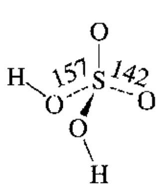
using V_2O_5 or another suitable catalyst in a multiple-stage catalytic converter (multiple stages are necessary to achieve high yields of SO_3). The SO_3 then reacts with water to form sulfuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

If SO_3 is passed directly into water, a fine aerosol of H_2SO_4 droplets is formed. To avoid this, the SO_3 is absorbed into 98% H_2SO_4 solution to form disulfuric acid, $H_2S_2O_7$ (oleum):

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

TABLE 8-13
Molecules and Ions Containing Sulfur and Oxygen

Formula	*Name*	*Structure*[a]	*Notes*
SO_2	Sulfur dioxide		mp = −75.5°C; bp = −10.0°C; colorless, choking gas; product of combustion of elemental sulfur
SO_3	Sulfur trioxide		mp = 16.9°C; bp = 44.6°C; formed from oxidation of SO_2: $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$; in equilibrium with trimer S_3O_9 in liquid and gas phases; reacts with water to form sulfuric acid
	Trimer		
SO_3^{2-}	Sulfite		Conjugate base of HSO_3^-, formed when SO_2 dissolves in water
SO_4^{2-}	Sulfate		T_d symmetry, extremely common ion, used in gravimetric analysis
$S_2O_3^{2-}$	Thiosulfate		Moderate reducing agent, used in analytical determination of I_2: $I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_4O_6^{2-}$
$S_2O_4^{2-}$	Dithionite		Very long S—S bond; dissociates into SO_2^-: $S_2O_4^{2-} \rightleftharpoons 2\,SO_2^-$; Zn and Na salts used as reducing agents
$S_2O_8^{2-}$	Peroxodisulfate		Useful oxidizing agent, readily reduced to sulfate: $S_2O_8^{2-} + 2\,e^- \rightleftharpoons 2\,SO_4^{2-}$, $\mathscr{E}° = 2.01$ V
H_2SO_4	Sulfuric acid		C_2 symmetry; mp = 10.4°C; bp = ~300°C (dec); strong acid in aqueous solution; undergoes autoionization: $2\,H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$, $pK = 3.57$ at 25° C

SOURCE: N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, pp. 821–854.

NOTE: [a]Distances in pm.

The $H_2S_2O_7$ is then mixed with water to form sulfuric acid:

$$H_2S_2O_7 + H_2O \longrightarrow 2\,H_2SO_4$$

Sulfuric acid is a dense ($1.83\ \text{g cm}^{-3}$) viscous liquid that reacts very exothermically with water. When concentrated sulfuric acid is diluted with water, it is therefore essential to add the acid carefully to water; adding water to the acid is likely to lead to spattering (the solution at the top may boil). Sulfuric acid also has a high affinity for water. For example, it causes sugar to char (by removing water, leaving carbon behind) and can cause rapid and serious burns to human tissue.

Anhydrous H_2SO_4 undergoes significant autoionization:

$$2\,H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad K = 2.7 \times 10^{-4} \text{ at } 25^\circ\text{ C}$$

Many compounds and ions containing sulfur and oxygen are known; many of these are important acids or conjugate bases. Some useful information about these compounds and ions is summarized in Table 8-13.

Other elements

Selenium, a highly poisonous element, and tellurium also exist in a variety of allotropic forms, whereas polonium, a radioactive element, exists in two metallic allotropes. Selenium is a photoconductor, a poor conductor ordinarily, but a good conductor in the presence of light. It is used extensively in xerography, photoelectric cells, and semiconductor devices.

8-9 GROUP 17 (VIIA): THE HALOGENS

8-9-1 THE ELEMENTS

Compounds containing the halogens (Greek, *halos* + *gen*, salt former) have been used since antiquity, with the first use probably that of rock or sea salt (primarily NaCl) as a food preservative. Isolation and characterization of the neutral elements, however, has occurred comparatively recently.[50] Chlorine was first recognized as a gas by J. B. van Helmont in approximately 1630, first studied carefully by C. W. Scheele in the 1770s (hydrochloric acid, which was used in these early syntheses, had been prepared by the alchemists around the year 900 A.D.). Iodine was next, obtained by Courtois in 1811 by subliming the product of the reaction of sulfuric acid with seaweed ash. A. J. Balard obtained bromine in 1826 by reacting chlorine with $MgBr_2$, which was present in saltwater marshes. Although hydrofluoric acid had been used to etch glass since the latter part of the 17th century, elemental fluorine was not isolated until 1886, when H. Moissan obtained a small amount of the very reactive gas by the electrolysis of KHF_2 in anhydrous HF. Astatine, one of the last of the nontransuranium elements to be produced, was first synthesized in 1940 by D. R. Corson, K. R. Mackenzie, and E. Segre by bombardment of ^{209}Bi with alpha particles. All isotopes of astatine are radioactive (the longest lived isotope has a half-life of 8.1 hours) and, consequently, the chemistry of this element has been studied only with the greatest difficulty.

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[50] M. E. Weeks, "The Halogen Family," in *Discovery of the Elements*, 7th ed, revised by H. M. Leicester, Journal of Chemical Education, Easton, PA, 1968, pp. 701–749.

All neutral halogens are diatomic and readily reduced to halide ions. All combine with hydrogen to form gases which, except for HF, are strong acids in aqueous solution. Some physical properties of the halogens are summarized in Table 8-14.

TABLE 8-14
Properties of the Group 17 (VIIA) Elements: The Halogens[a]

				Halogen Molecules, X_2			
Element	*Ionization Energy ($kJ\ mol^{-1}$)*	*Electron Affinity ($kJ\ mol^{-1}$)*	*Electro-negativity*	*Melting Point (°C)*	*Boiling Point (°C)*	*X—X Distance (pm)*	*ΔH of Dissociation ($kJ\ mol^{-1}$)*
F	1681	328	4.193	−218.6	−188.1	143	158.8
Cl	1251	349	2.869	−101.0	−34.0	199	242.6
Br	1140	325	2.685	−7.25	59.5	228	192.8
I	1008	295	2.359	113.6[a]	185.2	266	151.1
At	930[b]	270[b]	2.39[b]	302[b]			

Source: See Table 8-3. Ionization energy for At is from J. Emsley, *The Elements*, Oxford University Press, New York, 1989, p. 23.

Notes: [a]Sublimes readily.

[b]Approximate value.

The chemistry of the halogens is governed in large part by their tendency to acquire an electron to attain a noble gas electron configuration. Consequently, the halogens are excellent oxidizing agents, with F_2 being the strongest oxidizing agent of all the elements. The tendency of the halogen atoms to attract electrons is also shown in their high electron affinities and electronegativities.

F_2 is extremely reactive and cannot be handled except by special techniques; it is ordinarily prepared by electrolysis of molten fluorides such as KF. Cl_2 is a yellow gas and has an odor that is recognizable as the characteristic scent of "chlorine" bleach (an alkaline solution of the hypochlorite ion, ClO^-, which exists in equilibrium with small amounts of Cl_2). Br_2 is a dark-red liquid that evaporates easily and is also a strong oxidizing agent. I_2 is a black lustrous solid, readily sublimable at room temperature to produce a purple vapor, and, like the other halogens, highly soluble in nonpolar solvents. The color of iodine solutions varies significantly with the donor ability of the solvent as a consequence of charge transfer interactions, as described in Chapter 6. Iodine is also a moderately good oxidizing agent, but the weakest of the halogens. Because of its radioactivity, astatine has not been studied extensively; it would be interesting to be able to compare its properties and reactions with those of the other halogens.

Several trends in physical properties of the halogens are immediately apparent, as can be seen in Table 8-14. As the atomic number increases, the ability of the nucleus to attract outermost electrons decreases; consequently, fluorine is the most electronegative and has the highest ionization energy, and astatine is lowest in both properties. With increasing size and number of electrons of the diatomic molecules in going down the periodic table, the London interactions between the molecules increase: F_2 and Cl_2 are gases, Br_2 is a liquid, and I_2 is a solid as a consequence of these interactions. The trends are not entirely predictable because fluorine and its compounds exhibit some behavior that is substantially different than would be predicted by extrapolation of the characteristics of the other members of the group.

One of the most striking properties of F_2 is its remarkably low bond dissociation enthalpy, an extremely important factor in the high reactivity of this molecule. Extrapolation from the bond dissociation enthalpies of the other halogens would yield a value of approximately 290 $kJ\ mol^{-1}$, nearly double the actual value. Several suggestions have been made to account for this low value. It is likely that the weakness of the F—F bond is largely a consequence of repulsions between the nonbonding electron pairs.[51] The small size of the fluorine atom brings these pairs into close proximity when F—F bonds are formed. Electrostatic repulsions between these pairs on neighboring atoms result in weaker bonding and an equilibrium bond distance significantly greater than would be expected in the absence of such repulsions. In orbital terms, the small size of the fluorine atoms leads to poorer overlap in the formation of bonding molecular orbitals and to improved overlap of antibonding π^* orbitals than would be expected by extrapolation from the other halogens.

For example, the covalent radius obtained for other compounds of fluorine is 64 pm; an F—F distance of 128 pm would therefore be expected in F_2. However, the actual distance is 143 pm. In this connection, it is significant that oxygen and nitrogen share similar anomalies with fluorine; the O—O bonds in peroxides and the N—N bonds in hydrazines are longer than the sums of their covalent radii, and these bonds are weaker than the corresponding S—S and P—P bonds in the respective groups of these elements. In the case of oxygen and nitrogen, it is likely that the repulsion of electron pairs on neighboring atoms also plays a major role in the weakness of these bonds.[52] The weakness of the fluorine-fluorine bond, in combination with the small size and high electronegativity of fluorine, account in large part for the very high reactivity of F_2.

Of the hydrohalic acids, HF is by far the weakest in aqueous solution ($pK_a = 3.2$ at 25° C); HCl, HBr, and HI are all strong acids. Although HF reacts with water, strong hydrogen bonding occurs between F^- and the hydronium ion (F^-—H^+—OH_2) to form the ion pair $H_3O^+F^-$, reducing the activity coefficient of H_3O^+. As the concentration of HF increases, however, its tendency to form H_3O^+ increases as a result of further reaction of this ion pair with HF:

$$H_3O^+F^- + HF \rightleftharpoons H_3O^+ + HF_2^-$$

This view is supported by X-ray crystallographic studies of the ion pairs $H_3O^+F^-$ and $H_3O^+F_2^-$.[53]

Chlorine and chlorine compounds are used as bleaching and disinfecting agents in many industries. Perhaps the most commonly known of these compounds is hypochlorite, OCl^-, a common household bleach prepared by dissolving chlorine gas in sodium or calcium hydroxide:

$$Cl_2 + 2\,OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

The redox potentials supporting this reaction and others are shown in the Frost diagram in Figure 8-29. The disproportionation of Cl_2 to Cl^- and OCl^- in basic solution can be seen in Figure 8-29 because Cl_2 is above the line between Cl^- and OCl^-. The free energy change from Cl_2 to OCl^- is positive (higher on the $-n\mathscr{E}^\circ$ scale), but the free energy change from Cl_2 to Cl^- is negative and larger in magnitude, resulting in a net negative free energy change and a spontaneous reaction. The oxidizing power of the higher oxidation number species in acid is also evident. Perchlorate is an extremely strong oxidizing agent, and ammonium perchlorate is used as a rocket fuel. In the fall of 2001, chlorine dioxide, ClO_2, was used to disinfect U.S. mail and at least one congressional office that may have been infected with anthrax. This gas is also used as an alternative to Cl_2 for purifying drinking water and as a bleaching agent in the paper industry.

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[51] J. Berkowitz and A. C. Wahl, *Adv. Fluorine Chem.*, **1973**, *7*, 147.

[52] Anomalous properties of fluorine, oxygen, and nitrogen have been discussed by P. Politzer in *J. Am. Chem. Soc.*, **1969**, *91*, 6235, and *Inorg. Chem.*, **1977**, *16*, 3350.

[53] D. Mootz, *Angew. Chem., Int. Ed.*, **1981**, *20*, 791.

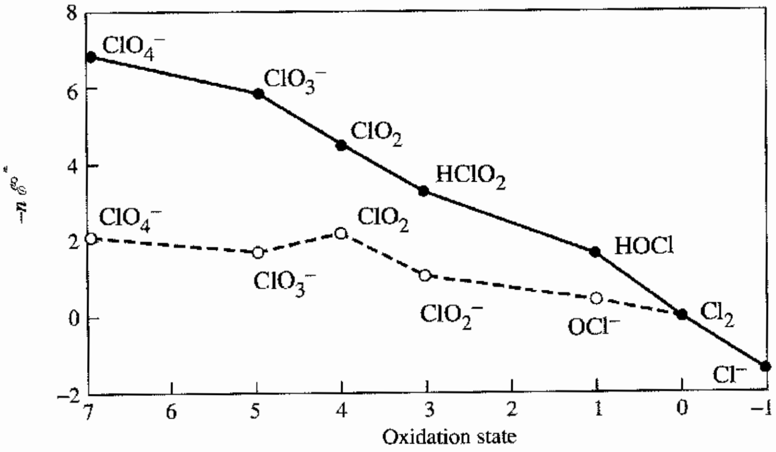


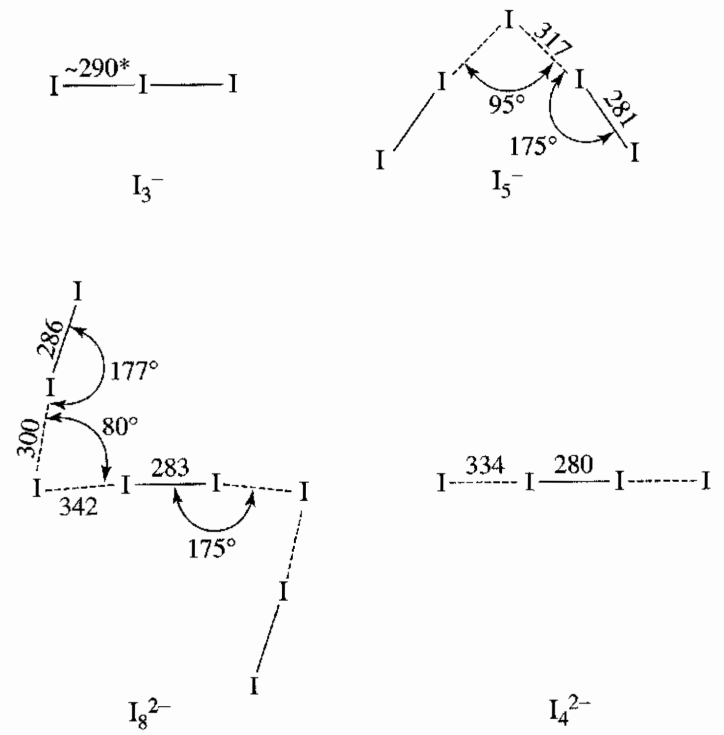
FIGURE 8-29 Frost Diagram for Chlorine Species. The solid line is for acidic solutions and the dashed line is for basic solutions.

Polyatomic ions

In addition to the common monatomic halide ions, numerous polyatomic species, both cationic and anionic, have been prepared. Many readers will be familiar with the brown triiodide ion, I_3^-, formed from I_2 and I^-:

$$I_2 + I^- \rightleftharpoons I_3^- \qquad K \approx 698 \text{ at } 25^\circ \text{ C in aqueous solution}$$

Many other polyiodide ions have been characterized; in general, these may be viewed as aggregates of I_2 and I^- (sometimes I_3^-). Examples are shown in Figure 8-30.



*Distances in triiodide vary depending on the cation. In some cases both I—I distances are identical, but in the majority of cases they are different. Differences in I—I distances as great as 33 pm have been reported.

FIGURE 8-30 Polyiodide Ions. (Bond angles and distances, in pm, are from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984, pp. 396–399.)

The halogens Cl_2, Br_2, and I_2 can also be oxidized to cationic species. Examples include the diatomic ions Br_2^+ and I_2^+ (Cl_2^+ has been characterized in low-pressure discharge tubes but is much less stable), I_3^+, and I_5^+. I_2^+ dimerizes into I_4^{2+}:

$$2\,I_2^+ \rightleftharpoons I_4^{2+}$$

Interhalogens

Halogens form many compounds containing two or more different halogens. Like the halogens themselves, these may be diatomic (such as ClF) or polyatomic (such as ClF_3, BrF_5, or IF_7). In addition, polyatomic ions containing two or more halogens have been synthesized for many of the possible combinations. Selected neutral boxed and ionic interhalogen species are listed in Table 8-15. The effect of the size of the central atom can readily be seen, with iodine the only element able to have up to seven fluorine atoms in a neutral molecule, whereas chlorine and bromine have a maximum of five fluorines. The effect of size is also evident in the ions, with iodine being the only halogen large enough to exhibit ions of formula XF_6^+ and XF_8^-.

TABLE 8-15
Interhalogen Species

Formation Oxidation State of Central Atom	*Number of Lone Pairs on Central Atom*	*Compounds and Ions*						
+7	0			$\boxed{IF_7}$				
				IF_6^+				
				IF_8^-				
+5	1	$\boxed{ClF_5}$	$\boxed{BrF_5}$	$\boxed{IF_5}$				
		ClF_4^+	BrF_4^+	IF_4^+				
			BrF_6^-	IF_6^-				
+3	2	$\boxed{ClF_3}$	$\boxed{BrF_3}$	$\boxed{IF_3}$		$\boxed{I_2Cl_6}$		
		ClF_2^+	BrF_2^+	IF_2^+		ICl_2^+	IBr_2^+	$IBrCl^+$
		ClF_4^-	BrF_4^-	IF_4^-		ICl_4^-		
+1	3	$\boxed{ClF}$	$\boxed{BrF}$	$\boxed{IF}$	$\boxed{BrCl}$	$\boxed{ICl}$	$\boxed{IBr}$	
		ClF_2^-	BrF_2^-	IF_2^-	$BrCl_2^-$	ICl_2^-	IBr_2^-	
					Br_2Cl^-	I_2Cl^-	I_2Br^-	$IBrCl^-$

Neutral interhalogens can be prepared in a variety of ways, including direct reaction of the elements (the favored product often depending on the ratio of halogens used) and reaction of halogens with metal halides or other halogenating agents. Examples include

$$Cl_2 + F_2 \longrightarrow 2\,ClF \qquad T = 225°C$$

$$I_2 + 5\,F_2 \longrightarrow 2IF_5 \qquad \text{Room temperature}$$

$$I_2 + 3\,XeF_2 \longrightarrow 2\,IF_3 + 3\,Xe \qquad T < -30°C$$

$$I_2 + AgF \longrightarrow IF + AgI \qquad 0°C$$

Interhalogens can also serve as intermediates in the synthesis of other interhalogens:

$$ClF + F_2 \longrightarrow ClF_3 \qquad T = 200°C \text{ to } 300°C$$

$$ClF_3 + F_2 \longrightarrow ClF_5 \qquad h\nu, \text{ room temperature}$$

Several interhalogens undergo autoionization in the liquid phase and have been studied as nonaqueous solvents. Examples of these are

$$3\,IX \rightleftharpoons I_2X^+ + IX_2^- \quad (X = Cl, Br)$$

$$2\,BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$I_2Cl_6 \rightleftharpoons ICl_2^+ + ICl_4^-$$

$$IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

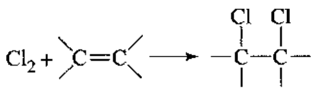
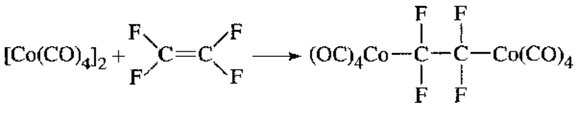
Examples of acid-base reactions in the autoionizing solvents BrF_3 and IF_5 have been discussed in Chapter 6.

Pseudohalogens

Parallels have been observed between the chemistry of the halogens and a number of other dimeric species. Dimeric molecules showing considerable similarity to the halogens are often called **pseudohalogens**. Some of the most important parallels in chemistry between the halogens and pseudohalogens include those illustrated for chlorine in Table 8-16.

For example, there are many similarities between the halogens and cyanogen, NCCN. The monoanion, CN^-, is, of course, well known; it combines with hydrogen to form the weak acid HCN and, with Ag^+ and Pb^{2+}, to form precipitates of low solubility in water. Interhalogen compounds such as FCN, ClCN, BrCN, and ICN are all known. Cyanogen, like the halogens, can add across double or triple carbon-carbon bonds. The pseudohalogen idea is a useful classification tool, although not many cases are known in which all six characteristics are satisfied. Some examples of pseudohalogens are given in Table 8-16.[54]

TABLE 8-16
Pseudohalogens

Characteristics	*Examples*[a]		
Neutral diatomic species	Cl_2	$(CN)_2$	$[Co(CO)_4]_2$
Ion of 1− charge	Cl^-	CN^-	$[Co(CO)_4]^-$
Formation of hydrohalic acids	HCl	HCN	$HCo(CO)_4$ (strong)[b]
Formation of interhalogen compounds	ICl, BrCl, ClF	$Cl_2 + (CN)_2 \longrightarrow 2\,ClCN$	$[Co(CO)_4]_2 + I_2 \longrightarrow 2\,ICo(CO)_4$
Formation of heavy metal salts of low solubility	AgCl, $PbCl_2$	AgCN	$AgCo(CO)_4$
Addition to unsaturated species			

NOTES: [a]Metal carbonyl (CO) compounds will be discussed in Chapters 13 to 15.

[b]However, $HCo(CO)_4$ is only slightly soluble in water.

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[54] For additional examples of pseudohalogens, see J. Ellis, *J. Chem. Educ.*, 1976, *53*, 2.

8-10 GROUP 18 (VIIIA): THE NOBLE GASES

The elements in Group 18 (VIIIA), long designated the "inert" or "rare" gases, no longer satisfy these early labels. They are now known to have an interesting, although somewhat limited, chemistry, and they are rather abundant. Helium, for example, is the second most abundant element in the universe, and argon is the third most abundant component of dry air, approximately 30 times as abundant by volume as carbon dioxide.

8-10-1 THE ELEMENTS

The first experimental evidence for the noble gases was obtained by Henry Cavendish in 1766. In a series of experiments on air, he was able to sequentially remove nitrogen (then known as "phlogisticated air"), oxygen ("dephlogisticated air"), and carbon dioxide ("fixed air") from air by chemical means, but a small residue, no more than one part in 120, resisted all attempts at reaction.[55] The nature of Cavendish's unreactive fraction of air remained a mystery for more than a century. This fraction was, of course, eventually shown to be a mixture of argon and other noble gases.[56]

During a solar eclipse in 1868, a new emission line, matching no known element, was found in the spectrum of the solar corona. J. N. Locklear and E. Frankland proposed the existence of a new element named, appropriately, helium (Greek, *helios*, sun). The same spectral line was subsequently observed in the gases of Mount Vesuvius.

In the early 1890s, Lord Rayleigh and William Ramsay observed a discrepancy in the apparent density of nitrogen isolated from air and from ammonia. The two researchers independently performed painstaking experiments to isolate and characterize what seemed to be either a new form of nitrogen (the formula N_3 was one suggestion) or a new element. Eventually the two worked cooperatively, with Ramsay apparently the first to suggest that the unknown gas might fit into the periodic table after the element chlorine. In 1895, they reported the details of their experiments and evidence for the element they had isolated, argon (Greek, *argos*, no work, lazy).[57]

Within 3 years, Ramsay and M. W. Travers had isolated three additional elements by low-temperature distillation of liquid air, neon (Greek, *neos*, new), krypton (Greek, *kryptos*, concealed), and xenon (Greek, *xenos*, strange). The last of the noble gases, radon, was isolated as a nuclear decay product in 1902.

Helium is fairly rare on Earth, but it is the second most abundant element in the universe (76% H, 23% He) and is a major component of stars. Commercially, helium is obtained from natural gas. The other noble gases, with the exception of radon, are present in small amounts in air (see Table 8-16) and are commonly obtained by fractional distillation of liquid air. Helium is used as an inert atmosphere for arc welding, in weather and other balloons, and in gas mixtures used in deep-sea diving, where it gives voices a higher pitch, but is less soluble in blood than nitrogen. Recently, liquid helium (with a boiling point of 4.2 K) has increasingly been used as a coolant for superconducting magnets in NMR instruments. Argon, the least expensive noble gas, is commonly used as an inert atmosphere for studying chemical reactions, for high-temperature metallurgical processes, and for filling incandescent bulbs. One useful property of the noble gases is that they emit light of vivid colors when an electrical discharge is passed through them; neon's emission spectrum, for example, is responsible for the bright orange-red of neon signs. Other noble gases are also used in discharge tubes, in which the color depends on

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[55] H. Cavendish, *Philos. Trans.*, **1785**, *75*, 372.

[56] Cavendish's experiments and other early developments in noble gas chemistry have been described in E. N. Hiebert, "Historical Remarks on the Discovery of Argon: The First Noble Gas", in H. H. Hyman, ed., *Noble Gas Compounds*, University of Chicago Press, Chicago, 1963, pp. 3–20.

[57] Lord Rayleigh and W. Ramsay, *Philos. Trans. A*, **1895**, *186*, 187.

the gases used. All isotopes of radon are radioactive; the longest lived isotope, ^{222}Rn, has a half-life of only 3.825 days. There has been concern regarding the level of radon in many homes. A potential cause of lung cancer, radon is formed from the decay of trace amounts of uranium in certain rock formations and itself undergoes α decay, leaving radioactive daughter isotopes in the lungs. Radon commonly enters homes through basement walls and floors.

Important properties of the noble gases are summarized in Table 8-17.

TABLE 8-17
Properties of the Group 18 (VIIIA) Elements: The Noble Gases

Element	*Ionization Energy (kJ mol^{-1})*	*Melting Point (°C)*	*Boiling Point (°C)*	*Enthalpy of Vaporization (kJ mol^{-1})*	*Electronegativity*	*Abundance in Dry Air (% by Volume)*
He[a]	2372	—	−268.93	0.08	4.160	0.000524
Ne	2081	−248.61	−246.06	1.74	4.787	0.001818
Ar	1521	−189.37	−185.86	6.52	3.242	0.934
Kr	1351	−157.20	−153.35	9.05	2.966	0.000114
Xe	1170	−111.80	−108.13	12.65	2.582	0.0000087
Rn	1037	−71	−62	18.1	2.60[b]	Trace

SOURCE: See Table 8-3.

NOTES: [a] Helium cannot be frozen at 1 atm pressure.

[b] Approximate value.

8-10-2 CHEMISTRY

For many years, these elements were known as the "inert" gases because they were believed to be totally unreactive as a consequence of the very stable "octet" valence electron configurations of their atoms. Their chemistry was simple: they had none!

The first chemical compounds containing noble gases were known as **clathrates**, "cage" compounds in which noble gas atoms could be trapped. Experiments begun in the late 1940s showed that when water or solutions containing quinone (*p*-dihydroxybenzene, $HO—C_6H_4—OH$) were crystallized under high pressures of certain gases, hydrogen-bonded lattices having rather large cavities could be formed, with gas molecules of suitable size trapped in the cavities. Clathrates containing the noble gases argon, krypton, and xenon, as well as those containing small molecules such as SO_2, CH_4, and O_2, have been prepared. No clathrates have been found for helium and neon; these atoms are simply too small to be trapped.

Even though clathrates of three of the noble gases had been prepared by the beginning of the 1960s, no compounds containing covalently bonded noble gas atoms had been synthesized. Attempts had been made to react xenon with elemental fluorine, the most reactive of the elements, but without apparent success. However, in 1962, this situation changed dramatically. Neil Bartlett had observed that the compound PtF_6 changed color on exposure to air. With D. H. Lohmann, he demonstrated that PtF_6 was serving as a very strong oxidizing agent in this reaction and that the color change was due to the formation of $O_2^+[PtF_6]^-$.[58] Bartlett noted the similarity of the ionization energies of xenon (1169 kJ mol^{-1}) and O_2 (1175 kJ mol^{-1}) and repeated the experiment, reacting Xe with PtF_6. He observed a color change from the deep red of PtF_6 to orange-yellow and reported the product as $Xe^+[PtF_6]^-$.[59] Although the product of this reaction later proved to be a complex mixture of several xenon compounds, these were the first covalently bonded

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[58] N. Bartlett and D. H. Lohmann, *Proc. Chem. Soc.*, **1962**, 115.

[59] N. Bartlett, *Proc. Chem. Soc.*, **1962**, 218.

noble gas compounds to be synthesized, and their discovery stimulated study of the chemistry of the noble gases in earnest. In a matter of months, the compounds XeF_2 and XeF_4 had been characterized, and other noble gas compounds soon followed.[60]

Scores of compounds of noble gas elements are now known, although the number remains modest in comparison with the other groups. The known noble gas compounds of xenon are by far the most diverse, and most of the other chemistry of this group is of compounds of krypton. There is evidence for the formation of such radon compounds as RnF_2, but the study of radon chemistry is hampered by the element's high radioactivity. Recently, the first "stable" compound of argon, HArF, has been reported.[61] This compound was synthesized by condensing a mixture of argon and an HF-pyridine polymer onto a CsI substrate at 7.5 K. Although stable at a low temperature, HArF decomposes at room temperature and above. Transient species containing helium and neon have been observed using mass spectrometry. However, most of the stable noble gas compounds are those of xenon with the highly electronegative elements F, O, and Cl; a few compounds have also been reported with Xe—N, Xe—C, and even Xe—transition metal bonds. Some of the compounds and ions of the noble gases are shown in Table 8-18.

TABLE 8-18
Noble Gas Compounds and Ions

Formal Oxidation State of Noble Gas	*Number of Lone Pairs on Central Atom*	*Compounds and Ions*			
+2	3	KrF^+	XeF^+		
		KrF_2	XeF_2		
+4	2		$XeF_3{}^+$		
			XeF_4	$XeOF_2$	
			$XeF_5{}^-$		
+6	1		$XeF_5{}^+$	$XeOF_4$	XeO_3
			XeF_6	XeO_2F_2	
			$XeF_7{}^-$	XeO_3F^-	
			$XeF_8{}^{2-}$	$XeOF_5{}^-$	
+8	0			XeO_3F_2	XeO_4
					$XeO_6{}^{4-}$

Several of these compounds and ions have interesting structures which have provided tests for models of bonding. For example, structures of the xenon fluorides have been interpreted on the basis of the VSEPR model (Figure 8-31). XeF_2 and XeF_4 have structures entirely in accord with their VSEPR descriptions: XeF_2 is linear (three lone pairs on Xe) and XeF_4 is planar (two lone pairs).

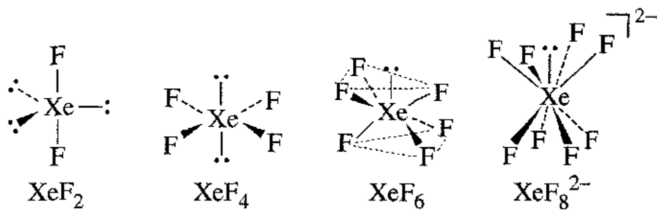

FIGURE 8-31 Structures of Xenon Fluorides.

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[60] For a discussion of the development of the chemistry of xenon compounds, see P. Laszlo and G. L. Schrobilgen, *Angew. Chem., Int. Ed.*, **1988**, *27*, 479.

[61] L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, and M. Räsänen, *Nature (London)*, **2000**, *406*, 874.

XeF_6 and $[XeF_8]^{2-}$, on the other hand, are more difficult to interpret by VSEPR. Each has a single lone pair on the central xenon. The VSEPR model would predict this lone pair to occupy a definite position on the xenon, as do single lone pairs in such molecules as NH_3, SF_4, and IF_5. However, no definite location is found for the central lone pair of XeF_6 or $XeF_8{}^{2-}$. One explanation is based on the degree of crowding around xenon. With a large number of fluorines attached to the central atom, repulsions between the electrons in the xenon-fluorine bonds are strong—too strong to enable a lone pair to occupy a well-defined position by itself. The central lone pair does play a role, however. In XeF_6, the structure is not octahedral but somewhat distorted as a consequence of the lone pair on xenon. Although the structure of XeF_6 in the gas phase has been very difficult to determine, spectroscopic evidence indicates that the lowest energy form has C_{3v} symmetry, as shown in Figure 8-31. This is not a rigid structure, however; the molecule apparently undergoes rapid rearrangement from one C_{3v} structure to another (the lone pair appears to move from the center of one face to another) by way of intermediates having other symmetry.[62] Solid XeF_6 contains at least four phases consisting of square-pyramidal $XeF_5{}^+$ ions bridged by fluoride ions, as shown for one of the phases in Figure 8-32.[63]

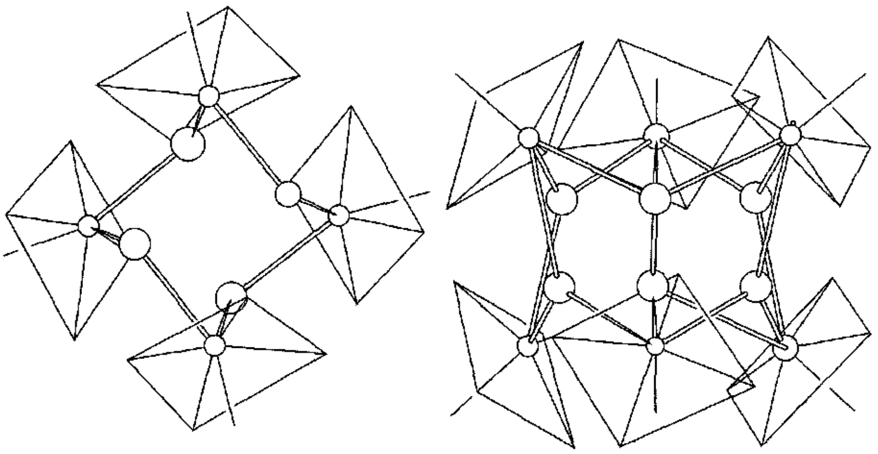

FIGURE 8-32 Xenon Hexafluoride (Crystalline Forms). (Reproduced with permission from R. D. Burbank and G. R. Jones, *J. Am. Chem. Soc.*, **1984**, *96*, 43. © 1974 American Chemical Society.)

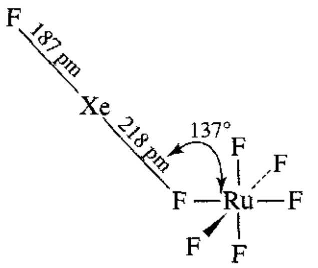

FIGURE 8-33 $[XeF]^+[RuF_6]^-$. (Data from N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell, and A. Zalkin, *Inorg. Chem.*, **1973**, *12*, 1717.)

The structure of $XeF_8{}^{2-}$ is also distorted, but very slightly. As shown in Figure 8-31, $XeF_8{}^{2-}$ is nearly a square antiprism (D_{4d} symmetry), but one face is slightly larger than the opposite face (resulting in approximate C_{4v} symmetry).[64] Although this distortion may be a consequence of the way in which these ions pack in the crystal, it is also possible that the distortion is caused by a lone pair exerting some influence on the size of the larger face.[65]

Positive ions containing xenon are also known. For example, Bartlett's original reaction of xenon with PtF_6 is now believed to proceed as follows:

$$Xe + 2PtF_6 \longrightarrow [XeF]^+[PtF_6]^- + PtF_5 \longrightarrow [XeF]^+[Pt_2F_{11}]^-$$

The ion XeF^+ does not ordinarily occur as a discrete ion but rather is attached covalently to a fluorine on the anion; an example, $[XeF]^+[RuF_6]^-$, is shown in Figure 8-33.[66]

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[62] K. Seppelt and D. Lentz, *Progr. Inorg. Chem.*, **1982**, *29*, 172–180; E. A. V. Ebsworth, D. W. H. Rankin, and S. Craddock, *Structural Methods in Inorganic Chemistry*, Blackwell Scientific Publications, Oxford, 1987, pp. 397–398.

[63] R. D. Burbank and G. R. Jones, *J. Am. Chem. Soc.*, **1974**, *96*, 43.

[64] S. W. Peterson, J. H. Holloway, B. A. Coyle, and J. M. Williams, *Science*, **1971**, *173*, 1238.

[65] The effect of lone pairs can be difficult to predict. For examples of sterically active and inactive lone pairs in ions of formula $AX_6{}^{n-}$, see K. O. Christe and W. Wilson, *Inorg. Chem.*, **1989**, *28*, 3275, and references therein.

[66] N. Bartlett, *Inorg. Chem.*, **1973**, *12*, 1717.

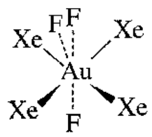

FIGURE 8-34 $[AuXe_4]^{2+}$ Structure in $[AuXe_4][Sb_2F_{11}]$.

A remarkable aspect of the chemistry of xenon is its ability to act as a ligand toward Au^{2+}. Figure 8-34 shows square planar $AuXe_4^{2-}$; other ions are *cis*-$[AuXe_2]^{2+}([Sb_2F_{11}]^-)_2$ and *trans*-$[AuXe_2]^{2+}([Sb_2F_6]^-)_2$.[67] Synthesis of $[AuXe_4][Sb_2F_{11}]_2$ occurs in the very strong acid HF-SbF_5, in which Xe is a stronger base than HF and can displace HF from $[Au(HF)_n]^{2+}$ complexes. Xe also serves as a weak reducing agent, reducing Au^{3+} to Au^{2+} rather than to Au^+ as expected.

Krypton forms several species with fluorine, including the ions KrF^+ and $Kr_2F_3^+$ as well as the neutral KrF_2. KrF_2 exists in two forms in the solid. In the alpha form, shown in Figure 8-35, all molecules are parallel to each other, with eight molecules centered at the corners of the unit cell and a ninth centered in the cell.[68]

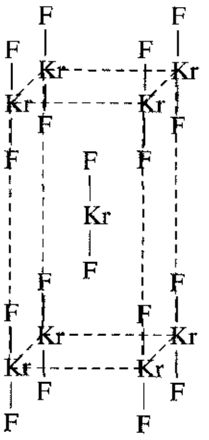

FIGURE 8-35 Krypton Fluoride Crystal Structure.

Several reactions of the noble gas compounds are worth noting. Interest in using noble gas compounds as reagents in organic and inorganic synthesis has been stimulated in part because the byproduct of such reactions is often the noble gas itself. The xenon fluorides XeF_2, XeF_4, and XeF_6 have been used as fluorinating agents for both organic and inorganic compounds. For example,

$$2\,SF_4 + XeF_4 \longrightarrow 2\,SF_6 + Xe$$

$$C_6H_5I + XeF_2 \longrightarrow C_6H_5IF_2 + Xe$$

XeF_4 can also selectively fluorinate aromatic positions in arenes such as toluene.

The oxides XeO_3 and XeO_4 are extremely explosive and must be handled under special precautions. XeO_3 is a powerful oxidizing agent in aqueous solution. The electrode potential of the half-reaction

$$XeO_3 + 6\,H^+ + 6\,e^- \longrightarrow Xe + 3\,H_2O$$

is 2.10 V. In basic solution, XeO_3 forms $HXeO_4^-$:

$$XeO_3 + OH^- \rightleftharpoons HXeO_4^- \qquad K = 1.5 \times 10^{-3}$$

The $HXeO_4^-$ ion subsequently disproportionates to form the perxenate ion, XeO_6^{4-}:

$$2\,HXeO_4^- + 2\,OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2\,H_2O$$

The perxenate ion is an even more powerful oxidizing agent than XeO_3 and is capable of oxidizing Mn^{2+} to permanganate, MnO_4^- in acidic solution.

The chemistry of krypton is much more limited, with fewer than a dozen compounds reported to date. The only neutral halide is KrF_2. Reports of other krypton compounds are sparse; two examples are $[F{-}Kr{-}N{\equiv}CH]^+AsF_6^-$[69] and $Kr(OTeF_5)_2$.[70] The radioactivity of radon has made the study of its chemistry difficult; RnF_2 and a few other compounds have been observed through tracer studies.

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[67] S. Seidel and K. Seppelt, *Science*, **2000**, *290*, 117; T. Drews, S. Seidel, and K. Seppelt, *Angew. Chem., Int. Ed.*, **2002**, *41*, 454.

[68] J. F. Lehmann, D. A. Dixon, and G. J. Schrobilgen, *Inorg. Chem.*, **2001**, *40*, 3002. This reference also has structural data on compounds containing KrF^+ and $Kr_2F_3^+$.

[69] P. J. MacDougall, G. J. Schrobilgen, and R. F. W. Bader, *Inorg. Chem.*, **1989**, *28*, 763.

[70] J. C. P. Saunders and G. J. Schrobilgen, *Chem. Commun. (Cambridge)*, **1989**, 1576.

GENERAL REFERENCES

More detailed descriptions of the chemistry of the main group elements can be found in N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, London, 1997, and in F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochman, *Advanced Inorganic Chemistry*, 6th ed., Wiley-Interscience, New York, 1999. A handy reference on the properties of the elements themselves, including many physical properties, is J. Emsley, *The Elements*, 3rd ed., Oxford University Press, 1998. For extensive structural information on inorganic compounds, see A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, 1984. Three useful references on the chemistry of nonmetals are R. B. King, *Inorganic Chemistry of Main Group Elements*, VCH Publishers, New York, 1995; P. Powell and P. Timms, *The Chemistry of the Nonmetals*, Chapman and Hall, London, 1974; and R. Steudel, *Chemistry of the Non-Metals*, Walter de Gruyter, Berlin, 1976 (English edition by F. C. Nachod and J. J. Zuckerman). The most complete reference on chemistry of the main group compounds through the early 1970s is the five-volume set, J. C. Bailar, Jr., H. C. Emeléus, R. Nyholm, and A. F. Trotman-Dickinson, eds., *Comprehensive Inorganic Chemistry*, Pergamon Press, Oxford, 1973. We encourage the reader to consult these references to supplement the information in this chapter.

PROBLEMS

8-1 The ions H_2^+ and H_3^+ have been observed in gas discharges.

a. H_2^+ has been reported to have a bond distance of 106 pm and a bond dissociation enthalpy of 255 kJ mol^{-1}. Comparable values for the neutral molecule are 74.2 pm and 436 kJ mol^{-1}. Are these values for H_2^+ in agreement with the molecular orbital picture of this ion? Explain.

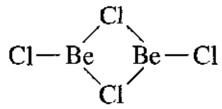
b. Assuming H_3^+ to be triangular (the probable geometry), describe the molecular orbitals of this ion and determine the expected H—H bond order.

8-2 The species He_2^+ and HeH^+ have been observed spectroscopically. Prepare molecular orbital diagrams for these two ions. What would you predict for the bond order of each?

8-3 The equilibrium constant for the formation of the cryptand $[Sr(cryptand(2.2.1)]^{2+}$ is larger than the equilibrium constants for the analogous calcium and barium cryptands. Suggest an explanation. (Reference: E. Kauffmann, J-M. Lehn, and J-P. Sauvage, *Helv. Chim. Acta*, **1976**, *59*, 1099.)

8-4 Gas phase BeF_2 is monomeric and linear. Prepare a molecular orbital description of the bonding in BeF_2.

8-5 In the gas phase $BeCl_2$ forms a dimer of structure



Describe the bonding of the chlorine bridges in this dimer in molecular orbital terms.

8-6 BF can be obtained by reaction of BF_3 with boron at 1850° C and low pressure; BF is highly reactive but can be preserved at liquid nitrogen temperature (77 K). Prepare a molecular orbital diagram of BF. How would the molecular orbitals of BF differ from CO, with which BF is isoelectronic?

8-7 $Al_2(CH_3)_6$ is isostructural with diborane, B_2H_6. On the basis of the orbitals involved, describe the Al—C—Al bonding for the bridging methyl groups in $Al_2(CH_3)_6$.

8-8 Referring to the description of bonding in diborane in Figure 8-12:

a. Show that the representation $\Gamma(p_z)$ reduces to $A_g + B_{1u}$.

b. Show that the representation $\Gamma(p_x)$ reduces to $B_{2g} + B_{3u}$.

c. Show that the representation $\Gamma(1s)$ reduces to $A_g + B_{3u}$.

d. Using the D_{2h} character table, verify that the sketches for the group orbitals match their respective symmetry designations (A_g, B_{2g}, B_{1u}, B_{3u}).

8-9 The compound $C(PPh_3)_2$ is bent at carbon; the P—C—P angle in one form of this compound has been reported as 130.1°. Account for the nonlinearity at carbon.