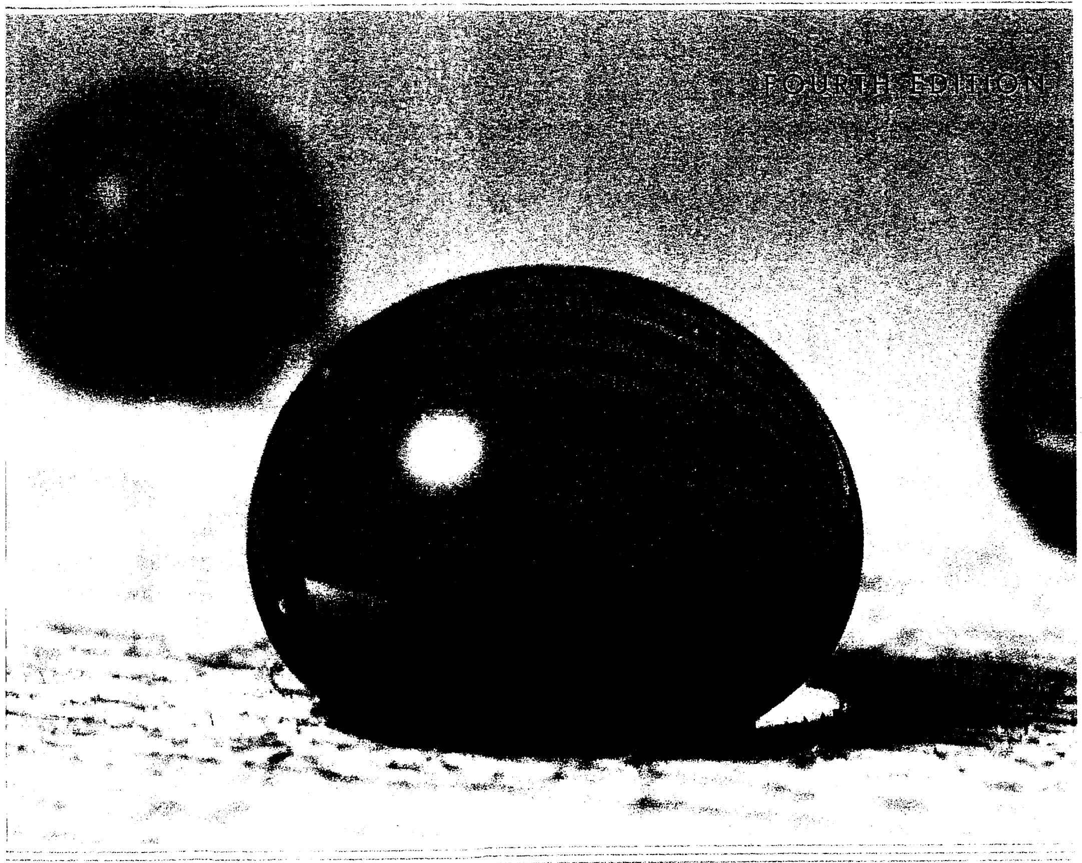
CHEMICAL PRINCIPLES

The Quest for Insight

基礎化学III (棚瀬)
補助教材

アトキンス·ジョーンズ　基礎化学　第2章　2008,
4th ed., ISBN-10:0-7167-7355-4,



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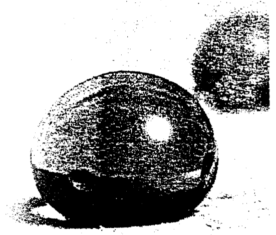
PETER ATKINS / LORETTA JONES

CHEMICAL BONDS



Chapter 2

What Are the Key Ideas? Bond formation is accompanied by a lowering of energy. That lowering of energy is due to the attractions between oppositely charged ions or between nuclei and shared electron pairs. The electron configurations of individual atoms control how the atoms combine with one another.

Why Do We Need to Know This Material? The existence of compounds is central to the science of chemistry; and by seeing how bonds form between atoms, we come to see how chemists design new materials. Research into artificial blood, new pharmaceuticals, agricultural chemicals, and the polymers used in materials such as compact discs, cellular phones, and synthetic fibers is based on an understanding of how atoms link together.

What Do We Need to Know Already? This chapter assumes that we know about atomic structure and electron configurations (Chapter 1), the basic features of energy, and the nature of the Coulomb interaction between charges (Section A). It is also helpful to be familiar with the nomenclature of compounds (Section D) and oxidation numbers (Section K).

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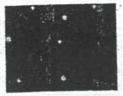
A **chemical bond** is the link between atoms. When a chemical bond forms between two atoms the resulting arrangement of the two nuclei and their electrons has a lower energy than the total energy of the separate atoms. If the lowest energy can be achieved by the *complete transfer* of one or more electrons from the atoms of one element to those of another, then ions form and the compound is held together by the electrostatic attraction between them. This attraction is called an **ionic bond**. Sodium and chlorine atoms, for example, bond together as ions because solid sodium chloride, which consists of Na^+ and Cl^- ions, has a lower energy than a collection of widely separated sodium and chlorine atoms. If the lowest energy can be achieved by *sharing* electrons, then the atoms link through a **covalent bond** and discrete molecules are formed. Hydrogen and nitrogen atoms bond together as molecules of ammonia, NH_3, for example, because a gas consisting of NH_3 molecules has a lower energy than a gas consisting of the same number of widely separated nitrogen and hydrogen atoms. A third type of bond is the **metallic bond**, in which large numbers of cations are held together by a sea of electrons. For example, a piece of copper consists of a stack of copper ions held together by a sea of electrons, each of which comes from one of the atoms in the sample (recall Fig. 1.53). We consider the metallic bond in more detail in Section 3.13 and Chapter 5.

The changes in energy responsible for the formation of bonds occur when the valence electrons of atoms, the electrons in the outermost shells, move to new locations. Therefore, bond formation depends on the electronic structures of atoms discussed in Chapter 1.

IONIC BONDS

The **ionic model**, the description of bonding in terms of ions, is particularly appropriate for describing binary compounds formed from a metallic element, especially an *s*-block metal, and a nonmetallic element. An **ionic solid** is an assembly of cations and anions stacked together in a regular array. In sodium chloride, sodium ions alternate with chloride ions, and large numbers of oppositely charged ions are lined up in all three dimensions (Fig. 2.1). Ionic solids are examples of **crystalline**



Animation Figure 2.1 Sodium chloride crystal melting

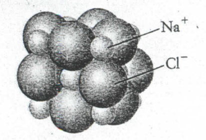


FIGURE 2.1 This tiny fragment of sodium chloride is an example of an ionic solid. The sodium ions are represented by pale red spheres and the chloride ions by green spheres. An ionic solid consists of an array of enormous numbers of cations and anions stacked together to give the lowest energy arrangement. The pattern shown here is repeated throughout the crystal.

Formulas of some common cations are shown in Fig. C.6.

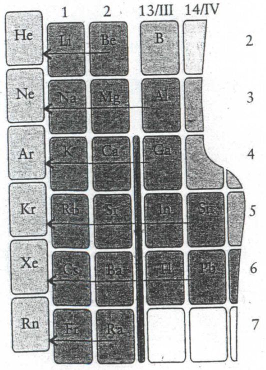


FIGURE 2.2 When a main-group metal atom forms a cation, it loses its valence *s*- and *p*-electrons and acquires the electron configuration of the preceding noble-gas atom. The heavier atoms in Groups 13/III and 14/IV retain their complete subshells of *d*-electrons.

solids, or solids that consist of atoms, molecules, or ions stacked together in a regular pattern. We explore these patterns in Chapter 5; here we concentrate on the changes in the valence electrons that accompany the formation of ions and the energetics of the formation of ionic solids.

2.1 The Ions That Elements Form

When an atom of a metallic element in the *s* block forms a cation, it loses electrons down to its noble-gas core (Fig. 2.2). In general, that core has an ns^2np^6 outer electron configuration, which is called an **octet** of electrons. For example, sodium ($[Ne]3s^1$) forms Na^+, which has the same electron configuration as neon, [Ne]. The Na^+ ions cannot lose more electrons in a chemical reaction, because the ionization energies of core electrons are too high. Hydrogen loses an electron to form a bare proton. Lithium ($[He]2s^1$) and beryllium ($[He]2s^2$) lose their *s*-electrons, leaving a heliumlike **duplet**, a pair of electrons with the configuration $1s^2$, when they become Li^+ and Be^{2+}. Some typical electron configurations of atoms and the ions they form are shown in Table 2.1.

Likewise, when the atoms of metals on the left of the *p* block in Periods 2 and 3 lose their valence electrons, they form ions with the electron configuration of the preceding noble gas. Aluminum, $[Ne]3s^23p^1$, for instance, forms Al^{3+} with the same configuration as neon, [Ne] ($[He]2s^22p^6$). However, when the metallic elements in Period 4 and later periods lose their *s*- and *p*-electrons, they leave a noble-gas core surrounded by an additional, complete subshell of *d*-electrons. For instance, gallium forms the ion Ga^{3+} with the configuration $[Ar]3d^{10}$. The *d*-electrons of the *p*-block atoms are gripped tightly by the nucleus and, in most cases, cannot be lost.

In the *d* block, the energies of the $(n-1)d$-orbitals lie below those of the *ns*-orbitals. Therefore, the *ns*-electrons are lost first, followed by a variable number of $(n-1)d$-electrons. For example, to obtain the configuration of the Fe^{3+} ion, we start from the configuration of the Fe atom, which is $[Ar]3d^64s^2$, and remove three electrons from it. The first two electrons removed are 4*s*-electrons. The third electron comes from the 3*d*-subshell, giving $[Ar]3d^5$.

Many metallic elements in the *p* and *d* blocks, have atoms that can lose a variable number of electrons. As we saw in Section 1.19, the inert-pair effect implies that the elements listed in Fig. 1.57 can lose either their valence *p*-electrons alone or all their valence *p*- and *s*-electrons. These elements and the *d*-block metals can form different compounds, such as tin(II) oxide, SnO, and tin(IV) oxide, SnO_2, for tin. The ability of an element to form ions with different charges is called **variable valence.**

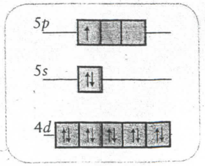
EXAMPLE 2.1 Writing the electron configurations of cations

Write the electron configurations of (a) In^+ and (b) In^{3+}.

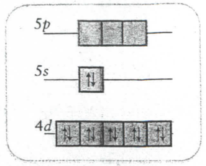
STRATEGY Determine the configuration of the neutral atom by referring to its position in the periodic table. Remove electrons from the valence-shell *p*-orbitals first, then from the *s*-orbitals, and finally, if necessary, from the *d*-orbitals in the next-lower shell, until the number of electrons removed equals the charge on the ion.

SOLUTION

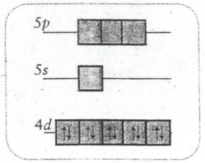
Determine the configuration of the neutral atom. — Indium is in Group 13/III, Period 5. Its ground-state configuration is therefore $[Kr]4d^{10}5s^25p^1$.



(a) Remove the outermost electron. — In^+ $[Kr]4d^{10}5s^2$



(b) Remove the next two electrons. — In^{3+} $[Kr]4d^{10}$



Self-Test 2.1A Write the electron configurations of (a) the copper(I) ion and (b) the copper(II) ion.

[*Answer:* (a) $[Ar]3d^{10}$; (b) $[Ar]3d^9$]

Self-Test 2.1B Write the electron configurations of (a) the manganese(II) ion and (b) the lead(IV) ion.

TABLE 2.1 Some Typical Electron Configurations of Atoms and the Ions They Form

Atom	Configuration	Ion	Configuration
Li	$[He]2s^1$	Li^+	[He] ($1s^2$)
Be	$[He]2s^2$	Be^{2+}	[He]
Na	$[Ne]3s^1$	Na^+	[Ne] ($[He]2s^22p^6$)
Mg	$[Ne]3s^2$	Mg^{2+}	[Ne]
Al	$[Ne]3s^23p^1$	Al^{3+}	[Ne]
N	$[He]2s^22p^3$	N^{3-}	[Ne] ($[He]2s^22p^6$)
O	$[He]2s^22p^4$	O^{2-}	[Ne]
F	$[He]2s^22p^5$	F^-	[Ne]
S	$[Ne]3s^23p^4$	S^{2-}	[Ar] ($[Ne]3s^23p^6$)
Cl	$[Ne]3s^23p^5$	Cl^-	[Ar]

Nonmetals rarely lose electrons in chemical reactions because their ionization energies are too high. However, a nonmetal atom can acquire enough electrons to complete its valence shell and form an anion with an octet corresponding to the configuration of the next noble gas ($1s^2$ in the case of the hydride ion, H^-), Fig. 2.3. It does not gain more electrons, because any additional electrons would have to be accommodated in a higher-energy shell. To form a monatomic anion, we add enough electrons to complete the valence shell. For example, nitrogen has five valence electrons (**1**); so three more electrons are needed to reach a noble-gas configuration, that of neon. Therefore, the ion will be N^{3-} (**2**). Notice that in each case the ion has the electron configuration of the next noble gas.

Formulas of some common anions are shown in Fig. C.7.

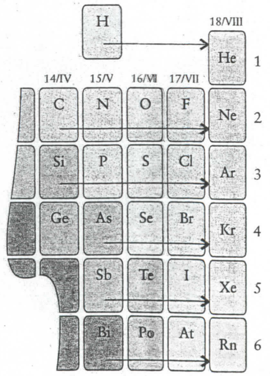
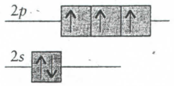


FIGURE 2.3 When nonmetal atoms acquire electrons and form anions, they do so until they have reached the electron configuration of the next noble gas.

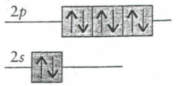
Self-Test 2.2A Predict the chemical formula and electron configuration of the phosphide ion.

[*Answer:* P^{3-}, $[Ne]3s^23p^6$]

Self-Test 2.2B Predict the chemical formula and electron configuration of the iodide ion.



1 N $[He]2s^22p^3$



2 N^{3-} $[He]2s^22p^6$

To predict the electron configuration of a monatomic cation, remove outermost electrons in the order np, ns, and (n − 1)d; for a monatomic anion, add electrons until the next noble-gas configuration has been reached. The transfer of electrons results in the formation of an octet (or duplet) of electrons in the valence shell on each of the atoms: metals achieve an octet (or duplet) by electron loss and nonmetals achieve it by electron gain.

2.2 Lewis Symbols

As will become apparent as this chapter progresses, many of our basic ideas on the chemical bond were proposed by G. N. Lewis, one of the greatest of all chemists, in the early years of the twentieth century. Lewis devised a simple way to keep track of valence electrons when atoms form ionic bonds. He represented each valence electron as a dot and arranged the dots around the symbol of the element. A single dot represents an electron alone in an orbital; a pair of dots represents two paired electrons sharing an orbital. Examples of the Lewis symbols of atoms are

$$\mathrm{H}\cdot \quad \mathrm{He}: \quad :\dot{\mathrm{N}}\cdot \quad \cdot\underset{\cdot\cdot}{\dot{\mathrm{O}}}\cdot \quad :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot \quad \mathrm{K}\cdot \quad \mathrm{Mg}:$$

The Lewis symbol for nitrogen, for example, represents the valence electron configuration $2s^22p_x^{\ 1}2p_y^{\ 1}2p_z^{\ 1}$ (see 1), with two electrons paired in a 2*s*-orbital and three unpaired electrons in different 2*p*-orbitals. The Lewis symbol is a visual summary of the valence-shell electron configuration of an atom and allows us to see what happens to the electrons when an ion forms.

To work out the formula of an ionic compound by using Lewis symbols, we first represent the cation by removing the dots from the symbol for the metal atom. Then we represent the anion by transferring those dots to the Lewis symbol for the nonmetal atom to complete its valence shell. We might need to adjust the numbers of atoms of each kind so that all the dots removed from the metal atom symbols are accommodated by the nonmetal atom symbols. Finally, we write the charge of each ion as a superscript in the normal way, using brackets to indicate that the charge is the overall charge of the ion. A simple example is the formula of calcium chloride. The calcium atom loses its two valence electrons when it forms the Ca^{2+} ion. Because each chlorine atom has one vacancy, two are required to accommodate the two electrons lost:

$$:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot + \mathrm{Ca}: + :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot \longrightarrow [:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:]^- \ \mathrm{Ca}^{2+} \ [:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:]^-$$

The ratio of two chloride ions for each calcium ion results in the formula $\mathrm{CaCl_2}$. However, note that this is an empirical formula (Section E). There are no $\mathrm{CaCl_2}$ molecules. Crystals of $\mathrm{CaCl_2}$ contain many of these ions in three-dimensional arrays.

Formulas of compounds consisting of the monatomic ions of main-group elements can be predicted by assuming that cations have lost all their valence electrons and anions have gained electrons in their valence shells until each ion has an octet of electrons, or a duplet in the case of H, Li, and Be.

2.3 The Energetics of Ionic Bond Formation

To understand why a crystal of sodium chloride, an ionic compound, has a lower energy than widely separated sodium and chlorine atoms, we picture the formation of the solid as taking place in three steps: sodium atoms release electrons, these electrons attach to chlorine atoms, and then the resulting cations and anions clump together as a crystal. Chemists often analyze complex processes by breaking them down into simpler steps such as these, and often consider hypothetical steps (steps that do not actually occur).

Sodium is in Group 1 of the periodic table and can be expected to form a +1 ion. However, the valence electron is tightly held by the effective nuclear charge—it does not just fall off. In fact, the ionization energy of sodium is 494 kJ·mol^{-1} (see Fig. 1.50), and so we must supply that much energy to form the cations:

$$\mathrm{Na(g)} \longrightarrow \mathrm{Na^+(g)} + \mathrm{e^-(g)} \qquad \text{energy required} = 494\ \mathrm{kJ\cdot mol^{-1}}$$

The electron affinity of chlorine atoms is +349 kJ·mol^{-1} (see Fig. 1.54), and so we know that 349 kJ·mol^{-1} of energy is *released* when electrons attach to chlorine atoms to form anions:

A positive electron affinity signifies a release of energy when an electron attaches to a gas-phase atom or ion (Section 1.18).

$$\mathrm{Cl(g)} + \mathrm{e^-(g)} \longrightarrow \mathrm{Cl^-(g)} \qquad \text{energy released} = 349\ \mathrm{kJ\cdot mol^{-1}}$$

At this stage, the net change in energy (energy required − energy released) is 494 − 349 kJ·mol^{-1} = +145 kJ·mol^{-1}, an *increase* in energy. A gas of widely separated $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions has a higher energy than a gas of neutral Na and Cl atoms.

Now consider what happens when gaseous $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions come together to form a crystalline solid. Their mutual attraction releases a lot of energy, and experimentally it is found that

$$\mathrm{Na^+(g)} + \mathrm{Cl^-(g)} \longrightarrow \mathrm{NaCl(s)} \qquad \text{energy released} = 787\ \mathrm{kJ\cdot mol^{-1}}$$

Therefore, the net change in energy for the overall process

$$\mathrm{Na(g)} + \mathrm{Cl(g)} \longrightarrow \mathrm{NaCl(s)}$$

is 145 − 787 kJ·mol^{-1} = −642 kJ·mol^{-1} (Fig. 2.4), a huge *decrease* in energy. We conclude that a solid composed of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions has a lower energy than does a collection of widely separated Na and Cl atoms.

We can now begin to understand the formation of ionic bonds and learn when to expect them. There is a net lowering of energy below that of the individual atoms, provided the net attraction between ions is greater than the energy needed to make them. The major contribution to the energy requirement is normally the ionization energy of the element that forms the cation. Although some of this energy may be recovered from the electron affinity of the nonmetal when the anion is formed, in some cases energy is also needed to make the anion. For instance, we saw in Section 1.18 that the formation of an $\mathrm{O^{2-}}$ ion from an O atom *requires* 703 kJ·mol^{-1} and adds to the energy that must be recovered from the interactions between ions. Typically, *only metallic elements have ionization energies that are low enough for the formation of cations to be energetically feasible.*

The energy required for the formation of ionic bonds is supplied largely by the attraction between oppositely charged ions.

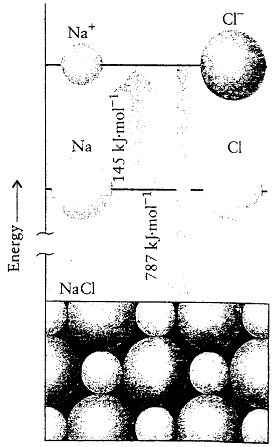


FIGURE 2.4 Considerable energy is needed to produce cations and anions from neutral atoms: the ionization energy of the metal atoms is only partly recovered from the electron affinity of the nonmetal atoms. The overall lowering of energy that drags the ionic solid into existence arises from the strong attraction between cations and anions that occurs in the solid. In Chapter 6, we see how to take into account the chemical reaction between Na(s) and $\mathrm{Cl_2(g)}$: this illustration is for the relative energies of Na(g) and Cl(g).

2.4 Interactions Between Ions

We have seen that a key contribution to the formation of ionic bonds is the strength of the interaction between ions in a solid: it must be strong enough to overcome the energy investment needed to make the ions. However, a very important point to note is that an ionic solid is not held together by bonds between specific pairs of ions: *all* the cations interact to a greater or lesser extent with *all* the anions, *all* the cations repel each other, and *all* the anions repel each other. An ionic bond is a "global" characteristic of the entire crystal, a net lowering of energy of the entire crystal. We need to assess this interaction quantitatively and see what determines the **lattice energy** of the solid, the difference in energy between the ions packed together in a solid and the ions widely separated as a gas. A high lattice energy indicates that the ions interact strongly with one another to give a tightly bonded solid.

The strong attraction between oppositely charged ions accounts for the typical properties of ionic solids, such as their high melting points and their brittleness. A high temperature is required before the ions are able to move past one

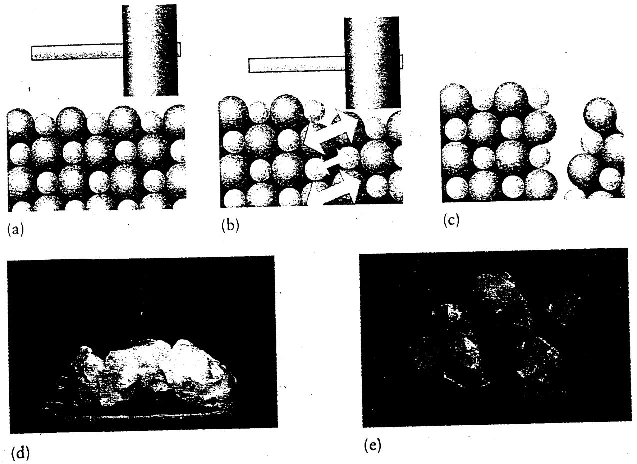


FIGURE 2.5 This sequence of images illustrates why ionic solids are brittle. (a) The original solid consists of an orderly array of cations and anions. (b) A hammer blow can push ions with like charges into adjacent positions; this proximity of like charges raises strong repulsive forces (as depicted by the double-headed arrows). (c) As the result of these repulsive forces, the solid breaks apart into fragments. (d) This calcite rock consists of several large crystals joined together. (e) The blow of a hammer has shattered some of the crystals, leaving flat, regular surfaces consisting of planes of ions. Compare this image with the result of striking a metallic crystal (Fig. 5.46).

another to form a liquid. Ionic solids are brittle because of the same strong attractions and repulsions. We cannot just push a block of ions past another block; instead, when we strike an ionic solid, ions with like charges come into contact and repel one another. The resulting repulsions cause it to shatter into fragments (Fig. 2.5).

Our starting point for understanding the interaction between ions in a solid is the expression for the Coulomb potential energy of the interaction of two individual ions (Section A):

$$E_{P,12} = \frac{(z_1e) \times (z_2e)}{4\pi\varepsilon_0 r_{12}} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{12}} \qquad (1)^*$$

In this expression, e is the fundamental charge (the absolute value of the charge of an electron), z_1 and z_2 are the charge numbers of the two ions, r_{12} is the distance between the centers of the ions, and ε_0 is the vacuum permittivity (see inside the back cover for the value of this fundamental constant).

A note on good practice: A charge number, z, is positive for cations and negative for anions and the charge of an ion is ze. However, chemists almost always refer to z itself as the charge, and speak of a charge of +1, −1, and so on.

Each ion in a solid experiences attractions from all the other oppositely charged ions and repulsions from all the other like-charged ions. The total potential energy is the sum of all these contributions. Each cation is surrounded by anions, and there is a large negative (energy-lowering) contribution from the attraction of the opposite charges. Beyond those nearest neighbors, there are cations that contribute a positive (repulsive, energy-raising) term to the total potential energy of the central cation. There is also a negative contribution from the anions beyond those cations, a positive contribution from the cations beyond them, and so on, to the edge of the solid. These repulsions and attractions become progressively weaker as the distance from the central ion increases, but because the nearest neighbors of an ion give rise to a strong attraction, the net outcome of all these contributions is a lowering of energy. Our task is to assess how far the energy is lowered by using the Coulomb potential energy expression in Eq. 1.

HOW DO WE DO THAT?

To calculate the potential energy of an ionic solid we start with a simple model: a single line of uniformly spaced alternating cations and anions, with d (the distance between their centers) the sum of the ionic radii (Fig. 2.6). If the charge numbers of the ions have the same absolute value (+1 and −1, or +2 and −2, for instance), then $z_1 = +z$, $z_2 = -z$, and $z_1z_2 = -z^2$. The potential energy of the central ion is calculated by summing all the Coulomb potential energy terms, with negative terms representing attractions to oppositely charged ions and positive terms representing repulsions from like-charged ions. For the interaction arising from ions extending in a line to the right of the central ion, the total potential energy of the central ion is

$$E_P = \frac{1}{4\pi\varepsilon_0} \times \left(-\frac{z^2e^2}{d} + \frac{z^2e^2}{2d} - \frac{z^2e^2}{3d} + \frac{z^2e^2}{4d} - \cdots\right)$$
$$= -\frac{z^2e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right) = -\frac{z^2e^2}{4\pi\varepsilon_0 d} \times \ln 2$$

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In the last step, we have used the relation $1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ldots = \ln 2$. Finally, we multiply E_P by 2 to obtain the total energy arising from interactions on each side of the ion and then by Avogadro's constant, N_A, to obtain an expression for the potential energy per mole of ions. The outcome is

$$E_P = -2\ln 2 \times \frac{z^2 N_A e^2}{4\pi\varepsilon_0 d}$$

with $d = r_{\text{cation}} + r_{\text{anion}}$, the distance between the centers of neighboring ions.

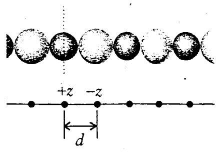


FIGURE 2.6 The arrangement used to calculate the potential energy of an ion in a line of alternating cations (red spheres) and anions (green spheres). We concentrate on one ion, the "central" ion denoted by the vertical dotted line.

We have found that the potential energy of an ion at the center of a line of alternating cations and anions has the form

$$E_P = -A \times \frac{z^2 N_A e^2}{4\pi\varepsilon_0 d} \qquad (2)$$

per mole of ions, with $A = 2 \ln 2$ (or 1.386) for this model system.

> ***What does this equation tell us?*** Because the potential energy is negative, there is a net attraction of the central ion to all the other ions, which means that the attraction between opposite charges overcomes the repulsion between like charges. The potential energy is strongly negative when the ions are highly charged (large values of z) and the separation between them is small (small values of d), which is the case when the ions themselves are small.

The calculation that led to Eq. 2 can be extended to more realistic three-dimensional arrays of ions with different charges, and the result has the same form but with different values of A and $|z_1z_2|$ (that is, the absolute value of z_1z_2, its value without the negative sign) in place of z^2. The factor A is a numerical coefficient called the **Madelung constant**; its value depends on how the ions are arranged about one another (Table 2.2). In all cases, the energy lowering that occurs when an ionic solid forms is greatest for small, highly charged ions. For example, there is a strong interaction between the Mg^{2+} and the O^{2-} ions in magnesium oxide, MgO, because the ions have high charges and small radii. This strong interaction is one reason why magnesium oxide survives at such high temperatures that it can be used for furnace linings. It is an example of a "refractory" material, a substance that can withstand high temperatures.

TABLE 2.2 Madelung Constants

Structural type*	A
cesium chloride	1.763
fluorite	2.519
rock salt	1.748
rutile	2.408

* For information about these structures, see Chapter 5.

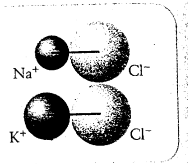
EXAMPLE 2.2 Sample exercise: Estimating the relative lattice energies of solids

The ionic solids NaCl and KCl form the same type of crystal structure. In which solid are the ions bound together more strongly by coulombic interactions?

SOLUTION

Compare the radii of the ions (Fig. 1.48), for they determine the size of the separation d.

The radius of Na^+ is 102 pm and that of K^+ is 138 pm; the radius of Cl^- is 181 pm.



The ions in NaCl should be bound together more strongly than those in KCl because the Na^+ ion has a smaller radius than the K^+ ion and d is smaller in NaCl than in KCl.

Self-Test 2.3A The ionic solids CaO and KCl crystallize to form structures of the same type. In which compound are the interactions between the ions stronger?
[*Answer:* CaO, higher charges and smaller radii]

Self-Test 2.3B The ionic solids KBr and KCl crystallize to form structures of the same type. In which compound are the interactions between ions stronger?

The potential energy in Eq. 2 becomes more and more negative as the separation d decreases. However, a collection of ions does not collapse to a point because repulsive effects between neighbors become important as soon as they come into contact, and the energy quickly rises again. To take the repulsion effects between close neighbors in an ionic solid into account it is commonly supposed that the repulsive contribution to the potential energy rises exponentially with decreasing separation and therefore has the form

$$E_P{}^* \propto e^{-d/d^*}$$

with d^* a constant (it is commonly taken to be 34.5 pm). The total potential energy is the sum of E_P and $E_P{}^*$ and passes through a minimum as the ion separation decreases and then rises sharply again (Fig. 2.7). The energy at the minimum is given by the **Born–Meyer equation** (which we do not derive here):

$$E_{P,\min} = -\frac{N_A|z_1z_2|e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)A \qquad (3)^*$$

What does this equation tell us? As before, the negative sign of this potential energy tells us that the ions have a lower potential energy when they are present as a solid rather than widely separated as a gas. The greatest stabilization is expected when the ions are highly charged (so $|z_1z_2|$ is large) and small (so d is small, but not smaller than d^*).

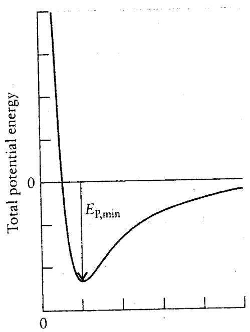


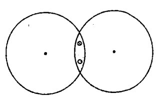
FIGURE 2.7 The potential energy of an ionic solid, taking into account the coulombic interaction of the ions and the exponential increase in their repulsion when they are in contact. The minimum potential energy is given by the Born-Meyer equation, Eq. 3.

We can now see why nature has adopted an ionic solid, calcium phosphate, for our skeletons: the doubly charged small Ca^{2+} ions and the triply charged $PO_4{}^{3-}$ ions attract one another very strongly and clump together tightly to form a rigid, insoluble solid (Fig. 2.8)

Ionic solids typically have high melting points and are brittle. The coulombic interaction between ions in a solid is large when the ions are small and highly charged.

COVALENT BONDS

Because nonmetals do not form monatomic cations, the nature of bonds between atoms of nonmetals puzzled scientists until 1916, when Lewis published his explanation. With brilliant insight, and before anyone knew about quantum mechanics or orbitals, Lewis proposed that a **covalent bond** is a pair of electrons shared between two atoms (3). The rest of this chapter and the next develop Lewis's vision of the covalent bond. In this chapter, we consider the types, numbers, and properties of bonds that can be formed by sharing pairs of electrons. In Chapter 3, we revisit Lewis's concept and see how to understand it in terms of orbitals.



3 Shared electron pair

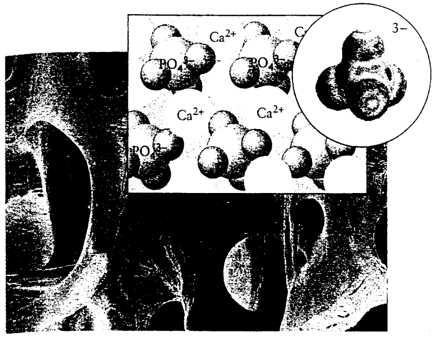


FIGURE 2.8 A micrograph of bone, which owes its rigidity to calcium phosphate. The overlay shows part of the crystal structure of calcium phosphate. Phosphate ions are polyatomic ions; however, as shown in the inset, they are nearly spherical and fit into crystal structures in much the same way as monatomic ions of charge −3.

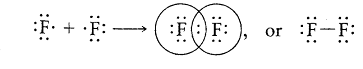
2.5 Lewis Structures

When ionic bonds form, the atoms of one element lose electrons and the atoms of the second element gain them until both types of atoms have reached a noble-gas configuration. The same idea can be extended to covalent bonds. However, when a covalent bond forms, atoms *share* electrons until they reach a noble-gas configuration. Lewis called this principle the **octet rule:**

In covalent bond formation, atoms go as far as possible toward completing their octets by sharing electron pairs.

For example, nitrogen $(:\dot{N}\cdot)$ has five valence electrons and needs three more electrons to complete its octet. Chlorine $(:\ddot{\underset{..}{Cl}}\cdot)$ has seven valence electrons and needs one more electron to complete its octet. Argon $(:\ddot{\underset{..}{Ar}}:)$ already has a complete octet and has no tendency to share any more electrons. Hydrogen $(H\cdot)$ needs one more electron to reach its helium-like duplet. Because hydrogen completes its duplet by sharing one pair of electrons, we say that it has a valence of 1 in all its compounds. In general, the **valence** of an element is the number of bonds that its atoms can form.

We can extend the Lewis symbols introduced in Section 2.2 to describe covalent bonding by using a line (—) to represent a shared pair of electrons. For example, the hydrogen molecule formed when two $H\cdot$ atoms share an electron pair (H:H) is represented by the symbol H—H. A fluorine atom has seven valence electrons and needs one more to complete its octet. It can achieve an octet by accepting a share in an electron supplied by another atom, such as another fluorine atom:



$$:\ddot{\underset{..}{F}}\cdot + \cdot\ddot{\underset{..}{F}}: \longrightarrow :\ddot{\underset{..}{F}}:\ddot{\underset{..}{F}}:, \quad \text{or} \quad :\ddot{\underset{..}{F}}-\ddot{\underset{..}{F}}:$$

The circles drawn around each F atom show how each one gets an octet by sharing one electron pair. The valence of fluorine is therefore 1, the same as that of hydrogen.

As well as a bonding pair of electrons, a fluorine molecule also possesses **lone pairs** of electrons; that is, pairs of valence electrons that do not take part in bonding. The lone pairs on one F atom repel the lone pairs on the other F atom, and this repulsion is almost enough to overcome the favorable attractions of the bonding pair that holds the atoms together. This repulsion is one of the reasons why fluorine gas is so reactive: the atoms are bound together as F_2 molecules only very weakly. Among the common diatomic molecules, only H_2 has no lone pairs.

The **Lewis structure** of a molecule shows atoms by their chemical symbols, covalent bonds by lines, and lone pairs by pairs of dots. For example, the Lewis structure of HF is $H-\ddot{\underset{..}{F}}:$. We shall see that Lewis structures are a great help in

It is sometimes necessary to write a Lewis structure at the end of a sentence or clause: be careful to distinguish electron dots from periods and colons!

understanding the properties of molecules, including their shapes and the reactions that they can undergo.

Self-Test 2.4A Write the Lewis structure for the "interhalogen" compound chlorine monofluoride, ClF, and state how many lone pairs each atom possesses in the compound.

[*Answer:* $:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}-\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:$; three on each atom]

Self-Test 2.4B Write the Lewis structure for the compound HBr and state how many lone pairs each atom in the compound possesses.

> *Nonmetal atoms share electrons until each has completed its octet (or duplet); a Lewis structure shows the arrangement of electrons as lines (bonding pairs) and dots (lone pairs).*

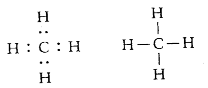
2.6 Lewis Structures for Polyatomic Species

Each atom in a polyatomic molecule completes its octet (or duplet for hydrogen) by sharing pairs of electrons with its immediate neighbors. Each shared pair counts as one covalent bond and is represented by a line between the two atoms. A Lewis structure does not portray the shape of a polyatomic molecule; it simply displays which atoms are bonded together and which atoms have lone pairs.

Let's construct the Lewis structure for the simplest organic molecule, the hydrocarbon methane, CH_4. First, we count the valence electrons available from all the atoms in the molecule. For methane, the Lewis symbols of the atoms are

$$:\dot{\underset{\cdot}{\mathrm{C}}}\quad \mathrm{H}\cdot\quad \mathrm{H}\cdot\quad \mathrm{H}\cdot\quad \mathrm{H}\cdot$$

and so there are eight valence electrons. The next step is to arrange the dots representing the electrons so that the C atom has an octet and each H atom has a duplet. We draw the arrangement shown on the left in (4); the Lewis structure of methane is then drawn as shown on the right in (4). Because the carbon atom is linked by four bonds to other atoms, we say that carbon is *tetravalent*: it has a valence of 4. We emphasize once again that a Lewis structure does not show the shape of the molecule, just the pattern of bonds, its "connectivity." In Chapter 3, we shall see that the three-dimensional arrangement of bonds in a methane molecule is in fact tetrahedral.

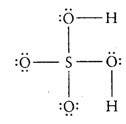

4 Methane, CH_4

The general procedure for constructing the Lewis structure of any molecule or ion is set out in Toolbox 2.1 at the end of this section, but the following information is essential for applying those rules.

A single shared pair of electrons is called a **single bond**. Two electron pairs shared between two atoms constitute a **double bond**, and three shared electron pairs constitute a **triple bond**. A double bond, such as C::O, is written C=O in a Lewis structure. Similarly, a triple bond, such as C:::C, is written C≡C. Double and triple bonds are collectively called **multiple bonds**. The **bond order** is the number of bonds that link a specific pair of atoms. The bond order in H_2 is 1; in the group C=O, it is 2; and, for C≡C in a molecule such as ethyne, C_2H_2, the bond order is 3.

To write a Lewis structure, we need to know which atoms are linked together in a molecule. A "terminal" atom is bonded to only one other atom; an H atom in methane is an example. Except in the strange compounds called the boranes (Section 14.14), an H atom is always a terminal atom. A "central" atom is bonded to at least two other atoms. Two examples are the O atom in a water molecule, HOH, and the C atom in methane. The arrangement of atoms in a molecule and the identity of the central atom are often known in advance (for instance, it is easy to remember the arrangements of atoms in CH_4, NH_3, and H_2O). If there is doubt, a good rule of thumb for molecules other than compounds of hydrogen is to *choose as the central atom the element with the lowest ionization energy*. This arrangement often results in the lowest energy because an atom in the central position shares more of its electrons than does a terminal atom. Atoms with higher ionization energies are more reluctant to share and are more likely to hold on to their electrons as lone pairs.

In Section 2.12, when we have met the concept of electronegativity, we shall see that another way to express this rule is to say that the central atom is usually the element with lowest electronegativity.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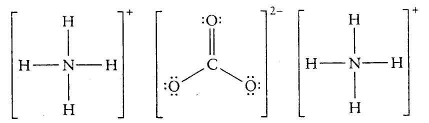

6

Another rule of thumb for predicting the structure of a molecule is to *arrange the atoms symmetrically around the central atom*. For instance, SO_2 is OSO, not SOO. One common exception to this rule is dinitrogen monoxide, N_2O (nitrous oxide), which has atoms in the asymmetrical arrangement NNO. Another clue for writing the correct arrangement of atoms is that, in simple chemical formulas, the central atom is often written first, followed by the atoms attached to it. For example, in the compound with the chemical formula OF_2, the arrangement of the atoms is actually FOF, not OFF; and, in SF_6, the S atom is surrounded by six F atoms. Acids are exceptions to this rule, because the H atoms are written first, as in H_2S, which has the arrangement HSH. If the compound is an oxoacid, then the acidic hydrogen atoms are attached to oxygen atoms, which in turn are attached to the central atom. For example, the arrangement of atoms in sulfuric acid, H_2SO_4, is $(HO)_2SO_2$ (5), and that in hypochlorous acid, HClO, is HOCl.

Finally, the same general procedure is used to determine the Lewis structures of polyatomic ions, except that we add or subtract electrons to account for the charge on the ion. We count the electrons available for bonds and lone pairs, arrange the atoms in the appropriate order, and then construct the Lewis structure. As for neutral molecules, it is essential to know the general arrangement of atoms in the ion. For oxoanions, it is usually the case that (except for H) the atom written first in the chemical formula is the central atom. In CO_3^{2-}, for instance, the C atom is surrounded by three O atoms. Each atom provides the number of dots (electrons) equal to the number of electrons in its valence shell, but we have to adjust the total number of dots to represent the overall charge. For a cation, we subtract one dot for each positive charge. For an anion, we add one dot for each negative charge. The cation and the anion must be treated separately: they are individual ions and are not linked by shared pairs. The Lewis structure of ammonium carbonate, $(NH_4)_2CO_3$, for instance, is written as three bracketed ions (6).

TOOLBOX 2.1 HOW TO WRITE THE LEWIS STRUCTURE OF A POLYATOMIC SPECIES

CONCEPTUAL BASIS

We look for ways of using all the valence electrons to complete the octets (or duplets).

PROCEDURE

Step 1 Count the number of valence electrons on each atom; for ions, adjust the number of electrons to account for the charge. Divide the total number of valence electrons in the molecule by 2 to obtain the number of electron pairs.

Step 2 Write down the most likely arrangements of atoms by using common patterns and the clues indicated in the text.

Step 3 Place one electron pair between each pair of bonded atoms.

Step 4 Complete the octet (or duplet, in the case of H) of each atom by placing any remaining electron pairs around the atoms. If there are not enough electron pairs, form multiple bonds.

Step 5 Represent each bonded electron pair by a line.

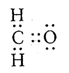
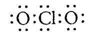
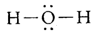
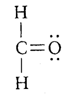
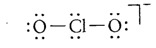
To check on the validity of a Lewis structure, verify that each atom has an octet or a duplet. As we shall see in Section 2.10, a common exception to this rule arises when the central atom is an atom of an element in Period 3 or higher. Such an atom can accommodate more than eight electrons in its valence shell. Consequently, the most stable Lewis structure may be one in which the central atom has more than eight electrons.

This procedure is illustrated in Examples 2.3 and 2.4.

EXAMPLE 2.3 **Sample exercise: Writing the Lewis structure of a molecule or an ion**

Write the Lewis structures of (a) water, H_2O; (b) methanal, H_2CO; and (c) the chlorite ion, ClO_2^-. Use the rules in Toolbox 2.1; note that we must add one electron for the negative charge of ClO_2^-.

SOLUTION

	(a) H_2O	(b) H_2CO	(c) ClO_2^-
Step 1 Count the valence electrons and adjust the number for charges on ions.	1 + 1 + 6 = 8	1 + 1 + 4 + 6 = 12	7 + 6 + 6 + 1 = 20
Count the electron pairs.	4	6	10
Step 2 Arrange the atoms.	H O H	H C O H	O Cl O
Step 3 Connect the atoms with bonding electron pairs.	H : O : H	H C : O H	O:Cl:O
Count electron pairs not yet located.	: : (2)	: : : (3)	: : : : : : : : (8)
Step 4 Complete the octets.			
Step 5 Represent the bonds and add any charges.			

SELF-TEST 2.5A Write a Lewis structure for the cyanate ion, CNO^- (the C atom is in the center).

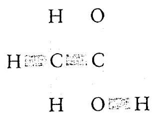
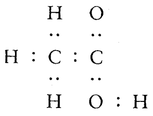
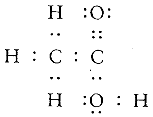
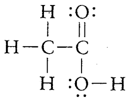
[*Answer:* $\ddot{N}=C=\ddot{O}^-$.]

SELF-TEST 2.5B Write a Lewis structure for NH_3.

EXAMPLE 2.4 **Sample exercise: writing Lewis structures for molecules with more than one "central" atom**

Write the Lewis structure for acetic acid, CH_3COOH, the carboxylic acid in vinegar formed when the ethanol in wine is oxidized. In the —COOH group, both O atoms are attached to the same C atom, and one of them is bonded to the final H atom. The two C atoms are bonded to each other.

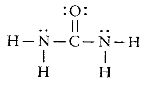
SOLUTION The formula for acetic acid suggests that it consists of two groups, with the central C atoms joined together: a CH_3— group and a —COOH group. We can anticipate that the CH_3— group, by analogy with methane, will consist of a C atom joined to three H atoms by single bonds.

	CH_3COOH
Step 1 Count the valence electrons.	4 + (3 × 1) + 4 + 6 + 6 + 1 = 24
Count the electron pairs.	12
Step 2 Arrange atoms (linked atoms are indicated by the rectangles).	
Step 3 Connect the atoms with bonding electron pairs.	
Count electron pairs not yet located.	: : : : : (5 pairs)
Step 4 Complete the octets.	
Step 5 Represent the bonds.	

SELF-TEST 2.6A Write a Lewis structure for the urea molecule, $(NH_2)_2CO$.

[*Answer:* See (7).]

SELF-TEST 2.6B Write a Lewis structure for hydrazine, H_2NNH_2.



7 Urea, $(NH_2)_2CO$

The Lewis structure of a polyatomic species is obtained by using all the valence electrons to complete the octets (or duplets) of the atoms present by forming single or multiple bonds and leaving some electrons as lone pairs.

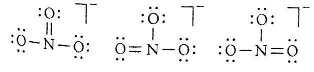
2.7 Resonance

Some molecules are not represented adequately by a single Lewis structure. For example, consider the nitrate ion, NO_3^-, which, as potassium nitrate, is used in fireworks and fertilizers. The three Lewis structures shown in (8) differ only in the position of the double bond. All are valid structures and have exactly the same energy. If one of the pictured structures were correct, we would expect the nitrate ion to have two long single bonds and one short double bond because a double bond between two atoms is shorter than a single bond between the same types of atoms. However, the experimental evidence is that the bond lengths in a nitrate ion are all the same. At 124 pm, they are longer than a typical N=O double bond (120 pm) but shorter than a typical N—O single bond (140 pm). The bond order in the nitrate ion lies between 1 (a single bond) and 2 (a double bond).

Bond length, the distance between the centers of bonded atoms, is discussed in more detail in Section 2.16.

Because all three bonds are identical, a better model of the nitrate ion is a *blend* of all three Lewis structures with each bond intermediate in properties between a single and a double bond. This blending of structures, which is called **resonance**, is depicted in (9) by double-headed arrows. The blended structure is a **resonance hybrid** of the contributing Lewis structures. A molecule does not flicker between different structures: a resonance hybrid is a blend of structures, just as a mule is a blend of a horse and a donkey, not a creature that flickers between the two.

Electrons that are shown in different positions in a set of resonance structures are said to be **delocalized**. Delocalization means that a shared electron pair is distributed over several pairs of atoms and cannot be identified with just one pair of atoms.



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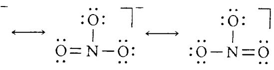


9 Nitrate ion, NO_3^-

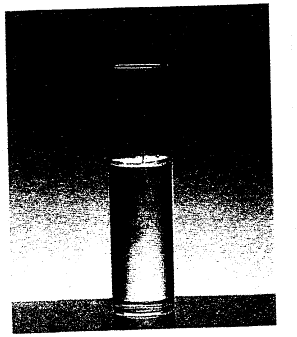


FIGURE 2.9 When bromine dissolved in a solvent (the brown liquid) is mixed with an alkene (the colorless liquid), the bromine atoms add to the alkene molecule at the double bond, resulting in colorless products.

EXAMPLE 2.5 Writing a resonance structure

Stratospheric ozone, O_3, protects life on Earth from harmful ultraviolet radiation from the Sun. Suggest two Lewis structures that contribute to the resonance structure for the O_3 molecule. Experimental data show that the two bond lengths are the same.

STRATEGY Write a Lewis structure for the molecule by using the method outlined in Toolbox 2.1. Decide whether there is another equivalent structure that results from the interchange of a single bond and a double or triple bond. Write the actual structure as a resonance hybrid of these Lewis structures.

SOLUTION

Count the valence electrons.

Oxygen is a member of Group 16/VI; so each atom has six valence electrons: $6 + 6 + 6 = 18$ electrons.

Draw a Lewis structure for the molecule.

$:\ddot{O}-\ddot{O}=\ddot{O}$

Draw a second Lewis structure by rearranging the bonds and lone pairs.

$\ddot{O}=\ddot{O}-\ddot{O}:$

Draw the resonance hybrid.

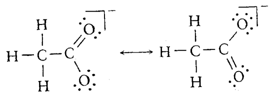
$:\ddot{O}-\ddot{O}=\ddot{O} \longleftrightarrow \ddot{O}=\ddot{O}-\ddot{O}:$

SELF-TEST 2.7A Write Lewis structures contributing to the resonance hybrid for the acetate ion, $CH_3CO_2^-$. The structure of CH_3COOH is described in Example 2.4; the acetate ion has a similar structure, except that it has lost the final H atom while keeping both electrons from the O—H bond.

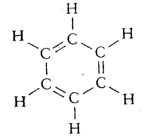
[*Answer:* See (10).]

SELF-TEST 2.7B Write Lewis structures contributing to the resonance hybrid for the nitrite ion, NO_2^-.

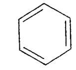
The German chemist Friedrich Kekulé first proposed (in 1865) that benzene has a cyclic structure with alternating single and double bonds.



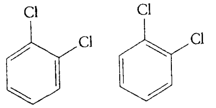
10 Acetate ion, $CH_3CO_2^-$



11 Kekulé structure



12 Kekulé structure, stick form



13 Dichlorobenzene, $C_6H_4Cl_2$

Benzene, C_6H_6, is another molecule best described as a resonance hybrid. It consists of a planar hexagonal ring of six carbon atoms, each one having a hydrogen atom attached to it. One Lewis structure that contributes to the resonance hybrid is shown in (11); it is called a **Kekulé structure**. The structure is normally written as a line structure (see Section C), a simple hexagon with alternating single and double lines (12).

The difficulty with a single Kekulé structure is that it does not fit all the experimental evidence:

- *Reactivity* Benzene does not undergo reactions typical of compounds with double bonds.

For example, when a solution of red-brown bromine is mixed with an alkene such as 1-hexene, $CH_2{=}CHCH_2CH_2CH_2CH_3$, the color due to bromine is lost as the Br_2 molecules attack the double bond to produce $CH_2Br{-}CHBrCH_2CH_2CH_2CH_3$ (Fig. 2.9). However, benzene does not react with bromine.

- *Bond lengths* All the carbon–carbon bonds in benzene are the same length.

A Kekulé structure suggests that benzene should have two different bond lengths: three longer single bonds (154 pm) and three shorter double bonds (134 pm). Instead, all the bonds are found experimentally to have the same intermediate length (139 pm).

- *Structural evidence* Only one dichlorobenzene in which the two chlorine atoms are attached to adjacent carbon atoms exists.

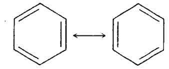
If the Kekulé structure were correct, there would be two distinct dichlorobenzenes in which the chlorine atoms are attached to adjacent carbon atoms (13), one in which the carbon atoms are joined by a single bond and one with a double bond. In fact, only one such compound is known.

We can use the concept of resonance to explain these characteristics of the benzene molecule. There are two Kekulé structures with exactly the same energy; they differ only in the positions of the double bonds. As a result of resonance between these two structures (14), the electrons shared in the C=C double bonds are delocalized over the whole molecule, thereby giving each bond a length intermediate between that of a single and that of a double bond. Resonance makes all six C—C bonds identical; this equivalence is implied by representing the double bonds in the resonance hybrid with a circle (15). We can see from (16) why there can be only one dichlorobenzene with Cl atoms on adjacent C atoms.

Other arrangements may be drawn, but they differ from the one shown only by a rotation of the molecule.

An important consequence of resonance is that it stabilizes a molecule by lowering its total energy. This stabilization makes benzene less reactive than expected for a molecule with three carbon–carbon double bonds. Resonance results in the greatest lowering of energy when the contributing structures have equal energies, as for the two Kekulé structures of benzene. However, in general, a molecule is a blend of all reasonable Lewis structures, including those with different energies. In these cases, the lowest energy structures contribute most strongly to the overall structure.

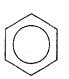
Resonance stabilization is a quantum mechanical effect: it is discussed further in Section 3.12.



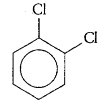
14 Benzene resonance structure

Resonance occurs only between structures with the same arrangement of atoms. For example, although we might be able to write two hypothetical structures for the dinitrogen oxide (nitrous oxide) molecule, NNO and NON, there is no resonance between them, because the atoms lie in different locations.

Resonance is a blending of structures with the same arrangement of atoms but different arrangements of electrons. It spreads multiple bond character over a molecule and results in a lower energy.



15 Benzene, C_6H_6



16 1,2-Dichlorobenzene, $C_6H_4Cl_2$

2.8 Formal Charge

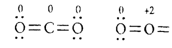
Different Lewis structures do not in general make the same contribution to a resonance structure. It is possible to decide which structures are likely to make the major contribution by comparing the number of valence electrons distributed around each atom in a structure with the number of valence electrons on each of the free atoms. The smaller these differences for a structure, the greater is its contribution to a resonance hybrid.

The **formal charge** on an atom in a given Lewis structure is the charge it would have if the bonding were perfectly covalent in the sense that the atom had exactly a half-share in the bonding electrons. That is, the formal charge takes into account the number of electrons that an atom can be regarded as "owning" in a molecule. It "owns" all its lone pairs and half of each shared bonding pair. The difference between this number and the number of valence electrons in the free atom is the formal charge:

$$\text{Formal charge} = V - (L + \tfrac{1}{2}B) \qquad (4)^*$$

where V is the number of valence electrons in the free atom, L is the number of electrons present on the bonded atom as lone pairs, and B is the number of bonding electrons on the atom. If the atom has more electrons in the molecule than when it is a free, neutral atom, then the atom has a negative formal charge, like a monatomic anion. If the assignment of electrons leaves the atom with fewer electrons than when it is free, then the atom has a positive formal charge, as if it were a monatomic cation.

Formal charge can be used to predict the most favorable arrangement of atoms in a molecule and the most likely Lewis structure for that arrangement: *a Lewis structure in which the formal charges of the individual atoms are closest to zero typically represents the lowest energy arrangement of the atoms and electrons.* A low formal charge indicates that an atom has undergone the least redistribution of electrons relative to the free atom. Such a structure has the lowest energy of all possible structures. For example, the formal charge rule suggests that the structure OCO is more likely for carbon dioxide than COO, as shown in (17). Similarly, it also suggests that the structure NNO is more likely than NON for dinitrogen monoxide, as shown in (18).



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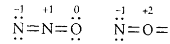


18

TOOLBOX 2.2 HOW TO USE FORMAL CHARGE TO DETERMINE THE MOST LIKELY LEWIS STRUCTURE

CONCEPTUAL BASIS

To assign a formal charge, we establish the "ownership" of the valence electrons of an atom in a molecule and compare that ownership with the free atom. An atom owns one electron of each bonding pair attached to it and owns its lone pairs completely. The most plausible Lewis structure will be the one in which the formal charges of the atoms are closest to zero.

PROCEDURE

Step 1 Decide on the number of valence electrons (V) possessed by each free atom by noting the number of its group in the periodic table.
Step 2 Draw the Lewis structures.
Step 3 For each bonded atom, count each electron in its lone pairs (L), plus one electron from each of its bonding pairs (B).
Step 4 For each bonded atom, subtract the total number of electrons it "owns" from V.

Each equivalent atom (the same element, the same number of bonds and lone pairs) has the same formal charge. A check on the calculated formal charges is that their sum is equal to the overall charge of the molecule or ion. For an electrically neutral molecule, the sum of the formal charges is zero. Compare the formal charges of each possible structure. The structure with the lowest formal charges represents the least disturbance of the electronic structures of the atoms and is the most plausible (lowest energy) structure.

This procedure is illustrated in Example 2.6.

EXAMPLE 2.6 Sample exercise: Selecting the most likely atom arrangement

One test for the presence of iron(III) ions in solution is to add a solution of potassium thiocyanate, KSCN, and obtain the blood-red color of a compound of iron and the thiocyanate ion. Write three Lewis structures with different atomic arrangements for the thiocyanate ion and select the most likely structure by identifying the structure with formal charges closest to zero. For simplicity, consider only structures with double bonds between neighboring atoms.

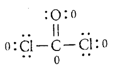
SOLUTION We proceed as set out in Toolbox 2.2.

	NCS^-	CNS^-	CSN^-
Step 1 Count the valence electrons V and, for ions, adjust for the charge.	C: 4, N: 5, S: 6 Charge: 1 Total: 16 electrons	C: 4, N: 5, S: 6 Charge: 1 Total: 16 electrons	C: 4, N: 5, S: 6 Charge: 1 Total: 16 electrons
Step 2 Draw Lewis structures.	$\ddot{N}=C=\ddot{S}$	$\ddot{C}=N=\ddot{S}$	$\ddot{C}=S=\ddot{N}$
Step 3 Assign electron ownership, $L + \frac{1}{2}B$.	$\overset{6}{N}=\overset{4}{C}=\overset{6}{S}$	$\overset{6}{C}=\overset{4}{N}=\overset{6}{S}$	$\overset{6}{C}=\overset{4}{S}=\overset{6}{N}$
Step 4 Find formal charge, $V - (L + \frac{1}{2}B)$.	$\overset{-1}{N}=\overset{0}{C}=\overset{0}{S}$	$\overset{-2}{C}=\overset{+1}{N}=\overset{0}{S}$	$\overset{-2}{C}=\overset{+2}{S}=\overset{-1}{N}$

The individual formal charges are closest to zero in the first column; the atom arrangement NCS^- is therefore the most likely one. The same conclusion would be reached if we considered Lewis structures based on the bonding pattern N≡C–S.

Self-Test 2.8A Suggest a likely structure for the poisonous gas phosgene, $COCl_2$. Write its Lewis structure and formal charges.

[*Answer:* See (19).]



19 Phosgene, $COCl_2$

Self-Test 2.8B Suggest a likely structure for the oxygen difluoride molecule. Write its Lewis structure and formal charges.

Although formal charge and oxidation number both give us information about the number of electrons around an atom in a compound, they are determined by different methods and often have different values. The formal charge exaggerates the covalent character of the bonds by assuming that the electrons are shared equally. Conversely, oxidation number (Sections D and K) is an exaggeration of the ionic character of bonds. It represents the atoms as ions, and all the electrons in a bond are assigned to the more electronegative atom. Thus, although the formal charge of C in structure **17** for CO_2 is 0, its oxidation number is +4 because all the bonding electrons are assigned to the oxygen atoms to give a structure that could be represented $O^{2-}C^{4+}O^{2-}$. Formal charges depend on the particular Lewis structure we write; oxidation numbers do not.

> *The formal charge gives an indication of the extent to which atoms have gained or lost electrons in the process of covalent bond formation; atom arrangements and Lewis structures with lowest formal charges are likely to have the lowest energy.*

EXCEPTIONS TO THE OCTET RULE

The octet rule accounts for the valences of many of the elements and the structures of many compounds. Carbon, nitrogen, oxygen, and fluorine obey the octet rule rigorously, provided there are enough electrons to go around. However, some compounds have an odd number of electrons. In addition, an atom of phosphorus, sulfur, chlorine, or another nonmetal in Period 3 and subsequent periods can accommodate more than eight electrons in its valence shell. The following two sections show how to recognize exceptions to the octet rule.

2.9 Radicals and Biradicals

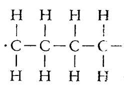
Some species have an odd number of valence electrons, and so at least one of their atoms cannot have an octet. Species having electrons with unpaired spins are called **radicals.** They are generally highly reactive. One example is the methyl radical, CH_3, which is so reactive that it cannot be stored. It occurs in the flames of burning hydrocarbon fuels. The single unpaired electron is indicated by the dot on the C atom in $\cdot CH_3$.

The older, still widely used term for radicals is *free radicals.*

Radicals are of crucial importance for the chemical reactions that take place in the upper atmosphere, where they contribute to the formation and decomposition of ozone. Radicals also play a role in our daily lives, sometimes a destructive one. They are responsible for the rancidity of foods and the degradation of plastics in sunlight. Damage from radicals can be delayed by an additive called an **antioxidant,** which reacts rapidly with radicals before the radicals have a chance to do their damage. Human aging is believed to be partly due to the action of radicals, and antioxidants such as vitamins C and E may delay the process (see Box 2.1). The nitric oxide molecule, NO, has an unpaired electron and plays an important role as a neurotransmitter. Because it is a radical, NO is very reactive and can be eliminated within a few seconds. Because it is small, the NO molecule can move easily throughout the body. These properties allow NO to play several roles, including controlling the supply of blood to various organs.

The role of radicals in the depletion of stratospheric ozone is developed further in Box 13.3.

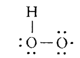
A **biradical** is a molecule with two unpaired electrons. The unpaired electrons are usually on different atoms, as depicted in (20). In that biradical, one unpaired electron is on one carbon atom of the chain and the second is on another carbon atom several bonds away. In some cases, though, both electrons are on the same atom. One of the most important examples is the oxygen atom itself. Its electron configuration is $[He]2s^22p_x^{\,2}2p_y^{\,1}2p_z^{\,1}$ and its Lewis symbol is $\cdot\ddot{O}\cdot$. The O atom has two unpaired electrons, and so it can be regarded as a special type of biradical.



20 A biradical

Self-Test 2.9A Write a Lewis structure for the hydrogenperoxyl radical, $HOO\cdot$, which plays an important role in atmospheric chemistry and which, in the body, has been implicated in the degeneration of neurons.

[*Answer:* See (21).]



21 Hydrogenperoxyl, $HO_2\cdot$

Self-Test 2.9B Write a Lewis structure for NO_2.

> *A radical is a species with an unpaired electron; a biradical has two unpaired electrons on either the same or different atoms.*

BOX 2.1はとばしてもよい。

BOX 2.1 **WHAT HAS THIS TO DO WITH . . . STAYING ALIVE?**

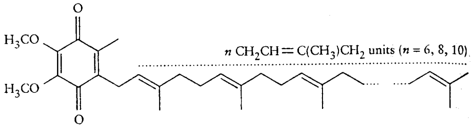
Chemical Self-Preservation

In nearly every pharmacy, supermarket, and health food store, you can find bottles of antioxidants and antioxidant-rich natural products, such as fish oils, *Gingko biloba* leaves, and wheat grass. These dietary supplements are intended to help the body control its population of radicals and, as a result, slow aging and degenerative diseases such as heart failure and cancer.

Radicals occur naturally in the body, partly as a by-product of metabolism. They serve many useful functions but can cause trouble if they are not eliminated when they are no longer needed. They often contain oxygen atoms and oxidize the *lipid* (fat) molecules that make up cell membranes and other vital tissues. This oxidation changes the structures of the lipid molecules and hence affects the function of the membranes. Cell membranes damaged in this way may not be able to protect cells against disease, and heart and nerve cells may lose their function. Recent evidence suggests that radical damage to living cells is the main factor in the aging process. When the nucleic acids such as DNA and RNA are attacked by radicals, they cannot replicate properly. These alterations result in defective cells with diminished function and a lessened ability to protect themselves against diseases such as cancer.

Leaves of the *Gingko biloba* tree, which originated in China. Extracts of these leaves are thought to have antioxidant properties. Some also believe that the extracts improve thinking ability by increasing oxygen flow to the brain.

The body maintains an antioxidant network consisting of vitamins A, C, and E, antioxidant enzymes, and a group of related compounds called coenzyme Q, for which the general formula is shown below. The *n* represents the number of times that a particular group is repeated; it can be 6, 8, or 10. *Antioxidants* are molecules that are easily oxidized, so they react readily with radicals before the radicals can react with other compounds in the body. Many common foods, such as green leafy vegetables, orange juice, and chocolate, contain antioxidants, as do coffee and tea.



Molecular structure of coenzyme Q, an antioxidant used by the body to control the level of radicals.

Harmful environmental conditions, such as ultraviolet radiation, ozone in the air we breathe, poor nutrition, and tobacco smoke can cause *oxidative stress*, a condition in which the concentration of radicals has become so high that the body's natural antioxidant network cannot cope. Premature aging of skin that has been overexposed to sunlight and lung cancer in smokers are two possible results. Herbal medicines containing certain *phytochemicals*, chemicals derived from plant sources and fish oils, are being investigated as antioxidants that can supplement the diet to protect against damage from free radicals. These same chemicals are also being studied for their ability to prolong life beyond the currently expected lifespan.

Related Exercises: 2.59, 2.60, 2.93, and 2.103.

For Further Reading: D. Harman, "The aging process," *Proceedings of the National Academy of Sciences*, 78 (2004), 7124. C. Goldberg, "The quest for immortality: Science at the frontiers of aging," *Science News*, **162** (August 31, 2002), 143.

2.10 Expanded Valence Shells

The octet rule tells us that eight electrons fill the outer shell of an atom to give a noble-gas ns^2np^6 valence-shell configuration. However, when the central atom in a molecule has empty *d*-orbitals, it may be able to accommodate 10, 12, or even more electrons. The electrons in such an **expanded valence shell** may be present as lone pairs or may be used by the central atom to form additional bonds.

A note on good practice: Although "expanded valence shell" is the logically precise term, most chemists still use the term *expanded octet.*

Because the additional electrons must be accommodated in valence orbitals, only nonmetal atoms in Period 3 or later periods can expand their valence shells.

Atoms of these elements have empty *d*-orbitals in the valence shell. Another factor—possibly the main factor—in determining whether more atoms than allowed by the octet rule can bond to a central atom is the size of that atom. A P atom is big enough for as many as six Cl atoms to fit comfortably around it, and PCl_5 is a common laboratory chemical. An N atom, though, is too small, and NCl_5 is unknown. A compound that contains an atom with more atoms attached to it than is permitted by the octet rule is called a **hypervalent compound**. This name leaves open the question of whether the additional bonds are due to valence-shell expansion or simply to the size of the central atom.

Elements that can expand their valence shells commonly show **variable covalence**, the ability to form different numbers of covalent bonds. Elements that have variable covalence can form one number of bonds in some compounds and a different number in others. Phosphorus is an example. It reacts directly with a limited supply of chlorine to form the toxic, colorless liquid phosphorus trichloride:

$$P_4(s) + 6\,Cl_2(g) \longrightarrow 4\,PCl_3(l)$$

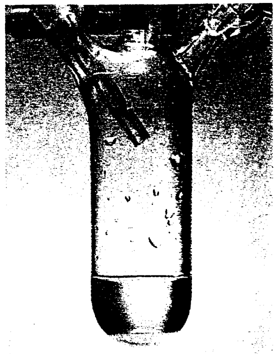
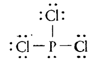


FIGURE 2.10 Phosphorus trichloride is a colorless liquid. When it reacts with chlorine (the pale yellow-green gas in the flask), it forms the very pale yellow solid phosphorus pentachloride (at the bottom of the flask).

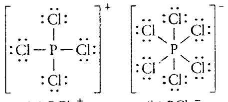
The Lewis structure of the PCl_3 molecule is shown in (22), and we see that it obeys the octet rule. However, when phosphorus trichloride reacts with more chlorine (Fig. 2.10), phosphorus pentachloride, a pale yellow crystalline solid, is produced:

$$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$$



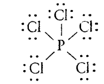
22 Phosphorus trichloride, PCl_3

Phosphorus pentachloride is an ionic solid consisting of PCl_4^+ cations and PCl_6^- anions; but, at 160°C, it vaporizes to a gas of PCl_5 molecules. The Lewis structures of the polyatomic ions and the molecule are shown in (23) and (24). In the anion, the P atom has expanded its valence shell to 12 electrons, by making use of two of its 3*d*-orbitals. In PCl_5, the P atom has expanded its valence shell to 10 electrons by using one 3*d*-orbital. Phosphorus pentachloride is therefore an example of a hypervalent compound in both its solid and its gaseous forms.



(a) PCl_4^+ (b) PCl_6^-

23 Phosphorus pentachloride, $PCl_5(s)$



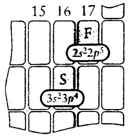
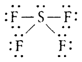
24 Phosphorus pentachloride, PCl_5

EXAMPLE 2.7 Writing a Lewis structure with an expanded valence shell

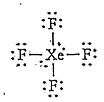
The fluoride SF_4 forms when a mixture of fluorine and nitrogen gases is passed over a film of sulfur at 275°C in the absence of oxygen and moisture. Write the Lewis structure of sulfur tetrafluoride and give the number of electrons in the expanded valence shell.

STRATEGY Because sulfur is in Period 3 and has empty 3*d*-orbitals available, it can expand its valence shell to accept additional electrons. After assigning all the valence electrons to bonds and lone pairs to give each atom an octet, assign any remaining electrons to the sulfur atom.

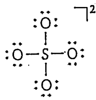
SOLUTION

Count the number of valence electrons.	6 from sulfur (·S̈·) 7 from each fluorine atom (:F̈·)	
Find the number of electron pairs.	There are 6 + (4 × 7) = 34 electrons, or 17 electron pairs.	
Construct the Lewis structure.	Give each F atom 3 lone pairs and 1 bonding pair shared with the central S atom; place the 2 extra electrons as a lone pair on the S atom.	

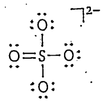
In this structure sulfur has 10 electrons in its expanded valence shell.



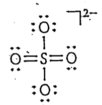
25 Xenon tetrafluoride, XeF_4



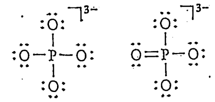
26a



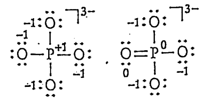
26b



26c



27



28

Self-Test 2.10A Write the Lewis structure for xenon tetrafluoride, XeF_4, and give the number of electrons in the expanded valence shell.

[*Answer:* See (25); 12 electrons]

Self-Test 2.10B Write the Lewis structure for the I_3^- ion and give the number of electrons in the expanded valence shell.

When different resonance structures are possible, some giving the central atom in a compound an octet and some an expanded valence shell, the dominant resonance structure is likely to be the one with the lowest formal charges. However, there are many exceptions and the selection of the best structure often depends on a careful analysis of experimental data.

EXAMPLE 2.8 Selecting the dominant resonance structure for a molecule

The sulfate ion, SO_4^{2-}, is present in a number of important minerals, including gypsum ($CaSO_4 \cdot 2H_2O$), which is used in cement, and Epsom salts ($MgSO_4 \cdot 7H_2O$), which is used as a purgative. Determine the dominant resonance structure of a sulfate ion from the three shown in (26) by calculating the formal charges on the atoms in each structure.

STRATEGY Follow the procedure in Toolbox 2.2. We need do only one calculation for equivalent atoms, such as the oxygen atoms in the first diagram, because they all have the same arrangement of electrons and hence the same formal charge.

SOLUTION We draw up the following table, in accord with Toolbox 2.2.

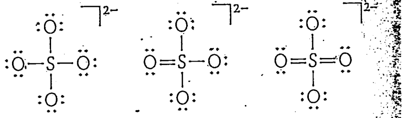
26a 26b 26c

Step 1 Count the valence electrons (V).

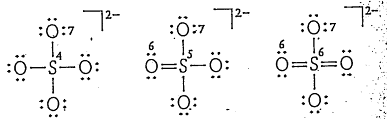
O: 6 S: 6

Total: 24 electrons, which provide 12 pairs of electrons

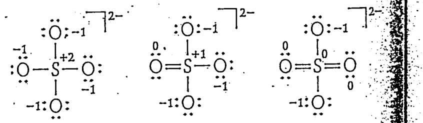
Step 2 Draw the Lewis structure.



Step 3 Assign electron ownership, ($L + \frac{1}{2}B$).



Step 4 Find the formal charge, $V - (L + \frac{1}{2}B)$.



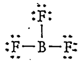
The individual formal charges are closest to zero in structure (26c); so that structure is likely to make the biggest contribution to the resonance hybrid, even though the valence shell on the S atom has expanded to hold 12 electrons.

Self-Test 2.11A Calculate the formal charges for the two Lewis structures of the phosphate ion shown in (27). Which structure is dominant?

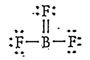
[*Answer:* See (28); the second structure.]

Self-Test 2.11B Calculate the formal charges for the three oxygen atoms in one of the Lewis structures of the ozone resonance structure (Example 2.5).

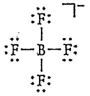
Octet expansion (expansion of the valence shell to more than eight electrons) can occur in elements of Period 3 and later periods. These elements can exhibit variable covalence and be hypervalent. Formal charge helps to identify the dominant resonance structure.



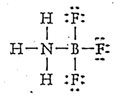
29 Boron trifluoride, BF_3



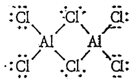
30 Boron trifluoride, BF_3



31 Tetrafluoroborate, BF_4^-



32 NH_3BF_3



33 Aluminum chloride, Al_2Cl_6

2.11 The Unusual Structures of Some Group 13/III Compounds

An unusual feature of the Lewis structure of the colorless gas boron trifluoride, BF_3 (29), is that the boron atom has an incomplete octet: its valence shell consists of only six electrons. We might expect the boron atom to complete its octet by sharing more electrons with fluorine, as depicted in (30), but fluorine has such a high ionization energy that it is unlikely to exist with a positive formal charge. Experimental evidence, such as the short B—F bond lengths, suggests that the true structure of BF_3 is a resonance hybrid of both types of Lewis structures, with the singly bonded structure making the major contribution.

The boron atom in BF_3 can complete its octet if an additional atom or ion with a lone pair of electrons forms a bond by providing *both* electrons. A bond in which both electrons come from one of the atoms is called a coordinate covalent bond. For example, the tetrafluoroborate anion, BF_4^- (31), forms when boron trifluoride is passed over a metal fluoride. In this anion, the formation of a coordinate covalent bond with a fluoride ion gives the B atom an octet. Another example of a coordinate covalent bond is that formed when boron trifluoride reacts with ammonia:

$$BF_3(g) + NH_3(g) \longrightarrow NH_3BF_3(s)$$

The Lewis structure of the product, a white molecular solid, is shown in (32). In this reaction, the lone pair on the nitrogen atom of ammonia, H_3N:, can be regarded as completing boron's octet in BF_3 by forming a coordinate covalent bond.

Boron trichloride, a colorless, reactive gas of BCl_3 molecules, behaves chemically like BF_3. However, the trichloride of aluminum, which is in the same group as boron, forms *dimers*, linked pairs of molecules. Aluminum chloride is a volatile white solid that vaporizes at 180°C to a gas of Al_2Cl_6 molecules. These molecules survive in the gas up to about 200°C and only then fall apart into $AlCl_3$ molecules. The Al_2Cl_6 molecule exists because a Cl atom in one $AlCl_3$ molecule uses one of its lone pairs to form a coordinate covalent bond to the Al atom in a neighboring $AlCl_3$ molecule (33). This arrangement can occur in aluminum chloride but not boron trichloride because the atomic radius of Al is bigger than that of B.

Compounds of boron and aluminum may have unusual Lewis structures in which boron and aluminum have incomplete octets or halogen atoms act as bridges.

黄色の部分は，自分で調べ学習してください。

IONIC VERSUS COVALENT BONDS

Ionic and covalent bonding are two extreme models of the chemical bond. Most actual bonds lie somewhere between purely ionic and purely covalent. When we describe bonds between nonmetals, covalent bonding is a good model. When a metal and nonmetal are present in a simple compound, ionic bonding is a good model. However, the bonds in many compounds seem to have properties between the two extreme models of bonding. Can we describe these bonds more accurately by improving the two basic models?

2.12 Correcting the Covalent Model: Electronegativity

All bonds can be viewed as resonance hybrids of purely covalent and purely ionic structures. For example, the structure of a Cl_2 molecule can be described as

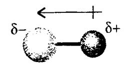
$$:\ddot{\underset{..}{Cl}}-\ddot{\underset{..}{Cl}}: \longleftrightarrow :\ddot{\underset{..}{Cl}}:^- \ \ddot{Cl}:^+ \longleftrightarrow :\ddot{Cl}^+ :\ddot{\underset{..}{Cl}}:^-$$

In this case, the ionic structures make only a small contribution to the resonance hybrid, and we regard the bond as almost purely covalent. Moreover, the two ionic structures have the same energy and make equal contributions to the hybrid; so the average charge on each atom is zero. However, in a molecule composed of different elements, such as HCl, the resonance

$$H-\ddot{\underset{..}{Cl}}: \longleftrightarrow H:^- \ \ddot{Cl}:^+ \longleftrightarrow H^+ :\ddot{\underset{..}{Cl}}:^-$$

has unequal contributions from the two ionic structures. The lower-energy ionic structure is $H^+ :\ddot{Cl}:^-$. Because the chlorine atom has a greater attraction for electrons than does the hydrogen atom, the structure with a negative charge on the Cl atom makes a bigger contribution than $H:^- \ddot{Cl}:^+$. As a result, there is a small net negative charge on the Cl atom and a small net positive charge on the H atom. Here we see the limitations of using formal charge alone to determine the distribution of electrons in a structure. The formal charge on each atom in HCl is zero.

The charges on the atoms in HCl are called **partial charges**. We show the partial charges on the atoms by writing $^{\delta+}H{-}Cl^{\delta-}$. A bond in which ionic contributions to the resonance result in partial charges is called a **polar covalent bond**. All bonds between atoms of different elements are polar to some extent. The bonds in homonuclear (same element) diatomic molecules and ions are nonpolar.



34 Dipole moment

The two atoms in a polar covalent bond form an **electric dipole**, a partial positive charge next to an equal but opposite partial negative charge. A dipole is represented by an arrow that points toward the negative partial charge (34). The size of an electric dipole—which is a measure of the magnitude of the partial charges—is reported as the **electric dipole moment**, μ (the Greek letter mu), in units called **debye** (D). The debye is defined so that a single negative charge (an electron) separated by 100. pm from a single positive charge (a proton) has a dipole moment of 4.80 D. The dipole moment associated with a Cl—H bond is about 1.1 D. We can think of this dipole as arising from a partial charge of about 23% of an electron's charge on the Cl atom and an equivalent positive charge on the H atom.

The debye is named for the Dutch chemist Peter Debye, who carried out important studies of dipole moments.

The SI unit of dipole moment is 1 C·m (1 coulomb meter). It is the dipole moment of a charge of 1 C separated from a charge of −1 C by a distance of 1 m; 1 D = 3.336 × 10^{-30} C·m.

A covalent bond is polar if one atom has a greater attraction for electrons than the other atom, because then the electron pair is more likely to be found closer to the former atom. In 1932, the American chemist Linus Pauling proposed a quantitative measure of electron distribution in bonds. The electron-pulling power of an atom when it is part of a molecule is called its **electronegativity**. Electronegativities are denoted χ (the Greek letter chi, pronounced "kye"). The atom of the element with the higher electronegativity has a stronger pulling power on electrons and tends to pull them away from the atom of the element with lower electronegativity (Fig. 2.11). Pauling based his scale on the dissociation energies, *D*, of the A—A, B—B, and A—B bonds, measured in electronvolts. He defined the difference in electronegativity of the two elements A and B as

Dissociation energies, a measure of the strengths of bonds, are discussed in Section 2.15.

$$|\chi_A - \chi_B| = 0.102\{D(A{-}B) - \tfrac{1}{2}[D(A{-}A) + D(B{-}B)]\}^{1/2} \qquad (5)$$

A simpler way of setting up a scale of electronegativities was devised by another American chemist, Robert Mulliken. In his approach, the electronegativity is the average of the ionization energy and electron affinity of the element (both expressed in electronvolts):

$$\chi = \tfrac{1}{2}(I + E_a) \qquad (6)$$

An atom gives up an electron reluctantly if the ionization energy is high. If the electron affinity is high, attaching electrons to an atom is energetically favorable. Elements with both these properties are reluctant to lose their electrons and tend to gain them; hence, they are classified as highly electronegative. Conversely, if the ionization energy and the electron affinity are both low, then it takes very little energy for the element to give up its electrons and it has little tendency to gain more; hence, the electronegativity is low.

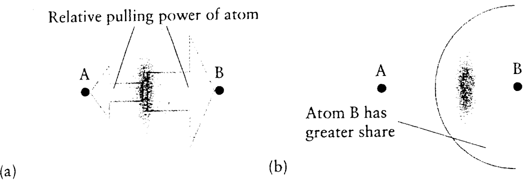
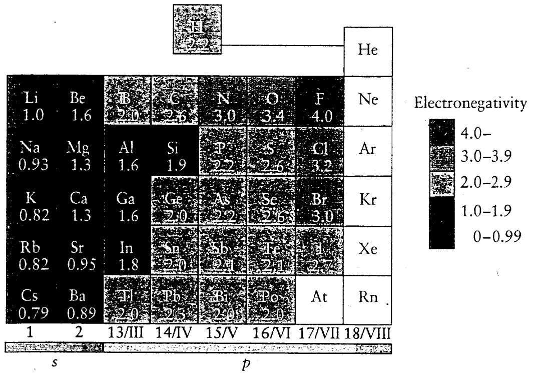


FIGURE 2.11 The electronegativity of an element is its electron-pulling power when it is part of a compound. (a) An atom with a high electronegativity (B) has a strong pulling power on the electrons (as represented by the larger arrow) that it shares with its neighbor, A. (b) The outcome of the tug-of-war is that the more electronegative atom has a greater share in the electron pair of the covalent bond. Electron density is symbolized by the green cloud in each image.



1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
			H 2.2				He
Li 1.0	Be 1.6	B 2.0	C 2.6	N 3.0	O 3.4	F 4.0	Ne
Na 0.93	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar
K 0.82	Ca 1.3	Ga 1.6	Ge 2.0	As 2.2	Se 2.6	Br 3.0	Kr
Rb 0.82	Sr 0.95	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7	Xe
Cs 0.79	Ba 0.89	Tl 2.0	Pb 2.3	Bi 2.0	Po 2.0	At	Rn

FIGURE 2.12 Variation in the electronegativity of the main-group elements (with the exception of the noble gases). Electronegativity tends to be high toward the upper-right corner of the periodic table and low on the lower left. Elements with low electronegativities (such as the *s*-block metals) are often called electropositive. These Pauling values are used throughout the text.

Figure 2.12 shows the variation in electronegativity for the main-group elements of the periodic table. Because ionization energies and electron affinities are highest at the top right of the periodic table (close to fluorine), it is not surprising to find that nitrogen, oxygen, bromine, chlorine, and fluorine are the elements with the highest electronegativities.

When the two atoms in a bond have only a small electronegativity difference, the partial charges are very small. As the difference in electronegativities increases, so do the partial charges. If the electronegativities are very different, then one atom can acquire the lion's share of the electron pair, and the corresponding ionic structure makes a large contribution to the resonance. Because it has largely robbed the other atom of its share of the electrons, the highly electronegative element resembles an anion and the other atom resembles a cation. We say that such a bond has considerable **ionic character**. If the difference in electronegativity is large, as in NaCl or KF, the ionic contribution dominates the covalent distribution, and it is better to regard the bond as ionic.

There is no hard-and-fast dividing line between ionic and covalent bonding. However, a good rule of thumb is that an electronegativity difference of about 2 means that there is so much ionic character present that the bond is best regarded as ionic (Fig. 2.13). For electronegativity differences smaller than about 1.5, a covalent description of the bond is probably reasonably reliable. For example, the electronegativities of carbon and oxygen are 2.6 and 3.4, an electronegativity difference of 0.8, and C—O bonds are best regarded as polar covalent. However, the electronegativity of calcium is 1.3, and Ca—O bonds, with an electronegativity difference of 2.1, are considered ionic.

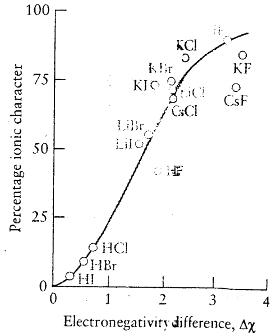


FIGURE 2.13 The dependence of the percentage ionic character of the bond on the difference in electronegativity, Δχ, between two bonded atoms for a number of halides.

Self-Test 2.12A In which of the following compounds do the bonds have greater ionic character: (a) P_4O_{10} or (b) PCl_3?

[*Answer:* (a)]

Self-Test 2.12B In which of the following compounds do the bonds have greater ionic character: (a) CO_2 or (b) NO_2?

Electronegativity is a measure of the pulling power of an atom on the electrons in a bond. A polar covalent bond is a bond between two atoms with partial electric charges arising from their difference in electronegativity. The presence of partial charges gives rise to an electric dipole moment.

2.13 Correcting the Ionic Model: Polarizability

All ionic bonds have some covalent character. To see how covalent character can arise, consider a monatomic anion (such as Cl^-) next to a cation (such as Na^+). As the cation's positive charge pulls on the anion's electrons, the spherical electron

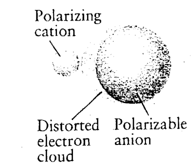


FIGURE 2.14 When a small, highly charged cation is close to a large anion, the electron cloud of the anion is distorted in the process we call polarization. The green sphere represents the shape of anion in the absence of a cation. The gray shadow shows how the shape of the sphere is distorted by the positive charge of the cation.

Cations are not significantly polarizable because their electrons are held so tightly.

cloud of the anion becomes distorted in the direction of the cation. We can think of this distortion as the tendency of an electron pair to move into the region between the two nuclei and to form a covalent bond (Fig. 2.14). Ionic bonds acquire more covalent character as the distortion of the electron cloud on the anion increases.

Atoms and ions that readily undergo a large distortion are said to be highly **polarizable**. An anion can be expected to be highly polarizable if it is large, such as an iodide ion, I^-. In such a large, highly polarizable ion, the ion's nucleus exerts only weak control over its outermost electrons because they are so far away. As a result, the electron cloud of the large anion is easily distorted.

Atoms and ions that can *cause* large distortions are said to have a high **polarizing power**. A cation can be expected to have a strong polarizing power if it is small and highly charged, such as an Al^{3+} cation. A small radius means that the center of charge of a highly charged cation can get very close to the anion, where it can exert a strong pull on the anion's electrons. Compounds composed of a small, highly charged cation and a large, polarizable anion tend to have bonds with considerable covalent character.

The polarizabilities of anions and the polarizing powers of cations follow the same diagonal relationships in the periodic table introduced in Section 1.20 and illustrated in Fig. 1.58. Cations become smaller, more highly charged, and hence more strongly polarizing, from left to right across a period. Thus, Be^{2+} is more strongly polarizing than Li^+, and Mg^{2+} is more strongly polarizing than Na^+. On the other hand, cations become larger and hence less strongly polarizing down a group. Thus, Na^+ is less strongly polarizing than Li^+, and Mg^{2+} is less strongly polarizing than Be^{2+}. Now we can see that, because polarizing power increases from Li^+ to Be^{2+} but decreases from Be^{2+} to Mg^{2+}, it follows that the polarizing power of the diagonal neighbors Li^+ and Mg^{2+} should be similar. We can expect such similarities in the properties of other diagonally related neighbors.

SELF-TEST 2.13A In which of the compounds NaBr and $MgBr_2$ do the bonds have greater covalent character?

[*Answer:* $MgBr_2$]

SELF-TEST 2.13B In which of the compounds CaS and CaO do the bonds have greater covalent character?

Compounds composed of highly polarizing cations and highly polarizable anions have a significant covalent character in their bonding.

THE STRENGTHS AND LENGTHS OF COVALENT BONDS

The characteristics of a covalent bond between two atoms are due mainly to the properties of the atoms themselves and vary only a little with the identities of the other atoms present in a molecule. Consequently, we can predict some characteristics of a bond with reasonable certainty once we know the identities of the two bonded atoms. For instance, the length of the bond and its strength are approximately the same regardless of the molecule in which it is found. Thus, to understand the properties of a large molecule, such as how DNA replicates in our cells and transmits genetic information, we can study the character of C=O and N—H bonds in much simpler compounds, such as formaldehyde, $H_2C{=}O$, and ammonia, NH_3.

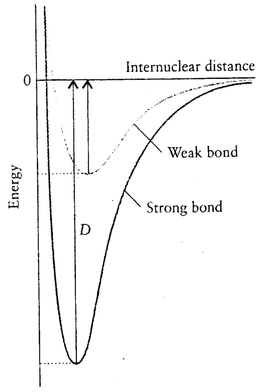


FIGURE 2.15 The variation of the energy of a diatomic molecule with internuclear separation for weak and strong bonds. The dissociation energy is a measure of the depth of the well. (In practice, we have to take into account the small zero-point energy of the vibrating molecule, and so the dissociation energy is slightly less than the depth of the well.)

2.14 Bond Strengths

The strength of a chemical bond is measured by its **dissociation energy**, *D*, the energy required to separate the bonded atoms. On a plot of the potential energy of a diatomic molecule as a function of the internuclear distance, the dissociation energy is the distance between the bottom of the energy well and the energy of the separated atoms (Fig. 2.15). The bond breaking is **homolytic**, which means that each atom retains one of the electrons from the bond. An example is

$$H{-}Cl(g) \longrightarrow \cdot H(g) + \cdot Cl(g)$$

A high dissociation energy indicates a deep potential energy well and therefore a strong bond that requires a lot of energy to break. The strongest known bond between two nonmetal atoms is the triple bond in carbon monoxide, for which the dissociation energy is 1062 kJ·mol^{-1}. One of the weakest bonds is that between the iodine atoms in molecular iodine, for which the dissociation energy is only 139 kJ·mol^{-1}.

The strength of a bond between two atoms is measured by its dissociation energy: the greater the dissociation energy, the stronger the bond.

TABLE 2.3 Bond Dissociation Energies of Diatomic Molecules (kJ·mol^{-1})

Molecule	Bond dissociation energy
H_2	424
N_2	932
O_2	484
CO	1062
F_2	146
Cl_2	230
Br_2	181
I_2	139
HF	543
HCl	419
HBr	354
HI	287

We shall not distinguish between the average dissociation energy and the average dissociation enthalpy, a concept to be introduced in Section 6.20. The two quantities differ by only a few kilojoules per mole.

2.15 Variation in Bond Strength

Tables 2.3 and 2.4 list a selection of typical dissociation energies. The values given in Table 2.4 are average dissociation energies for a number of different molecules. For instance, the strength quoted for a C—O single bond is the average strength of such bonds in a selection of organic molecules, such as methanol (CH_3—OH), ethanol (CH_3CH_2—OH), and dimethyl ether (CH_3—O—CH_3). The values should therefore be regarded as typical rather than as accurate values for a particular molecule.

TABLE 2.4 Average Bond Dissociation Energies (kJ·mol^{-1})

Bond	Average bond dissociation energy	Bond	Average bond dissociation energy
C—H	412	C—I	238
C—C	348	N—H	388
C=C	612	N—N	163
C⋯C*	518	N=N	409
C≡C	837	N—O	210
C—O	360	N=O	630
C=O	743	N—F	195
C—N	305	N—Cl	381
C—F	484	O—H	463
C—Cl	338	O—O	157
C—Br	276		

*In benzene.

The trends in bond strengths shown in Table 2.3 are explained in part by the Lewis structures for the molecules. Consider, for example, the diatomic molecules of nitrogen, oxygen, and fluorine (Fig. 2.16). Note the decline in bond strength as the bond order decreases—from 3 in N_2 to 1 in F_2. The triple bond in nitrogen is the origin of the inertness mentioned at the beginning of the chapter. A multiple bond is always stronger than a single bond between the same two atoms because more electrons bind the multiply bonded atoms. A triple bond between two atoms is always stronger than a double bond between the same two atoms, and a double bond is always stronger than a single bond between the same two atoms. However, a double bond between two carbon atoms is not twice as strong as a single bond, and a triple bond is a lot less than three times as strong. For example, we see that the average dissociation energy of a C=C double bond is 612 kJ·mol^{-1}, whereas it takes 696 kJ·mol^{-1} to break two C—C single bonds; similarly, the average dissociation energy of a C≡C triple bond is 837 kJ·mol^{-1}, but it takes 1044 kJ·mol^{-1} to break three C—C single bonds (Fig. 2.17). The origin of these differences is in part the repulsions between the electron pairs in a multiple bond, so each pair is not quite as effective at bonding as a pair of electrons in a single bond. Another contributing factor is that, as will be described in Section 3.4, the electrons in double and triple bonds are not as concentrated between the two atoms as they are in a single bond.

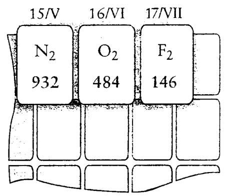


FIGURE 2.16 The bond dissociation energies, in kilojoules per mole of nitrogen, oxygen, and fluorine molecules. Note how the bonds weaken in the change from a triple bond in N_2 to a single bond in F_2.

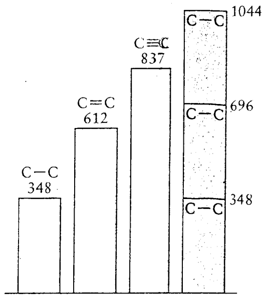


FIGURE 2.17 The strengths (in kilojoules per mole) of single and multiple bonds between two carbon atoms. Note that, for bonds between carbon atoms, a double bond is less than twice as strong as a single bond and a triple bond is less than three times as strong as a single bond, as shown by the fourth column.

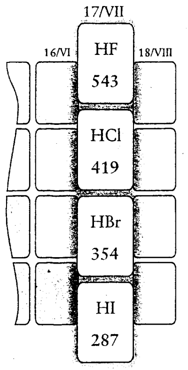


FIGURE 2.18 The bond dissociation energies of the hydrogen halide molecules in kilojoules per mole of molecules. Note how the bonds weaken as the halogen atom becomes larger.

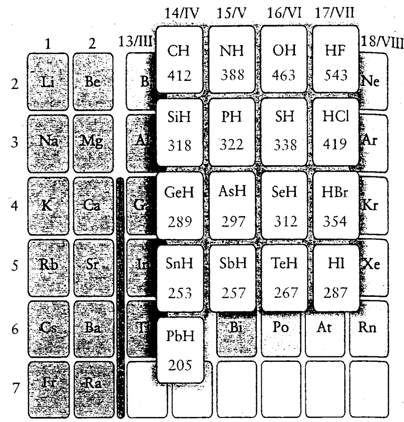
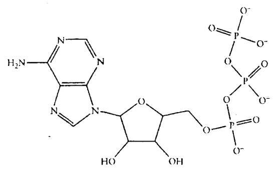


FIGURE 2.19 The dissociation energies for bonds between hydrogen and the *p*-block elements. The bond strengths decrease down each group as the atoms increase in size.

The values in Table 2.4 show how resonance affects the strengths of bonds. For example, the strength of a carbon–carbon bond in benzene is intermediate between that of a single and that of a double bond. Resonance spreads multiple bond character over the bonds between atoms: as a result, what were single bonds are strengthened and what were double bonds are weakened. The net effect overall is a stabilization of the molecule.

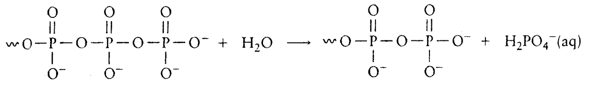
The presence of lone pairs may influence the strengths of bonds. Lone pairs repel each other; and, if they are on neighboring atoms, that repulsion can weaken the bond. This repulsion between lone pairs helps to explain why the bond in F_2 is weaker than the bond in H_2, because the latter molecule has no lone pairs.

Trends in bond strengths correlate with trends in atomic radii. If the nuclei of the bonded atoms cannot get very close to the electron pair lying between them, the two atoms will be only weakly bonded together. For example, the bond strengths of the hydrogen halides decrease from HF to HI, as shown in Fig. 2.18. The strength of the bond between hydrogen and a Group 14/IV element also decreases down the group (Fig. 2.19). This weakening of the bond correlates with a decrease in the stability of the hydrides down the group. Methane, CH_4, can be kept indefinitely in air at room temperature. Silane, SiH_4, bursts into flame on contact with air. Stannane, SnH_4, decomposes into tin and hydrogen. Plumbane, PbH_4, has never been prepared, except perhaps in trace amounts.



35

The relative strengths of bonds are important for understanding the way that energy is used in bodies to power our brains and muscles. For instance, adenosine triphosphate, ATP (35), is found in every living cell. The triphosphate part of this molecule is a chain of three phosphate groups. One of the phosphate groups is removed in a reaction with water. The P—O bond in ATP requires only 276 kJ·mol^{-1} to break and the new P—O bond formed in $H_2PO_4^-$ releases 350 kJ·mol^{-1} when it forms. As a result, the conversion of ATP to adenosine diphosphate, ADP, in the reaction



$$\sim O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O^- + H_2O \longrightarrow \sim O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O^- + H_2PO_4^-(aq)$$

(where the wiggly line indicates the rest of the molecule) can release energy that is used to power energy-demanding processes in cells.

Closely related to the strength of a bond is its stiffness (its resistance to stretching and compressing), with strong bonds typically being stiffer than weak bonds. The stiffness of bonds is studied by infrared (IR) spectroscopy, as described in Major Technique 1, which follows this chapter, and is used to identify compounds.

> *The bond strength increases as the multiplicity of a bond increases, decreases as the number of lone pairs on neighboring atoms increases, and decreases as the atomic radii increase. Bonds are strengthened by resonance.*

2.16 Bond Lengths

A **bond length** is the distance between the centers of two atoms joined by a covalent bond. It corresponds to the internuclear distance at the potential energy minimum for the two atoms (see Fig. 2.15). Bond lengths affect the overall size and shape of a molecule. The transmission of hereditary information in DNA, for instance, depends on bond lengths because the two strands of the double helix must fit together like pieces of a jigsaw puzzle (Section 19.15). Bond lengths are also crucial to the action of enzymes because only a molecule of the right size and shape will fit into the active site of the enzyme molecule (Section 13.15). As we see from Table 2.5, the lengths of bonds between Period 2 elements typically lie in the range from 100 pm to 150 pm. Bond lengths are determined experimentally by using either spectroscopy or x-ray diffraction (Box 2.2).

Bonds between heavy atoms tend to be longer than those between light atoms because heavier atoms have larger radii than lighter ones (Fig. 2.20). *Multiple bonds are shorter than single bonds* between the same two elements because the additional bonding electrons attract the nuclei more strongly and pull the atoms closer together: compare the lengths of the various carbon–carbon bonds in Table 2.5. We can also see the averaging effect of resonance: the length of the carbon–carbon bond in benzene is intermediate between the lengths of the single and double bonds of a Kekulé structure (but closer to that of a double bond). For bonds between atoms of the same two elements, *the stronger the bond, the shorter it is.* Thus, a C≡C triple bond is both stronger and shorter than a C=C double bond. Similarly, a C=O double bond is both stronger and shorter than a C—O single bond.

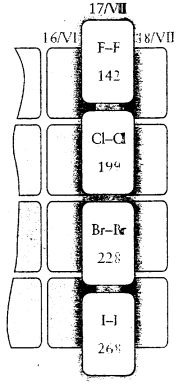


FIGURE 2.20 Bond lengths (in picometers) of the diatomic halogen molecules. Notice how the bond lengths increase down the group as the atomic radii become larger.

TABLE 2.5 Average and Actual Bond Lengths

Bond	Average bond length (pm)	Molecule	Bond length (pm)
C—H	109	H_2	74
C—C	154	N_2	110
C=C	134	O_2	121
C⩦C*	139	F_2	142
C≡C	120	Cl_2	199
C—O	143	Br_2	228
C=O	112	I_2	268
O—H	96		
N—H	101		
N—O	140		
N=O	120		

*In benzene.

BOX 2.2はとばしてもよい。

BOX 2.2 HOW DO WE KNOW . . . THE LENGTH OF A CHEMICAL BOND?

Because a chemical bond is only about 10^{-10} m long, special techniques have to be used to measure its length. There are two principal techniques: one for solids and the other for gases. The technique used for solids, x-ray diffraction, is described in Major Technique 3, following Chapter 5. *Microwave spectroscopy*, discussed here, is used to determine bond lengths in gas-phase molecules. This branch of spectroscopy makes use of the ability of rotating molecules to absorb microwave radiation, which has a wavelength close to 1 cm.

According to classical physics, a solid body such as a ball can rotate with any energy. According to quantum mechanics, however, rotational energy is quantized, and a body can rotate only with certain energies—that is, only at certain speeds. Let's see what that means for a diatomic molecule AB, with atomic masses m_A and m_B and bond length R. The molecule can rotate only with the following energies:

$$E = \frac{h^2 J(J+1)}{8\pi^2 \mu R^2} \qquad J = 0,1,2,\ldots$$

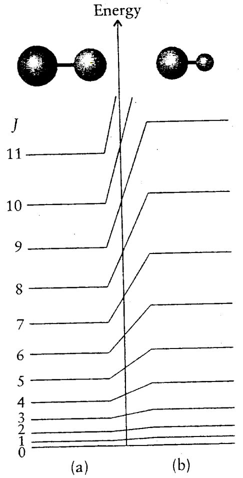
where $\mu = m_A m_B/(m_A + m_B)$, h is Planck's constant, and J is a quantum number. These energy levels are shown in the illustration (right) for two kinds of molecules, one with heavy atoms and a long bond (such as ICl) and the other with light atoms and a short bond (such as HF). We see that the energy levels are much closer together for the heavier molecule than for the lighter molecule. The minimum energy needed to excite a molecule into rotation from rest (corresponding to $J = 0$ and $E = 0$) is

$$\Delta E = \frac{h^2}{4\pi^2 \mu R^2}$$

Perhaps surprisingly, less energy is needed to excite a large heavy molecule than a small light molecule.

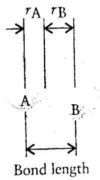
Because the energy needed to change the rotational state of a molecule depends on the masses of its atoms and the bond length we can calculate the bond length if we can measure the minimum energy needed to excite the molecule into rotation. Photons corresponding to microwave radiation can supply the energy needed to excite the molecule to higher rotational energies. Therefore, to determine a bond length, we pass a beam of microwave radiation through a gaseous sample, vary its frequency, and determine the frequency, ν (nu), that results in a strong absorption. The energy of the photons corresponding to this frequency is $h\nu$, and this value can be set equal to the expression for the energy difference given above. We then solve the resulting expression for the value of R, the bond length.

The technique as we have described it works only for polar molecules, because only they can interact with microwave radiation. However, variations of these spectroscopic methods can be used to investigate nonpolar molecules, too. A major limitation of the technique is that only the spectra of simple molecules can be interpreted. For complex molecules, we use solid samples and x-ray diffraction techniques.



The rotational energy levels of (a) a heavy diatomic molecule and (b) a light diatomic molecule. Note that the energy levels are closer together for the heavy diatomic molecule. Microwaves are absorbed when transitions take place between neighboring energy levels.

Each atom makes a characteristic contribution, called its **covalent radius**, to the length of a bond (Fig. 2.21). A bond length is approximately the sum of the covalent radii of the two atoms (36). The O—H bond length in ethanol, for example, is the sum of the covalent radii of H and O, 37 + 74 pm = 111 pm. We also see from Fig. 2.21 that the covalent radius of an atom taking part in a multiple bond is smaller than that for a single bond of the same atom.



36 Covalent radii

Covalent radii typically decrease from left to right across a period. The reason is the same as for atomic radii (Section 1.15): the increasing effective nuclear charge draws in the electrons and makes the atom more compact. Like atomic radii, covalent radii increase down a group because, in successive periods, the valence electrons occupy shells that are more distant from the nucleus and are better shielded by the inner core of electrons.

The covalent radius of an atom is the contribution it makes to the length of a covalent bond; covalent radii are added together to estimate the lengths of bonds in molecules.

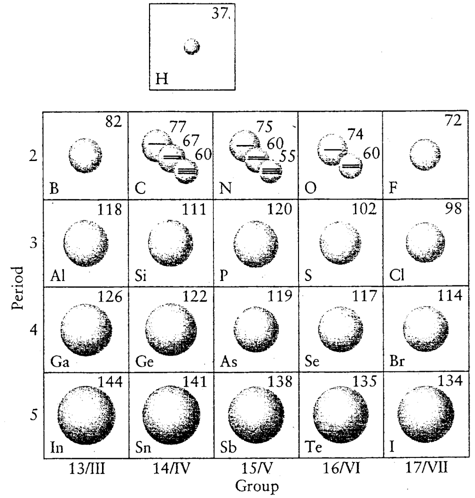


FIGURE 2.21 Covalent radii of hydrogen and the *p*-block elements (in picometers). Where more than one value is given, the values refer to single, double, and triple bonds. Covalent radii tend to become smaller toward fluorine. A bond length is approximately the sum of the covalent radii of the two participating atoms.

SKILLS YOU SHOULD HAVE MASTERED

- ☐ 1 Write the electron configuration for an ion (Example 2.1 and Self-Test 2.2).
- ☐ 2 Compare the relative lattice energies of two ionic compounds (Example 2.2).
- ☐ 3 Draw the Lewis structures of molecules and ions (Toolbox 2.1 and Examples 2.3, 2.4, and 2.7).
- ☐ 4 Write the resonance structures for a molecule (Example 2.5).
- ☐ 5 Use formal charge calculations to evaluate alternative Lewis structures (Toolbox 2.2 and Examples 2.6 and 2.8).
- ☐ 6 Predict which of two bonds has greater ionic or covalent character (Self-Tests 2.12 and 2.13).
- ☐ 7 Predict and explain periodic trends in the polarizability of anions and the polarizing power of cations (Section 2.13).
- ☐ 8 Predict and explain relative bond strengths and lengths (Sections 2.14–2.16).

練習問題をレポート課題とします。

EXERCISES

Ionic Bonds

2.1 Use data in Appendix 2D to predict which of the following pairs of ions would have the greatest coulombic attraction in a solid compound: (a) K^+, O^{2-}; (b) Ga^{3+}, O^{2-}; (c) Ca^{2+}, O^{2-}.

2.2 Use data from Appendix 2D to predict which of the following pairs of ions would have the greatest coulombic attraction in a solid compound: (a) Mg^{2+}, S^{2-}; (b) Mg^{2+}, Se^{2-}; (c) Mg^{2+}, O^{2-}.

2.3 Explain why the lattice energy of lithium chloride (861 kJ·mol^{-1}) is greater than that of rubidium chloride (695 kJ·mol^{-1}), given that they have similar arrangements of ions in the crystal lattice. See Appendix 2D.

2.4 Explain why the lattice energy of silver bromide (903 kJ·mol^{-1}) is greater than that of silver iodide (887 kJ·mol^{-1}), given that they have similar arrangements of ions in the crystal lattice. See Appendix 2D.

Electron Configurations of Ions

2.5 Give the number of valence electrons for each of the following elements: (a) Sb; (b) Si; (c) Mn; (d) B.

2.6 Give the number of valence electrons for each of the following elements: (a) I; (b) Ni; (c) Re; (d) Sr.

2.7 Give the ground-state electron configuration expected for each of the following ions: (a) S^{2-}; (b) As^{3+}; (c) Ru^{3+}; (d) Ge^{2+}.

2.8 Give the ground-state electron configuration expected for each of the following ions: (a) I^-; (b) Ni^{2+}; (c) Re^{4+}; (d) Sr^{2+}.

2.9 Give the ground-state electron configuration expected for each of the following ions: (a) Cu^+; (b) Bi^{3+}; (c) Ga^{3+}; (d) Tl^{3+}.

2.10 Give the ground-state electron configuration expected for each of the following ions: (a) Al^{3+}; (b) Tc^{4+}; (c) Ra^{2+}; (d) I^-.

2.11 The following species have the same number of electrons: Cd, In^+, and Sn^{2+}. (a) Write the electron configurations for each species. Are they the same or different? Explain. (b) How many unpaired electrons, if any, are present in each species? (c) What neutral atom, if any, has the same electron configuration as that of In^{3+}?

2.12 The following species have the same number of electrons: Ca, Ti^{2+}, and V^{3+}. (a) Write the electron configurations for each ion. Are they the same or different? Explain. (b) How many unpaired electrons, if any, are present in each species? (c) What neutral atom, if any, has the same electron configuration as that of Ti^{3+}?

2.13 Which M^{2+} ions (where M is a metal) are predicted to have the following ground-state electron configurations: (a) $[Ar]3d^7$; (b) $[Ar]3d^6$; (c) $[Kr]4d^4$; (d) $[Kr]4d^3$?

2.14 Which E^{3+} (where E is an element) ions are predicted to have the following ground-state electron configurations: (a) $[Xe]4f^{14}5d^8$; (b) $[Xe]4f^{14}5d^5$; (c) $[Kr]4d^{10}5s^25p^2$; (d) $[Ar]3d^{10}4s^2$?

2.15 Which M^{3+} ions (where M is a metal) are predicted to have the following ground-state electron configurations: (a) $[Ar]3d^6$; (b) $[Ar]3d^5$; (c) $[Kr]4d^5$; (d) $[Kr]4d^3$?

2.16 Which M^{2+} ions (where M is a metal) are predicted to have the following ground-state electron configurations: (a) $[Ar]3d^7$; (b) $[Kr]4d^7$; (c) $[Kr]4d^{10}5s^2$; (d) $[Xe]4f^{14}5d^{10}$?

2.17 For each of the following ground-state atoms, predict the type of orbital (1*s*, 2*p*, 3*d*, 4*f*, etc.) from which an electron will need to be removed to form the +1 ions: (a) Zn; (b) Cl; (c) Al; (d) Cu.

2.18 For each of the following ground-state ions, predict the type of orbital (1*s*, 2*p*, 3*d*, 4*f*, etc.) from which an electron will need to be removed to form the ions of one greater positive charge: (a) Ti^{3+}; (b) In^+; (c) Te^{2-}; (d) Ag^+.

2.19 Write the most likely charge for the ions formed by each of the following elements: (a) Br; (b) Te; (c) Cs; (d) Ga; (e) Cd.

2.20 Write the most likely charge for the ions formed by each of the following elements: (a) Sr; (b) Pb; (c) Sc; (d) I; (e) O.

2.21 Predict the number of valence electrons present for each of the following ions: (a) Mn^{4+}; (b) Rh^{3+}; (c) Co^{3+}; (d) P^{3+}.

2.22 Predict the number of valence electrons present for each of the following ions: (a) In^+; (b) Tc^{2+}; (c) Ta^{2+}; (d) Re^+.

2.23 Give the ground-state electron configuration and number of unpaired electrons expected for each of the following ions: (a) Sb^{3+}; (b) Sn^{4+}; (c) W^{2+}; (d) Br^-; (e) Ni^{2+}.

2.24 Give the ground-state electron configuration and number of unpaired electrons expected for each of the following ions: (a) Ga^+; (b) Cu^{2+}; (c) Pb^{2+}; (d) Se^{2-}.

2.25 For each of the following ground-state ions, predict the type of orbital (1*s*, 2*p*, 3*d*, 4*f*, etc.) that the electrons of highest energy will occupy: (a) Ca^{2+}; (b) In^+; (c) Te^{2-}; (d) Ag^+.

2.26 For each of the following ground-state ions, predict the type of orbital (1*s*, 2*p*, 3*d*, 4*f*, etc.) that the electrons of highest energy will occupy: (a) Fe^{2+}; (b) Bi^{3+}; (c) Si^{4+}; (d) Br^-.

2.27 Chlorine can exist in both positive and negative oxidation states. What is the maximum (a) positive and (b) negative oxidation number that chlorine can have? (c) Write the electron configuration for each of these states. (d) Explain how you arrived at these values.

2.28 Sulfur can exist in both positive and negative oxidation states. What is the maximum (a) positive and (b) negative oxidation number that sulfur can have? (c) Write the electron configuration for each of these states. (d) Explain how you arrived at these values.

2.29 On the basis of the expected charges on the monatomic ions, give the chemical formula of each of the following compounds: (a) magnesium arsenide; (b) indium(III) sulfide; (c) aluminum hydride; (d) hydrogen telluride; (e) bismuth(III) fluoride.

2.30 On the basis of the expected charges on the monatomic ions, give the chemical formula of each of the following compounds: (a) manganese(II) telluride; (b) barium arsenide; (c) silicon nitride; (d) lithium bismuthide; (e) zirconium(IV) chloride.

2.31 On the basis of the expected charges of the monatomic ions, give the chemical formula of each of the following compounds: (a) bismuth(III) oxide; (b) lead(IV) oxide; (c) thallium(III) oxide.

2.32 On the basis of the expected charges of the monatomic ions, give the chemical formula of each of the following compounds: (a) iron(II) sulfide; (b) cobalt(III) chloride; (c) magnesium phosphide.

Covalent Bonds

2.33 Write the Lewis structure of (a) CCl_4; (b) $COCl_2$; (c) ONF; (d) NF_3.

2.34 Write the Lewis structure of (a) SCl_2; (b) AsH_3; (c) $GeCl_4$; (d) $SnCl_2$.

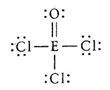
2.35 Write the Lewis structure of (a) tetrahydridoborate ion, BH_4^-; (b) hypobromite ion, BrO^-; (c) amide ion, NH_2^-.

2.36 Write the Lewis structure of (a) nitronium ion, ONO^+ (b) chlorite ion, ClO_2^-; (c) peroxide ion, O_2^{2-}; (d) formate ion, HCO_2^-.

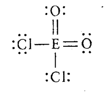
2.37 Write the complete Lewis structure for each of the following compounds: (a) formaldehyde, HCHO, which as its aqueous solution "formalin" is used to preserve biological specimens; (b) methanol, CH_3OH, the toxic compound also called wood alcohol; (c) glycine, $H_2C(NH_2)COOH$, the simplest of the amino acids, the building blocks of proteins.

2.38 Write the Lewis structure of each of the following organic compounds: (a) ethanol, CH_3CH_2OH, which is also called ethyl alcohol or grain alcohol; (b) methylamine, CH_3NH_2, a putrid-smelling substance formed when flesh decays; (c) formic acid, HCOOH, a component of the venom injected by ants.

2.39 The following Lewis structure was drawn for a Period 3 element. Identify the element.



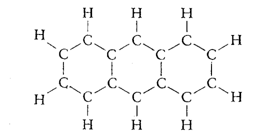
2.40 The following Lewis structure was drawn for a Period 3 element. Identify the element.



2.41 Write the complete Lewis structure for each of the following compounds: (a) ammonium chloride; (b) potassium phosphide; (c) sodium hypochlorite.

2.42 Write the complete Lewis structure for each of the following compounds: (a) zinc cyanide; (b) potassium tetrafluoroborate; (c) barium peroxide (the peroxide ion is O_2^{2-}).

2.43 Anthracene has the formula $C_{14}H_{10}$. It is similar to benzene but has 3 six-membered rings that share common C—C bonds, as shown below. Complete the structure by drawing in multiple bonds to satisfy the octet rule at each carbon atom. Resonance structures are possible. Draw as many as you can find.



2.44 Write the Lewis structures that contribute to the resonance hybrid of the guanadinium ion, $C(NH_2)_3^+$.

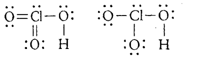
2.45 Draw the Lewis structures that contribute to the resonance hybrid of nitryl chloride, $ClNO_2$ (N is the central atom).

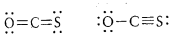
2.46 Do H—C≡N and H—N≡C form a pair of resonance structures? Explain your answer.

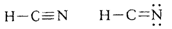
2.47 Draw the Lewis structure and determine the formal charge on each atom in (a) NO^+; (b) N_2; (c) CO; (d) C_2^{2-}; (e) CN^-.

2.48 Using only Lewis structures that obey the octet rule, draw the Lewis structures and determine the formal charge on each atom in (a) CH_3^+; (b) OCl^-; (c) BF_4^-.

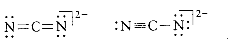
2.49 Determine the formal charge on each atom in the following molecules. Identify the structure of lower energy in each pair.

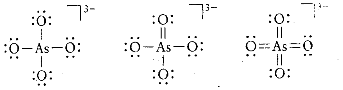
(a) 

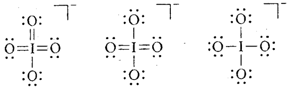
(b) 

(c) 

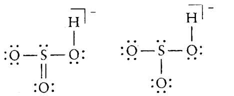
2.50 Determine the formal charge on each atom in the following ions. Identify the structure of lowest energy in each case.

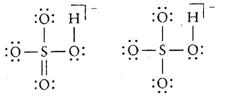
(a) 

(b) 

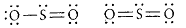
(c) 

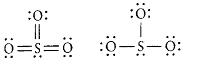
2.51 Two contributions to the resonance structure are shown below for each species. Determine the formal charge on each atom and then, if possible, identify the Lewis structure of lower energy for each species.

(a) 

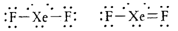
(b) 

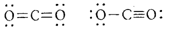
2.52 Two Lewis structures are shown below for each species. Determine the formal charge on each atom and then, if appropriate, identify the Lewis structure of lower energy for each species.

(a) 

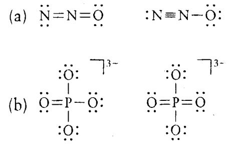
(b) 

2.53 Select from each of the following pairs of Lewis structures the one that is likely to make the dominant contribution to a resonance hybrid. Explain your selection.

(a) 

(b) 

2.54 Select from each of the following pairs of Lewis structures the one that is likely to make the dominant contribution to a resonance hybrid. Explain your selection.



Exceptions to the Octet Rule

2.55 Write the Lewis structure, including typical contributions to the resonance structure (where appropriate, allow for the possibility of octet expansion, including double bonds in different positions), for (a) sulfite ion; (b) hydrogen sulfite ion; (c) perchlorate ion; (d) nitrite ion.

2.56 Write the Lewis structure, including typical contributions to the resonance structure (where appropriate, allow for the possibility of octet expansion), for (a) dihydrogen phosphate ion; (b) chlorite ion; (c) chlorate ion; (d) nitrate ion.

2.57 Which of the following species are radicals? (a) NO_2^-; (b) CH_3; (c) OH; (d) CH_2O.

2.58 Which of the following species are radicals? (a) ClO_2; (b) Cl_2O; (c) BF_4^-; (d) BrO.

2.59 Write the Lewis structure of each of the following reactive species, all of which are found to contribute to the destruction of the ozone layer, and indicate which are radicals: (a) chlorine monoxide, ClO; (b) dichloroperoxide, Cl—O—O—Cl; (c) chlorine nitrate, $ClONO_2$ (the central O atom is attached to the Cl atom and to the N atom of the NO_2 group).

2.60 Write the Lewis structure of each of the following species and indicate which are radicals: (a) the superoxide ion, O_2^-; (b) the methoxy group, CH_3O; (c) XeO_4; (d) $HXeO_4^-$.

2.61 Determine the numbers of electron pairs (both bonding and lone pairs) on the iodine atom in (a) ICl_2^+; (b) ICl_4^-; (c) ICl_3; (d) ICl_5.

2.62 Determine the numbers of electron pairs (both bonding and lone pairs) on the phosphorus atom in (a) PCl_3; (b) PCl_5; (c) PCl_4^+; (d) PCl_6^-.

2.63 Write the Lewis structure for each of the following molecules or ions and give the number of electrons about the central atom: (a) SF_6; (b) XeF_2; (c) AsF_6^-; (d) $TeCl_4$.

2.64 Write the Lewis structure for each of the following molecules or ions and give the number of electrons about the central atom: (a) SiF_6^{2-}; (b) IF_7; (c) ClF_3; (d) BrF_2^+.

2.65 Write the Lewis structure and state the number of lone pairs on xenon, the central atom of each of the following compounds: (a) $XeOF_2$; (b) XeF_4; (c) $XeOF_4$.

2.66 Write the Lewis structure and state the number of lone pairs on the central atom of each of the following compounds: (a) ClF_3; (b) AsF_5; (c) SF_4.

Ionic Versus Covalent Bonds

2.67 List the halogens in order of increasing electronegativity.

2.68 Just as some elements are electronegative, others can be *electropositive*, a term meaning that the element will readily give up electrons. Elements that are least electronegative are the most electropositive. What trend exists among the alkali metals and the alkaline earth metals with respect to their electropositive character?

2.69 Place the following elements in order of increasing electronegativity: antimony, tin, selenium, indium.

2.70 Place the following elements in order of increasing electronegativity: oxygen, carbon, nitrogen, fluorine, silicon, phosphorus, sulfur.

2.71 For each pair, determine which compound has bonds with greater ionic character: (a) HCl or HI; (b) CH_4 or CF_4; (c) CO_2 or CS_2.

2.72 For each pair, determine which compound has bonds with greater ionic character: (a) PH_3 or NH_3; (b) SO_2 or NO_2; (c) SF_6 or IF_5.

2.73 Arrange the cations Rb^+, Be^{2+}, and Sr^{2+} in order of increasing polarizing power. Give an explanation of your arrangement.

2.74 Arrange the cations K^+, Mg^{2+}, Al^{3+}, and Cs^+ in order of increasing polarizing power. Give an explanation of your arrangement.

2.75 Arrange the anions Cl^-, Br^-, N^{3-}, and O^{2-} in order of increasing polarizability and give reasons for your decisions.

2.76 Arrange the anions N^{3-}, P^{3-}, I^-, and At^- in order of increasing polarizability and give reasons for your decisions.

The Strengths and Lengths of Covalent Bonds

2.77 Place the following molecules or ions in order of *decreasing* bond length: (a) the CO bond in CO, CO_2, CO_3^{2-}; (b) the SO bond in SO_2, SO_3, SO_3^{2-}; (c) the CN bond in HCN, CH_2NH, CH_3NH_2. Explain your reasoning.

2.78 Place the following molecules or ions in order of *decreasing* bond order: (a) NO bond in NO, NO_2, NO_3^-; (b) CC bond in C_2H_2, C_2H_4, C_2H_6; (c) CO bond in CH_3OH, CH_2O, CH_3OCH_3. Explain your reasoning.

2.79 Use the information in Fig. 2.21 to estimate the bond length of (a) the NN bond in hydrazine, H_2NNH_2; (b) the CO bond in CO_2; (c) the CO and CN bonds in urea, $OC(NH_2)_2$; (d) the NN bond in nitrogen hydride, HNNH.

2.80 Use the information in Fig. 2.21 to estimate the indicated bond length of (a) the CO bond in formaldehyde, H_2CO; (b) the CO bond in dimethyl ether, CH_3OCH_3; (c) the CO bond in methanol, CH_3OH; (d) the CS bond in methanethiol, CH_3SH.

2.81 Use the covalent radii in Fig. 2.21 to calculate the bond lengths in the following molecules. Account for the trends in your calculated values. (a) CF_4; (b) SiF_4; (c) SnF_4.

2.82 Which do you predict to have the strongest CN bond: (a) $NHCH_2$, (b) NH_2CH_3, or (c) HCN? Explain.

Integrated Exercises

2.83 In 1999, Karl Christe synthesized and characterized a salt that contained the N_5^+ cation, in which the five N atoms are connected in a long chain. This cation is the first all-nitrogen species to be isolated in more than 100 years. Draw the most important Lewis structure for this ion, including all equivalent resonance structures. Calculate the formal charges on all atoms.

2.84 Write three Lewis structures that follow the octet rule (including the most important structure) for the isocyanate ion, CNO^-. State which of the three Lewis structures is the most important and explain why it is probably the most important.

2.85 Write the Lewis structure, including resonance structures where appropriate, for (a) the oxalate ion, $C_2O_4^{2-}$ (there is a C—C bond with two oxygen atoms attached to each carbon atom); (b) BrO^+; (c) the acetylide ion, C_2^{2-}. Assign formal charges to each atom.

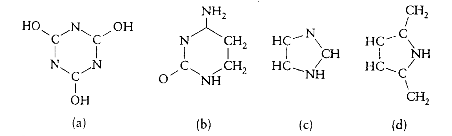
2.86 Draw resonance structures for the trimethylenemethane anion $C(CH_2)_3^{2-}$ in which a central carbon atom is attached to three CH_2 groups (CH_2 groups are referred to as methylene).

2.87 Show how resonance can occur in the following organic ions: (a) acetate ion, $CH_3CO_2^-$; (b) enolate ion, $CH_2COCH_3^-$, which has one resonance structure with a C=C double bond and an $-O^-$ group on the central carbon atom; (c) allyl cation, $CH_2CHCH_2^+$; (d) amidate ion, CH_3CONH^- (the O and the N atoms are both bonded to the second C atom).

2.88 White phosphorus is composed of tetrahedral molecules of P_4 in which each P atom is connected to three other P atoms. Draw the Lewis structure for this molecule. Does it obey the octet rule?

2.89 Nitrogen, oxygen, phosphorus, and sulfur exist as N_2, O_2, tetrahedral P_4, and cyclic S_8 molecules. Explain this fact in terms of the abilities of the atoms to form different types of bonds with one another.

2.90 Draw the most important Lewis structure for each of the following ring molecules (which have been drawn without showing the locations of the double bonds). Show all lone pairs and nonzero formal charges. If there are equivalent resonance forms, draw them.



2.91 An important principle in chemistry is the *isolobal analogy*. This very simple principle states that chemical fragments with similar valence orbital structures can replace one another in molecules. For example, $\cdot\dot{C}-H$ and $\cdot\dot{Si}-H$ are isolobal fragments, each having three electrons with which to form bonds in addition to the bond to H. An isolobal series of molecules would be HCCH, HCSiH, HSiSiH. Similarly, a lone pair of electrons can be used to replace a bond so that $\cdot\ddot{N}\colon$ is isolobal with $\cdot\dot{C}-H$ with the lone pair taking the place of the C—H bond. The isolobal set here is HCCH, HCN, NN. (a) Draw the Lewis structures for the molecules HCCH, HCSiH, HSiSiH, HCN, and NN. (b) Using the isolobal principle, draw Lewis structures for molecules based on the structure of benzene, C_6H_6, in which one or more CH groups are replaced with N atoms.

2.92 The cyclopentadienide ion, $C_5H_5^-$, is a common organic anion that forms very stable complexes with metal cations. The anion is derived by removing a proton from cyclopentadiene, C_5H_6, with strong base. The molecule has a five-membered ring of carbon atoms, with four carbon atoms attached to only one proton and one carbon atom bonded to two. Draw the Lewis structure of cyclopentadiene. Are resonance forms possible for this molecule? The ion $C_5H_5^-$ consists of a planar five-membered ring of carbon atoms, with one hydrogen atom attached to each carbon atom. Draw the Lewis structure for $C_5H_5^-$. How many resonance structures can you draw for this anion?

2.93 Hydrogen peroxide is a powerful oxidizing agent that can damage lung tissue. However, your body is capable of handling small doses of strong oxidizers, because the surface of your lungs is covered with epithelial lining fluid. This thin layer of fluid has several antioxidants dissolved in it, including vitamin C (ascorbic acid, $C_6H_8O_6$). Antioxidants react with oxidizing agents like hydrogen peroxide to form nontoxic products, as shown in the reaction below.

$$C_6H_8O_6 + H_2O_2 \longrightarrow C_6H_6O_6 + 2\,H_2O$$

(a) Verify, using oxidation numbers, whether, in this reaction, H_2O_2 is being reduced or oxidized. Is ascorbic acid being oxidized or reduced? (b) Calculate the formal charges of the atoms in H_2O_2 and H_2O. Which are more useful for determining whether the compound has been oxidized or reduced, oxidation numbers or formal charges? Justify your answer.

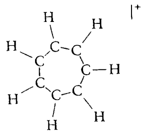
2.94 (a) Confirm that lattice energies are inversely proportional to the distance between the ions in MX (M = alkali metal, X = halide ion) by plotting the lattice energies of KF, KCl, and KI against the internuclear distances d_{M-X}. The lattice energies of KF, KCl, and KI are 826, 717, and 645 kJ·mol^{-1}, respectively. Use the ionic radii found in Appendix 2D to calculate d_{M-X}. How good is the correlation? You should use a standard graphing program to make the plot that will generate an equation for the line and calculate a correlation coefficient for the fit (see the Web site for this book). (b) Estimate the lattice energy of KBr from your graph. (c) Find an experimental value for the lattice energy of KBr in the chemical literature and compare that value with the value that you calculated in Part (b). How well do they agree?

2.95 (a) Explore whether the lattice energies of the alkali metal iodides are inversely proportional to the distances between the ions in MI (M = alkali metal) by plotting the lattice energies given below against the internuclear distances d_{M-I}.

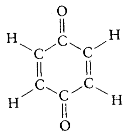
Alkali metal iodide	Lattice energy (kJ·mol^{-1})
LiI	759
NaI	700
KI	645
RbI	632
CsI	601

Use the ionic radii found in Appendix 2D to calculate d_{M-X}. How good is the correlation? Is a better fit obtained by plotting the lattice energies against $(1 - d^*/d)/d$, as suggested by the Born–Meyer equation? You should use a standard graphing program to make the plot that will generate an equation for the line and calculate a correlation coefficient for the fit (see the Web site for this book). (b) From the ionic radii given in Appendix 2D and the plot given in part (a), estimate the lattice energy for silver iodide. (c) Compare your results from part (b) with the experimentally determined value of 886 kJ·mol^{-1}. If they do not agree, provide an explanation for the deviation.

2.96 The framework for the tropylium cation, $C_7H_7^+$, is a seven-membered ring of carbon atoms with a hydrogen atom attached to each carbon atom. Complete the structural drawing by adding the multiple bonds as appropriate. Resonance structures are possible. Draw as many as you can find. Determine the C—C bond order.



2.97 Quinone, $C_6H_4O_2$, is an organic molecule with the structure shown below; it can be reduced to the anion $C_6H_4O_2^{2-}$. (a) Draw the Lewis structure of the reduced product. (b) On the basis of formal charges derived from the Lewis structure, predict which atoms in the molecule are most negatively charged. (c) If two protons are added to the reduced product, where are they most likely to bond?



2.98 In air, the NO radical can react with O_2. What is the most likely product of the reaction? Answer this question by drawing Lewis structures of the reactants and products.

2.99 The atomic numbers (Z), electronic configurations, and numbers of unpaired electrons for five ions are listed in the following table. Assume that all unpaired electrons have parallel spins. Indicate the element symbol, charge, and energy state (that is, ground state or excited state) for each of the five cases.

Z	Configuration	No. of unpaired electrons	Element	Charge	Energy state
26	$[Ar]3d^6$	4			
52	$[Kr]4d^{10}5s^2 5p^5 6s^1$	2			
16	$[Ne]3s^2 3p^6$	0			
39	$[Kr]4d^1$	1			
30	$[Ar]4s^2 3d^8$	2			

2.100 The atomic numbers (Z), electronic configurations, and numbers of unpaired electrons for five ions are listed in the following table. Assume that all unpaired electrons have parallel spins. Indicate the element symbol, charge, and energy state (that is ground state, excited state, etc.) for each of the five cases.

Z	Configuration	No. of unpaired electrons	Element	Charge	Energy state
38	$[Kr]5p^1$	1			
45	$[Kr]4d^7$	3			
43	$[Kr]4d^5 5s^1$	6			
8	[Ne]	0			
21	$[Ar]3d^1 4s^1$	2			

2.101 Draw the most important Lewis structure for each of the following molecules. Show all lone pairs and formal charges. Draw all equivalent resonance forms. (a) HONCO; (b) H_2CSO; (c) H_2CNN; (d) ONCN.

2.102 Determine the formal charges for the atoms in (a) CN^-; (b) CNO^-; (c) N_3^-.

2.103 A common biologically active radical is the pentadienyl radical, RCHCHCHCHCHR′, where the carbons form a long chain, with R and R′, which can be a number of different organic groups, at each end. Draw three resonance structures for this compound that maintain carbon's valence of four.

2.104 Sketch the qualitative molecular potential energy curves for the N—N bond on one graph for N_2H_4, N_2, and N_3^-.

2.105 Thallium and oxygen form two compounds with the following characteristics:

	Compound I	Compound II
Mass percentage Tl	89.49%	96.23%
Melting point	717°C	300°C

(a) Determine the chemical formulas of the two compounds. (b) Determine the oxidation number of thallium in each compound. (c) Assume that the compounds are ionic and write the electron configuration for each thallium ion. (d) Use the melting points to decide which compound has more covalent character in its bonds. Is your finding consistent with what you would predict from the polarizing abilities of the two cations?

2.106 How close are the Mulliken and Pauling electronegativity scales? (a) Use Eq. 6 to calculate the Mulliken electronegativities of C, N, O, and F. Use the values in $kJ \cdot mol^{-1}$ from Figs. 1.50 and 1.54 and divide each value by 230 $kJ \cdot mol^{-1}$ for this comparison. (b) Plot both sets of electronegativities as a function of atomic number on the same graph. (c) Which scale is more periodic (depends more consistently on position in the periodic table)?

2.107 The perchlorate ion, ClO_4^-, is described by resonance structures. (a) Draw the Lewis structures that contribute to the resonance hybrid and identify the most plausible Lewis structures by using formal charge arguments. (b) The average length of a single Cl—O bond is 172 pm and that of a double Cl=O bond can be estimated at 140 pm. The Cl—O bond length in the perchlorate ion is found experimentally to be 144 pm for all four bonds. Identify the most plausible Lewis structures of the perchlorate ion from these experimental data. (c) What is the oxidation number of chlorine in the perchlorate ion? Identify the most plausible Lewis structure by using the oxidation number, assuming that lone pairs belong to the atom to which they are attached but that all electrons shared in a bond belong to the atom of the more negative element. (d) Are these three approaches consistent? Explain why or why not.

2.108 Predict which bond will absorb light of shorter wavelength and explain why: C—H or C—Cl. Refer to Major Technique 1, which follows these exercises.

2.109 Infrared spectra show absorption due to C—H bond stretching at 3.38 μm for a methyl (—CH_3) group and at 3.1 μm for an alkyne (—C≡C—H) group. Which C—H bond is stiffer (has the larger force constant k), assuming that the vibrating atoms have the same effective mass? Refer to Major Technique 1, which follows these exercises.

2.110 Vibrational spectra are often so complicated that assignment of a particular absorption to a given bond is difficult. One way to confirm that an assignment is correct is to carry out selective isotopic substitution. For example, we can replace a hydrogen atom with a deuterium atom. If an iron-hydride (Fe—H) stretch occurs at 1950 cm^{-1}, at what energy will this stretch occur, approximately, for a compound that has deuterium in place of the hydrogen? Refer to Major Technique 1, which follows these exercises.

2.111 Certain gases, called greenhouse gases, contribute to global warming by absorbing infrared radiation. Only molecules with dipole moments or nonpolar molecules that undergo distortions that create momentary dipoles (such as CO_2, see Figure 2 in Major Technique 1, which follows these exercises) can absorb infrared radiation. Which of the following gases, all of which occur naturally in air, can function as greenhouse gases? (a) CO; (b) O_2; (b) O_3; (d) SO_2; (e) N_2O; (f) Ar.

2.112 One of the following compounds does not exist. Use Lewis structures to identify that compound. (a) C_2H_2; (b) C_2H_4; (c) C_2H_6; (d) C_2H_8.

2.113 Interhalogen compounds are compounds of two different halogens that have, with few exceptions, the general formula XX'_n. Examples include BrCl, ClF_3 and IF_5. Use Lewis structures to explain why n is always an odd number.

2.114 In the solid state, sulfur is sometimes found in rings of six atoms. (a) Draw a valid Lewis structure for S_6. (b) Is resonance possible in S_6? If so, draw one of the resonance structures.

2.115 Structural isomers are molecules that have the same formula but in which the atoms are connected in a different order. Two isomers of disulfur difluoride, S_2F_2, are known. In each the two S atoms are bonded to each other. In one isomer each of the S atoms is bonded to an F atom. In the other isomer, both F atoms are attached to one of the S atoms. (a) In each isomer the S—S bond length is approximately 190 pm. Are the S—S bonds in these isomers single bonds or do they have some double bond character? (b) Draw two resonance structures for each isomer. (c) Determine for each isomer which structure is favored by formal charge considerations. Are your conclusions consistent with the S—S bond lengths in the compounds?

2.116 Ionic compounds typically have higher boiling points and lower vapor pressures than covalent compounds. Predict which compound in the following pairs has the lower vapor pressure at room temperature: (a) Cl_2O or Na_2O; (b) $InCl_3$ or $SbCl_3$; (c) LiH or HCl; (d) $MgCl_2$ or PCl_3.

Chemistry Connections

2.117 The nitrogen oxides are common pollutants generated by internal combustion engines and power plants. They not only contribute to the respiratory distress caused by smog, but if they reach the stratosphere can also threaten the ozone layer that protects Earth from harmful radiation.

(a) The bond energy in NO is 632 $kJ \cdot mol^{-1}$ and that of each N—O bond in NO_2 is 469 $kJ \cdot mol^{-1}$. Using Lewis structures and the average bond energies in Table 2.4, explain the difference in bond energies between the two molecules and the fact that the bond energies of the two bonds in NO_2 are the same.

(b) The bond length in NO is 115 pm. Use Fig. 2.21 to predict the length of a single bond and a double bond between nitrogen and oxygen. Use Table 2.5 to estimate the length of a triple bond between nitrogen and oxygen. Predict the bond order in NO from its bond length and explain any difference from the calculated values.

(c) When the NO in smog reacts with NO_2 a bond forms between the two N atoms. Draw the Lewis structure of each reactant and the product and indicate the formal charge on each atom.

(d) The NO_2 in smog also reacts with NO_3 to form a product with an O atom between the two N atoms. Draw the Lewis structure of the most likely product and indicate the formal charge on each atom.

(e) Write the balanced chemical equation for the reaction of the product from part (d) with water to produce an acid. The acid produced acts as a secondary pollutant in the environment. Name the acid.

(f) If 4.05 g of the product from part (d) reacts with water as in part (e) to produce 1.00 L of acidic solution, what will be the concentration of the acid?

(g) Determine the oxidation number of nitrogen in NO, NO_2, and the products in parts (c) and (d). Which of these compounds would you expect to be the most potent oxidizing agent?