Chapter 4

A Survey of Inorganic Structures and Bonding

Molecular structure is the foundation on which chemistry, the study of matter and the changes it undergoes, rests. Much of chemistry is concerned with changes at the molecular level as structures are elucidated and chemical reactions occur. This is true not only in inorganic chemistry, but also in all areas of chemical science. Consequently, this chapter is devoted to an overview of some of the basic ideas concerning bonding and the structure of molecules. Although other aspects of bonding will be discussed in later chapters, this chapter is intended to provide an introduction to structural inorganic chemistry early in the study of the subject. More details concerning the structure of specific inorganic materials will be presented in later chapters, because most of the structures discussed here will be revisited in the context of the chemistry of the compounds. It should be kept in mind that for many purposes, a theoretical approach to bonding is not necessary. Accordingly, this chapter provides a nonmathematical view of molecular structure that is useful and adequate for many uses in inorganic chemistry. Because some of the principles are different for molecules that contain only single bonds, this topic will be introduced first.

In this chapter, the descriptions of molecular structure will be primarily in terms of a valence bond approach, but the molecular orbital method will be discussed in Chapter 5. As we shall see, construction of molecular orbital diagrams for polyatomic species is simplified by making use of symmetry, which will also be discussed in Chapter 5.
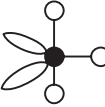
4.1 STRUCTURES OF MOLECULES HAVING SINGLE BONDS

One of the most important factors when describing molecules that have only single bonds is the repulsion that exists between electrons. Repulsion is related to the number of electron pairs both shared and unshared around the central atom. When only two pairs of electrons surround the central atom (as in BeH_2), the structure is almost always linear because that gives the configuration of lowest energy. When there are four pairs of electrons around the central atom (as in CH_4), the structure is tetrahedral. From your prior study of chemistry, the hybrid orbital types sp and sp^3 used to describe these cases are probably familiar. It is not unusual to hear someone say that CH_4 is tetrahedral because the carbon atom is sp^3 hybridized. However, CH_4 is tetrahedral because that structure represents the *configuration of lowest energy*, and our way of *describing* a set of orbitals that *matches* that geometry is by combining

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the wave functions for the $2s$ and three $2p$ orbitals. It can be shown that the four resulting orbitals point toward the corners of a tetrahedron.

Based on the requirement that repulsion should be minimized, idealized structures can be obtained based on the number of electrons surrounding the central atom. However, unshared pairs (sometimes called lone pairs) of electrons behave somewhat differently than do shared pairs. A shared pair of electrons is essentially localized in the region of space between the two atoms sharing the pair. An unshared pair of electrons is bound only to the atom on which they reside, and as a result, they are able to move more freely than a shared pair, so more space is required for an unshared pair. This has an effect on the structure of the molecule.

Figure 4.1 shows the common structural types that describe a very large number of inorganic molecules. Linear, trigonal planar, tetrahedral, trigonal bipyramid, and octahedral structures result when


■ **FIGURE 4.1**   Molecular structure based on hybrid orbital type.

there are 2, 3, 4, 5, and 6 bonding pairs, respectively, but no unshared pairs on the central atom. The hybrid orbital types for these structures are sp, sp^2, sp^3, sp^3d, and sp^3d^2, respectively.

Rationalizing the probable structure for a molecule involves finding the number of electrons around the central atom and placing them in orbitals pointing in directions that minimize repulsion. However, there are complications when the details of the structure are considered. For example, a molecule such as BF_3 has only three pairs of electrons around the central atom (three valence shell electrons from B and one from each F atom). Therefore, the structure that gives the lowest energy is a trigonal plane with bond angles of 120°,

$$
\begin{array}{c}
F \\
| \\
B \\
\diagup \quad \diagdown \\
F \qquad F
\end{array}
$$
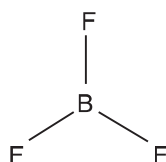
and the hybrid orbital type is sp^2. On the other hand, there are also six electrons around Sn in the gaseous $SnCl_2$ molecule (four valence electrons from Sn and one from each Cl atom). Molecules that have the same number of electrons are said to be *isoelectronic*. However, the hybrid orbital type may not be sp^2 because the bond angle certainly is *not* 120° in this case, and the structure of $SnCl_2$ is

$$
\begin{array}{c}
(\,\cdot\cdot\,) \\
Sn \\
\diagup \quad \diagdown \\
Cl \quad 95° \quad Cl
\end{array}
$$
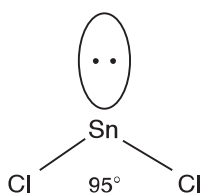
The unshared pair of electrons resides in an orbital that might be considered as sp^2, but since the electrons are held to only one atom, there is more space required than there is for a shared pair. A shared pair is more restricted in its motion because of being attracted to two atoms simultaneously. As a result, the repulsion between the unshared pair and the shared pairs is sufficient to force the bonding pairs closer together, which causes the bond angle to be much smaller than the expected 120°. In fact, the bond angle is much closer to that expected if p orbitals are used by Sn. On the other hand, the Sn–Cl bonds are quite polar, so the bonding electron pairs reside much closer to the Cl atoms, which makes it easier for the bond angle to be small than if they were residing close to the Sn atom.

In some molecules that involve sp^2 hybrid orbitals on the central atom, the bond angles deviate considerably from 120°. For example in F_2CO, the bond angle is 108°:

$$
\begin{array}{c}
F \\
\diagdown \\
108° \qquad C = O \\
\diagup \\
F
\end{array}
$$
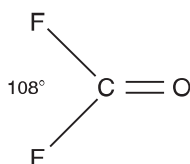
Various explanations have been proposed for the large deviation of the bonding from that expected on the basis of sp^2 hybrids. One simple approach to this problem is to consider that C–F bonds are quite polar with the shared electron pairs drawn closer to the fluorine atoms. Therefore, those bonding pairs are farther apart than they would be if they were being shared equally by C and F. There is less repulsion between the bonding pairs of electrons, and the effect of the C–O double bond is that the π orbitals give rise to some repulsion with the C–F bonding pairs, forcing them closer together. Using this approach, we would expect the bond angle in phosgene, Cl$_2$CO, to be *larger* than it is in F$_2$CO because the electron pairs in the C–Cl bonds will reside closer to the carbon atom than if the bonds were C–F. Therefore, the bonding electron pairs would be closer to each other in F$_2$CO than in Cl$_2$CO. In either case, the carbon atom is at the positive end of the bond dipole because both F and Cl atoms have higher electronegativities than carbon. The structure of Cl$_2$CO,
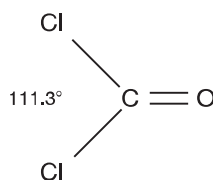
indicates that this interpretation is correct. Of course, the Cl atoms are larger than the F atoms, so it is tempting to attribute the larger bond angle in Cl$_2$CO to that cause. The structure of formaldehyde, H$_2$CO, is useful in this connection because the H atom is *smaller* than either F or Cl. However, the structure
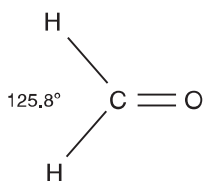
indicates that repulsion between the terminal atoms may not be significant. In this case, the H–C–H bond angle is *larger* than that expected for sp^2 hybrids on the central atom. When the polarity of the C–H bonds is considered, it is found that the carbon atom is at the *negative* end of the bond dipoles (see Chapter 6). Therefore, the C–H bonding pairs of electrons reside closer to the carbon atom (and hence closer to each other), and we should expect repulsion between them to cause the bond angle to be larger than 120°. The measured bond angle is in agreement with this rationale.

It is interesting to also see the difference in the bond angles in OF$_2$ and OCl$_2$, which have the structures
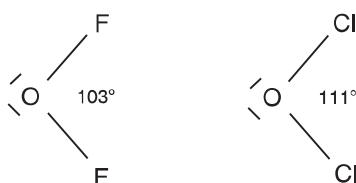
Although it might be tempting to ascribe this difference in bond angles to the difference in size between F and Cl, the location of *bonding* pairs of electrons is also important. The O–F bonds are polar with the bonding pairs closer to the fluorine atoms (and thus farther away from O and each other) allowing the bond angle to be smaller. The O–Cl bonds are polar, but with oxygen having the higher electronegativity, the shared pairs of electrons are closer to the oxygen atom (and to each other). As a result, there should be greater repulsion between the *bonding* pairs in OCl_2 than in OF_2, and the OCl_2 bond angle is the larger of the two in agreement with this rationale. In both cases, there are two unshared pairs of electrons on the oxygen atom, and the bond angle deviates from the tetrahedral angle. If the situation were as simple as the effect produced by the unshared pairs, we would expect the bond angle to be *slightly* larger in OCl_2 because the Cl atoms are larger than F. A difference of 8° probably indicates more repulsion between *bonding* pairs also.

In the CH_4 molecule, the bond angle is the expected value, 109° 28′. There are eight electrons around the carbon atom (four valence shell electrons from C and one from each H atom), which results in a regular tetrahedral structure. In the ammonia molecule, the nitrogen atom has eight electrons around it (five from the N atom and one from each H atom), but one pair of electrons is an unshared pair.
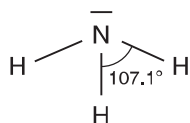
Although the hybrid orbital type used by N is sp^3, the bond angles in the NH_3 molecule are 107.1° rather than 109° 28′ found in a regular tetrahedron. The reason for this difference is that the unshared pair requires more space and forces the bonding pairs slightly closer together. Although a structure such as that just shown displays a *static* model, the ammonia actually undergoes a vibrational motion known as *inversion*. In this vibration, the molecule passes from the structure shown to that which is inverted by passing through a trigonal planar transition state:
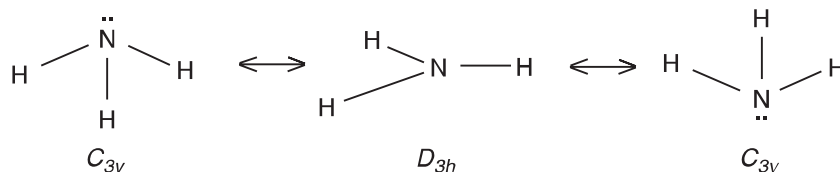
This vibration has a frequency that is approximately 1010 sec^{-1}. The barrier height for inversion is 2076 cm^{-1}, but the difference between the first and second vibrational states is only 950 cm^{-1}, which is equivalent to 1.14 kJ mol^{-1}. Using the Boltzmann distribution law, we can calculate that the second vibrational state is populated only to the extent of 0.0105, so clearly there is not a sufficient amount of thermal energy available to cause the *rapid* inversion if the molecule must pass *over* a barrier that is 2076 cm^{-1} in height. In this case, the inversion involves *quantum mechanical tunneling*, which means that the molecule passes from one structure to the other without having to pass *over* the barrier.

The structure of the H_2O molecule shows the effect of two unshared pairs of electrons:
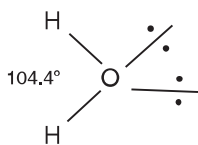
In this case, the two unshared pairs of electrons force the bonding pairs closer together so the observed bond angle is only 104.4°. Two unshared pairs in the H_2O molecule cause a greater effect than does one unshared pair in the NH_3 molecule. The effects that produce slight deviations from the bond angles expected for regular geometric structures are the result of a principle known as *valence shell electron pair repulsion*, VSEPR. The basis for this principle is that in terms of repulsion,

$$\text{unshared pair} - \text{unshared pair} > \text{shared pair} - \text{unshared pair} > \text{shared pair} - \text{shared pair}$$
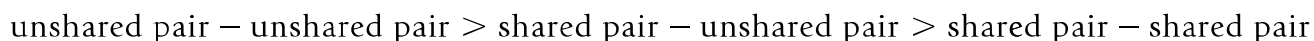
When the effects of unshared pairs are considered according to this scheme, not only is the correct overall structure often deduced, but also the slight deviations from regular bond angles are often predicted.

An interesting application of VSEPR is illustrated by the structure of SF_4. The sulfur atom has 10 electrons around it (six valence shell electrons from S and one from each of the four F atoms). We predict that the structure will be based on a trigonal bipyramid, but there are two possible structures:

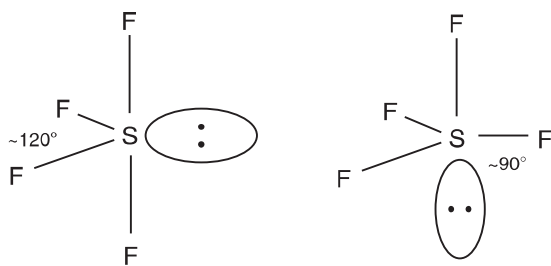Only one of these structures is observed for the SF_4 molecule. In the structure on the left, the unshared pair of electrons is located at ~90° from two bonding pairs and ~120° from the other two bonding pairs. In the structure on the right, the unshared pair is located at ~90° from three bonding pairs and 180° from the other bonding pair. These two possibilities may not look very different, but the repulsion between electron pairs is inversely related to the distance of separation raised to an exponent that may be as large as 6. A small difference in distance leads to a substantial difference in repulsion. As a result, the structure that has only two bonding electron pairs at 90° from the unshared pair is lower in energy, and the structure on the left is the correct one for SF_4. *In structures based on a trigonal bipyramid, unshared pairs of electrons are found in equatorial positions.*

Note that violations of the octet rule by the central atom occur with atoms such as sulfur and phosphorus. These are atoms that have *d* orbitals as part of their valence shells, so they are not limited to

a maximum of eight electrons. There is another interesting feature for molecules that are based on the trigonal bipyramid model for five bonds. If we consider the molecules PF_5 and PCl_5, there are 10 electrons around the phosphorus atom (five bonds) that point toward the corners of a trigonal bipyramid:
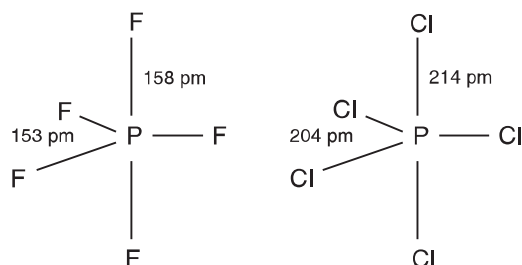
However, the bonds in the axial positions are slightly longer than those in the equatorial positions. For this type of structure, the hybrid bond type on the phosphorus atom is considered as sp^3d. However, the hybrid orbital type that gives three bonds in a trigonal plane is sp^2, and it can be shown that the dp combination is one that gives two orbitals directed at 180° from each other. Therefore, sp^3d hybrids can be considered as $sp^2 + dp$, and the bond lengths reflect the fact that the orbitals used in bonding three of the chlorine atoms are different than for the other two. This is a general characteristic of molecules having five pairs of electrons around the central atom in a structure based on a trigonal bipyramid, and the axial bonds are usually longer than those in the equatorial plane.

One of the interesting aspects of the structure in which five pairs of electrons surround the central atom is that the equatorial positions make use of sp^2 hybrids whereas the axial bonds are dp. As we have seen, any *unshared* pairs of electrons are found in *equatorial* positions. A further consequence of this is that peripheral atoms of high electronegativity bond best to orbitals of low s character, and peripheral atoms of low electronegativity bond better to orbitals of high s character. The result of this preference is that if the mixed halide PCl_3F_2 is prepared, the fluorine atoms are found in axial positions. Also, atoms that can form multiple bonds (which usually have lower electronegativity) bond better to orbitals of higher s character (the sp^2 equatorial positions).

In view of the principles just described, the molecule PCl_2F_3 would be expected to have two fluorine atoms in the axial positions and two chlorine atoms and one fluorine atom in equatorial positions. However, at temperatures greater than $-22\,°C$, the nuclear magnetic resonance (NMR) spectrum of PCl_2F_3 shows only one doublet, which results from the splitting of the fluorine resonance by the ^{31}P. When the NMR is taken at $-143\,°C$, the NMR spectrum is quite different and shows the presence of fluorine atoms bonded in more than one way. It is evident that at temperatures above $-22\,°C$ either all of the fluorine atoms are equivalent or somehow they exchange rapidly so that only fluorine atoms in one environment are present. Earlier, the inversion vibration of the NH_3 molecule, which has a frequency that is on the order of 1010 sec^{-1}, was described. The question arises as to what type of structural change could occur in PCl_2F_3 or PF_5 that would make the fluorine atoms in equatorial and axial positions appear

equivalent on the time scale of NMR experiments. A mechanism that is believed to correctly describe this situation is known as the *Berry pseudorotation,* and it is illustrated in the following scheme:
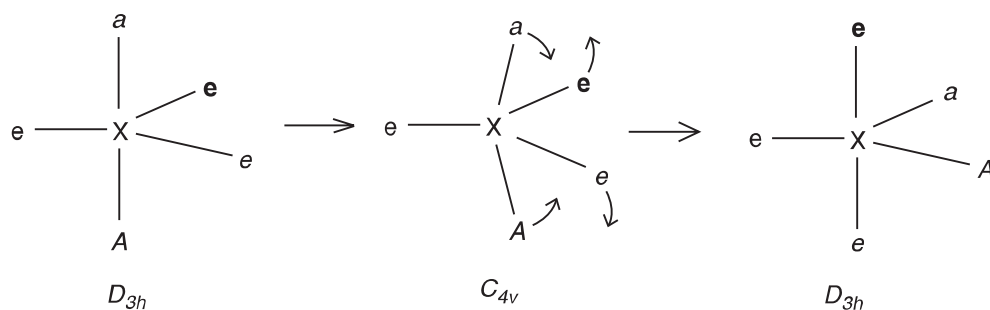
In this process, the groups initially in equatorial positions are e, *e*, and **e**, whereas those in axial positions are *a* and *A*. These designations are only to keep track of the positions, because all peripheral atoms would have to be identical for the symmetry designations to be correct. The molecule passes through a square base pyramid configuration as the rotation of four of the groups occurs. This mechanism is similar to the inversion of the ammonia molecule except for the fact that the movement of atoms is by *rotational* motion. At very low temperature, thermal energy is low and the vibration occurs slowly enough that the fluorine resonance indicates fluorine atoms in two different environments (axial and equatorial). At higher temperatures, the structural change is rapid, and only one fluorine environment is indicated. As we saw for NH_3, not all molecules have static structures.

Perhaps no other pair of molecules exhibits the effect of molecular structure on reactivity like SF_4 (sp^3d orbitals) and SF_6 (sp^3d^2 orbitals), whose structures are
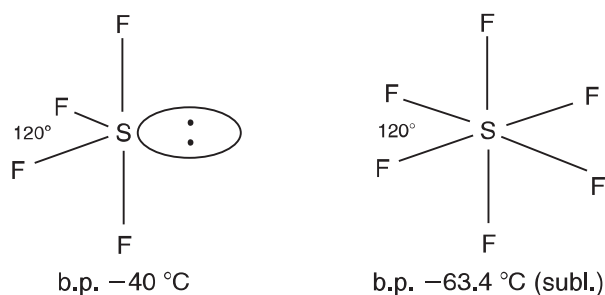
SF_6 is a remarkably inert compound. In fact, it is so unreactive that it is used as a gaseous dielectric material. Also, the gas can be mixed with oxygen to create a kind of synthetic atmosphere, and rats can breathe the mixture for several hours with no ill effects. On the other hand, SF_4 is a very reactive molecule that reacts with H_2O rapidly and vigorously:

$$SF_4 + 3\,H_2O \rightarrow 4\,HF + H_2SO_3 \tag{4.1}$$

Because of the instability of H_2SO_3, this reaction can also be written as

$$SF_4 + 2\,H_2O \rightarrow 4\,HF + SO_2 \tag{4.2}$$

The fact that SF_6 does not react with water is not due to thermodynamic stability. Rather, it is because there is no low-energy pathway for the reaction to take place (kinetic stability). Six fluorine atoms surrounding the sulfur atom effectively prevent attack, and the sulfur atom has no unshared pairs of electrons where other molecules might attack. In SF_4, not only is there sufficient space for an attacking species to gain access to the sulfur atom, but also the unshared pair is a reactive site. As a result of these structural differences, SF_6 is relatively inert, whereas SF_4 is very reactive.

There are several compounds that consist of two different halogens. These *interhalogen* compounds have structures that contain only single bonds and unshared pairs of electrons. For example, in BrF_3, the bromine atom has 10 electrons surrounding it (seven valence shell electrons and one from each fluorine atom). The structure is drawn to place the unshared pairs of electrons in equatorial positions based on a trigonal bipyramid. Because of the effects of the unshared pairs of electrons, the axial bonds are forced closer together to give bond angles of 86°:
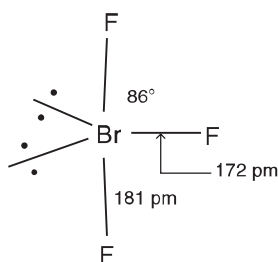
Except for slight differences in bond angles, this is also the structure for ClF_3 and IF_3. When IF_3 reacts with SbF_5, the reaction is

$$IF_3 + SbF_5 \rightarrow IF_2{}^+ + SbF_6{}^- \tag{4.3}$$

The structure of $IF_2{}^+$ can be deduced by recognizing that there are eight electrons around the iodine atom. There are seven valence electrons from I, one from each of the two fluorine atoms, but one electron has been removed, giving the positive charge. The electrons will reside in four orbitals pointing toward the corners of a tetrahedron, but two pairs are unshared.
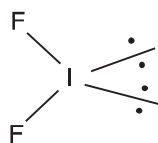
Note that the structures of many of these species are similar to the model structures shown in Figure 4.1. Although the hybrid orbital type is sp^3, the structure is characterized as bent or angular, not

tetrahedral. On the other hand, the IF_2^- ion, which has 10 electrons around the iodine atom, has a linear structure.
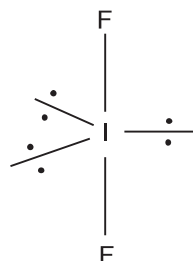
Note that in this case the unshared pairs of electrons are in equatorial positions, which results in a linear structure for IF_2^- even though the hybrid orbital type is sp^3d. It is the arrangement of *atoms*, not electrons, that determines the structure for a molecule or ion. It is apparent that the simple procedures described in this section are adequate for determining the structures of many molecules and ions in which there are only single bonds and unshared pairs of electrons.

Xenon forms several compounds with fluorine, among which are XeF_2 and XeF_4. With filled s and p valence shell orbitals, the xenon atom provides eight electrons while each fluorine atom contributes one electron. Therefore, in XeF_2, there are 10 electrons around the Xe atom, which makes the XeF_2 molecule isoelectronic with the IF_2^- ion. Both XeF_2 and IF_2^- are linear. In XeF_4, there are 12 electrons around the Xe atom, which results in the structure being
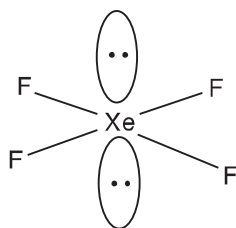

The molecule is square planar, as is IF_4^-, which is isoelectronic with XeF_4.

Although we have described the structures of several molecules in terms of hybrid orbitals and VSEPR, not all structures are this simple. The structures of H_2O (bond angle 104.4°) and NH_3 (bond angles 107.1°) were described in terms of sp^3 hybridization of orbitals on the central atom and *comparatively small* deviations from the ideal bond angle of 109° 28' caused by the effects of unshared pairs of electrons. If we consider the structures of H_2S and PH_3 in those terms, we have a problem. The reason is that the bond angle for H_2S is 92.3°, and the bond angles in PH_3 are 93.7°. Clearly, there is more than a minor deviation from the expected tetrahedral bond angle of 109° 28' caused by the effect of unshared pairs of electrons!

If the bond angles in H_2S and PH_3 were 90°, we would suspect that the orbitals used in bonding were the $3p$ valence shell orbitals. The sulfur atom has two of the p orbitals singly occupied, and overlap of hydrogen $1s$ orbital could produce two bonds at 90°. Similarly, the phosphorus atom has the three $3p$ orbitals singly occupied, and overlap of three hydrogen $1s$ orbitals could lead to three bonds at 90°. Although we were correct to assume that sp^3 orbitals were used by the central atoms in H_2O and NH_3, it appears that we are not justified in doing so for H_2S and PH_3.

Why does hybridization occur when the central atom is oxygen or nitrogen but not when it is S or P? The answer lies in the fact that there are two major results of hybridization of orbitals. The first is that the orbitals are directed in space at different angles than are the unhybridized atomic orbitals. We have already seen the types of structures that result and how less repulsion results. However, the other result of hybridization is that the orbitals are *changed in size*. The hybridization of 3s and 3p orbitals on sulfur or phosphorus would produce more favorable bond angles with regard to repulsion, but the overlap between those orbitals and the hydrogen 1s orbitals is less effective. The hydrogen orbital can overlap better with a smaller unhybridized p orbital on sulfur or phosphorus. The result is that the orbitals used by the central atom have a very slight degree of hybridization but closely resemble pure p orbitals. Based on this analysis, we would expect that H_2Se and AsH_3 would have bond angles that deviate even more from the tetrahedral bond angle. In accord with this, the bond angles for these molecules are 91.0° and 91.8°, respectively, indicating that the bonding orbitals on the central atoms are nearly pure p orbitals. The hydrogen compounds of the heavier members of groups V and VI have bond angles that are even closer to right angles (H_2Te, 90°; SbH_3, 91.3°).

4.2 RESONANCE AND FORMAL CHARGE

For many species, the approach taken earlier with molecules that have only single bonds and unshared pairs of electrons is inadequate. For example, the molecule CO has only 10 valence shell electrons with which to achieve an octet around each atom. The structure |C≡O| makes use of exactly 10 electrons, and that makes it possible to place an octet (three shared pairs and one unshared pair) around each atom. A simple procedure for deciding how to place the electrons is as follows:

1. Determine the total number of valence shell electrons from all of the atoms (N) that are available to be distributed in the structure.

2. Multiply the number of atoms present by eight to determine how many electrons would be required to give an octet around each atom (S).

3. The difference ($S–N$) gives the number of electrons that must be shared in the structure.

4. If possible, change the distribution of electrons to give favorable formal charges (discussed later in this chapter) on the atoms.

For CO, the total number of valence shell electrons is 10, and to give octets around two atoms would require 16 electrons. Therefore, $16 - 10 = 6$ electrons must be shared by the two atoms. Six electrons are equivalent to three pairs or three covalent bonds. Thus, we are led to the structure for CO that was shown earlier.

For a molecule such as SO_2, we find that the number of valence shell electrons is 18, whereas three atoms would require 24 electrons to make three octets. Therefore, $24 - 18 = 6$, the number of electrons that must be shared, which gives a total of three bonds between the sulfur atom and the two oxygen atoms. However, because we have already concluded that each atom in the molecule must have an octet of electrons around it, the sulfur atom must also have an unshared pair of electrons

that is localized in the atom in addition to the three pairs that it is sharing. This can be shown as in the structure
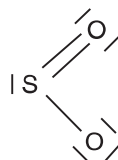
However, the same features are shown in the structure
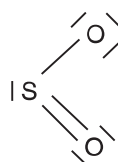
A situation in which the electrons can be arranged in more than one way constitutes *resonance*. In Chapter 3, the resonance structures HF and $H^+ F^-$ were used to describe HF, but in the case of SO_2 neither of the resonance structures contains ions. The structures just shown involve different ways of arranging the electrons that still conform to the octet rule. The true structure of SO_2 is one that lies halfway between the two structures shown (a hybrid made up of equal contributions from these two structures). It does *not* spend part of the time as one structure and part of the time as the other. The molecule is *all* of the time a *resonance hybrid* of the structures shown. In this case, the two structures contribute equally to the true structure, but this is not always the case. As a result of the unshared pair of electrons on the sulfur atom, the bond angle in SO_2 is 119.5°.

The double bond that is shown in each of the two structures just shown is not localized as is reflected by the two resonance structures. However, the two single bonds and the unshared pair are localized as a result of the hybrid orbitals in which they reside. The hybrid orbital type is sp^2, which accounts for the bond angle being 119.5°. There is one p orbital not used in the hybridization that is perpendicular to the plane of the molecule, which allows for the π bonding to the two oxygen atoms simultaneously. The π bond is described as being *delocalized*, and this can be shown as follows:
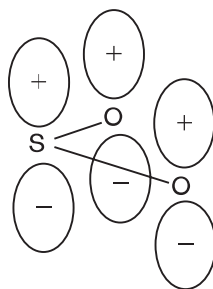

A single S–O bond has a length of approximately 150 pm, but as a result of the multiple bonding between sulfur and oxygen, the observed bond length in SO_2 where the bond order is 1.5 is 143 pm.

The following are rules that apply to drawing resonance structures. Remember that resonance relates to different ways of placing electrons in the structures, not ways of arranging the atoms themselves.

1. The atoms must be in the same relative positions in all structures drawn. For example, it can be demonstrated experimentally that the SO_2 molecule has a bent or angular structure. Structures showing the molecule with some other geometry (e.g., linear) are not permitted.

2. Structures that maximize the number of electrons used in bonding (consistent with the octet rule) contribute more to the true structure.

3. All resonance structures drawn must show the same number of unpaired electrons if there are any. A molecule or ion has a fixed number of unpaired electrons, and all resonance structures drawn for that species must show that number of unpaired electrons.

4. Negative formal charges normally reside on the atoms having higher electronegativity.

The NO_2 molecule illustrates the application of rule 3. Because the NO_2 molecule has a total of 17 valence shell electrons, there are eight pairs of electrons and one unpaired electron. Structures drawn for NO_2 must reflect this. Therefore, we draw the structure for NO_2 as
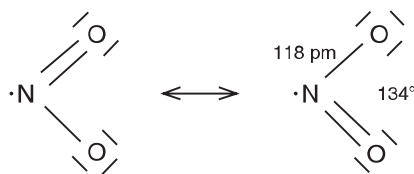
Note that the unpaired electron resides on the nitrogen atom, giving it a total of seven electrons. Because the oxygen atom has higher electronegativity, the oxygen atoms are given complete octets. This is also consistent with the observation that NO_2 dimerizes by pairing of electrons on two molecules as shown by the equation

$$2 \cdot NO_2 \rightleftharpoons O_2N : NO_2 \tag{4.4}$$

Note that in the NO_2 molecule the bond angle is much larger than the 120° expected when the central atom is using sp^2 hybrid orbitals. In this case, the nonbonding orbital located on the nitrogen atom contains only one electron, so repulsion between that orbital and the shared electron pairs is small. Therefore, the bond angle is larger because the repulsion between the bonding pairs is not balanced by the repulsion of the single electron in the nonbonding orbital. However, when the structure of NO_2^- is considered, there is an unshared *pair* of electrons on the nitrogen atom:
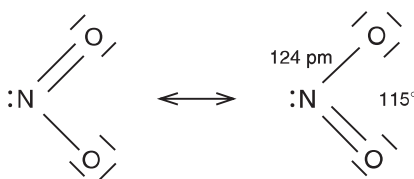
The repulsion between the unshared pair and the bonding electrons is much greater than in NO_2, as is reflected by the bond angle being only 115°. The N–O bond length is 124 pm in NO_2^- because the nitrogen atom has an octet of electrons. There is less residual attraction for the bonding pairs of electrons, so the N–O bonds are longer than in NO_2.

The concept of *formal* charges is a very useful one that is essentially a way of keeping track of electrons. In order to determine the formal charge on each atom in a structure, we must first apportion the electrons among the atoms. This is done according to the following procedure:

1. Any unshared pairs of electrons belong to the atom on which the electrons are located.

2. Shared electron pairs are divided equally between the atoms sharing them.

3. The total number of electrons on an atom in a structure is the sum from steps 1 and 2.

4. Compare the total number of electrons that appear to be on each atom to the number of valence shell electrons that it normally has. If the number of electrons in the valence shell is greater than indicated in step 3, the atom *appears* to have lost one or more electrons and has a *positive* formal charge. If the number indicated in step 3 is larger than the number in the valence shell, the atom *appears* to have gained one or more electrons and has a *negative* formal charge.

5. Structures that have formal charges with the same sign on adjacent atoms will contribute little to the true structure.

6. The sum of formal charges on the atoms must total the overall charge on the species.

Earlier we showed the structure |C≡O| for the carbon monoxide molecule. Each atom has one unshared pair of electrons and there are three shared pairs. The triple bond is only about 112.8 pm in length. If the shared pairs are divided equally, each atom appears to have three electrons from among those shared. Therefore, each atom in the structure *appears* to have a total of five electrons. Carbon normally has four electrons in its valence shell, so in the structure shown it has a formal charge of −1. An oxygen atom normally has six valence shell electrons, so it *appears* that the oxygen atom has lost one electron, giving it a formal charge of +1. Of course, the procedure is simply a bookkeeping procedure because no electrons have been lost or gained.

Formal charges can be used to predict the stable arrangement of atoms in many molecules. For example, nitrous oxide, N_2O, might have the structures shown as follows:

$$\overline{N} = O = \overline{N} \quad \text{and} \quad \overline{N} = N = \overline{O}$$

It might be tempting to assume that the structure on the left is correct, but not when the formal charges are considered. Note that the formal charges are circled to distinguish them from ionic charges. Following the procedure just outlined, the formal charges are

$$\overset{\ominus 1}{\underline{N}} = \overset{\oplus 2}{O} = \overset{\ominus 1}{\underline{N}}$$
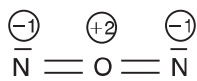
A +2 formal charge on oxygen, the atom with the second highest electronegativity, is not in agreement with the rules for distributing formal charges. Therefore, the correct structure is the one shown on the right, which also accounts for the fact that N_2O can react as an oxidizing agent because the oxygen atom is in a terminal position. *In general, the atom of lowest electronegativity will be found as the central atom*. Although we know that the arrangement of atoms is NNO, there is still the problem of resonance structures. For the N_2O molecule, three resonance structures can be shown as follows.

$$\overset{\ominus 1}{\underline{N}} = \overset{\oplus 1}{N} = \overset{0}{\underline{O}} \quad \longleftrightarrow \quad \overset{0}{|N} \equiv \overset{\oplus 1}{N} - \overset{\ominus 1}{\underline{O}|} \quad \longleftrightarrow \quad \overset{\ominus 2}{|\underline{N}} - \overset{\oplus 1}{N} \equiv \overset{\oplus 1}{O|}$$
$$\qquad\quad \text{I} \qquad\qquad\qquad\qquad \text{II} \qquad\qquad\qquad\qquad \text{III}$$
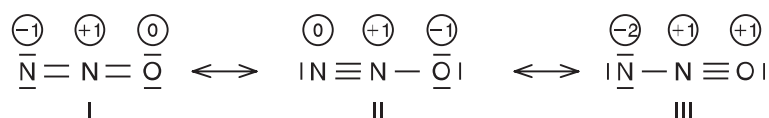
Structure III will contribute approximately 0% to the true structure because it has like formal charges on adjacent atoms, it has a positive formal charge on the oxygen atom while a nitrogen atom has a −2 formal charge, and it has higher formal charges overall. Deciding the relative contributions from structures I and II is somewhat more difficult. Although structure II has the negative formal charge on the oxygen atom, it also has a triple bond between the two nitrogen atoms, which results in six shared electrons in a small region of space. Two double bonds are generally preferred over a triple bond and a single bond. Structure I has two double bonds even though it places a negative formal charge on a nitrogen atom. As a result of these factors, we suspect that structures I and II would contribute about equally to the actual structure.

In this case, there is a simple experiment that will determine whether this is correct. Structure I places a negative formal charge on the terminal nitrogen atom, while structure II places a negative formal charge on the oxygen atom on the opposite end of the molecule. If the two structures contribute equally, these effects should cancel, which would result in a molecule that is not polar. In fact, the dipole moment of N_2O is only 0.17 D, so structures I and II must make approximately equal contributions.
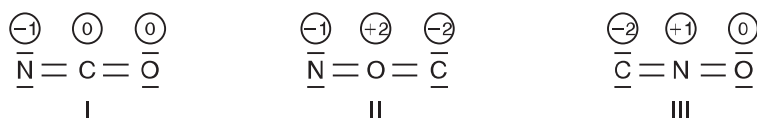
Bond lengths are also useful when deciding contributions from resonance structures. Structure I shows a double bond between N and O, while structure II shows the N–O bond as a single bond. If the structures contribute equally, the experimental N–O bond length should be approximately half way between the values for N–O and N=O, which is the case. Thus, we have an additional piece of evidence that indicates structures I and II contribute about equally to the actual structure. The observed bond lengths in the N_2O molecule are shown below (in picometers).

$$\overset{112.6}{N\text{———}N}\overset{118.6}{\text{———}O}$$
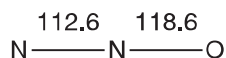
Known bond lengths for other molecules that contain bonds between N and O atoms are useful in assessing the contributions of resonance structures in this case. The N≡N bond length is 110 pm, whereas that for the N=N bond is usually approximately 120 to 125 pm depending on the type of molecule. Likewise, the nitrogen-to-oxygen bond length in the NO molecule in which the bond order is 2.5 is 115 pm. On the other hand, in NO^+ (which has a bond order of 3), the bond length is 106 pm. From these values, it can be seen that the observed bond lengths in N_2O are consistent with the fact that the true structure is a hybrid of structures I and II shown earlier.

We can also illustrate the application of these principles by means of other examples. Consider the cyanate ion, NCO^-. In this case, there are 16 valence shell electrons that need to be distributed. To provide

a total of three octets, 24 electrons would be needed. Therefore, eight electrons must be shared, which means that there will be a total of four bonds, two from the central atom to each of the terminal atoms. Four bonds in the form of two double bonds in each direction can be expected to give a linear structure. Our first problem is how to arrange the atoms. Showing the total of 16 electrons, the arrangements can be illustrated as follows (the formal charges also indicated):

$$
\underset{\text{I}}{\overset{\overset{(-1)}{\underline{\text{N}}}\;\;\overset{(0)}{}\;\;\overset{(0)}{}}{\underline{\text{N}} = \text{C} = \underline{\text{O}}}
\qquad
\underset{\text{II}}{\overset{\overset{(-1)}{\underline{\text{N}}}\;\;\overset{(+2)}{}\;\;\overset{(-2)}{}}{\underline{\text{N}} = \text{O} = \underline{\text{C}}}
\qquad
\underset{\text{III}}{\overset{\overset{(-2)}{\underline{\text{C}}}\;\;\overset{(+1)}{}\;\;\overset{(0)}{}}{\underline{\text{C}} = \text{N} = \underline{\text{O}}}
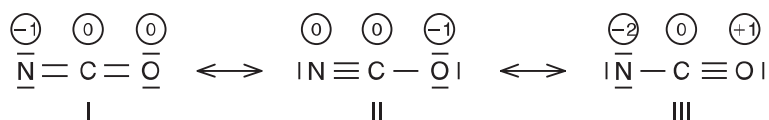$$

Deciding which arrangement of atoms is correct is based on the formal charge on the central atom. In the first structure, there are four shared pairs of electrons on the carbon atom, and dividing each pair equally leads to a total of four electrons around the carbon atom. Because a carbon atom normally has four valence-shell electrons, the carbon atom in structure I has a formal charge of 0. In structure II, dividing each of the bonding pairs equally leads to accounting for four electrons on the oxygen atom, which normally has six valence-shell electrons. Therefore, in structure II, the oxygen atom has a formal charge of +2. Of the three atoms in the structure, oxygen has the highest electronegativity, so this structure is very unfavorable. In structure III, dividing each bonding pair equally makes it *appear* that the nitrogen atom has four electrons on it, but there are five electrons in the valence shell of nitrogen. This results in a formal charge of +1 on the nitrogen atom and a −2 formal charge on the carbon atom.

Both structures II and III have an arrangement of atoms that places a positive formal charge on atoms that are higher in electronegativity than carbon. Consequently, the most stable arrangement of atoms is as shown in structure I. Some compounds containing the ion having structure III (the fulminate ion) are known, but they are much less stable than the cyanates (structure I). In fact, mercury fulminate has been used as a detonator.

As a general rule, we can see that for triatomic species containing 16 electrons, the fact that there must be four bonds to the central atom will result in a positive formal charge on that atom unless it is an atom that has only four valence-shell electrons. Therefore, in cases where one of the three atoms is carbon, that atom is likely to be the central atom. A nitrogen atom in the central position would be forced to have a +1 formal charge, and an oxygen atom would have a +2 formal charge. By considering the structures of numerous 16-electron triatomic species it will be generally found that the central atom is the one having the lowest electronegativity.

Now that we have determined that structure I is correct for the cyanate ion, we still need to consider resonance structures. In keeping with the rules given earlier, the acceptable resonance structures that can be devised are

$$
\underset{\text{I}}{\overset{\overset{(-1)}{\underline{\text{N}}}\;\;\overset{(0)}{}\;\;\overset{(0)}{}}{\underline{\text{N}} = \text{C} = \underline{\text{O}}}
\;\longleftrightarrow\;
\underset{\text{II}}{\overset{\overset{(0)}{}\;\;\overset{(0)}{}\;\;\overset{(-1)}{}}{|\text{N} \equiv \text{C} - \underline{\text{O}}|}}
\;\longleftrightarrow\;
\underset{\text{III}}{\overset{\overset{(-2)}{}\;\;\overset{(0)}{}\;\;\overset{(+1)}{}}{|\underline{\text{N}} - \text{C} \equiv \text{O}|}}
$$

In structure I, the formal charges are −1, 0, and 0 on the nitrogen, carbon, and oxygen atoms, respectively. In structure II, the corresponding formal charges are 0, 0, and −1. However, in structure III, the

formal charges on the atoms are nitrogen -2, carbon 0, and oxygen $+1$. Immediately, we see that the most electronegative atom, oxygen, has a positive formal charge, and we realize that if the actual structure is a resonance hybrid of these three structures, structure III will contribute approximately 0%. This structure essentially represents removing electron density from an oxygen atom and placing it on a nitrogen atom. We now must estimate the contributions of the other two structures.

Although structure II has a negative formal charge on the atom having the highest electronegativity, it also has a triple bond, which places a great deal of electron density in a small region of space. The repulsion that arises causes the bond to be less favorable than the -1 formal charge on the oxygen atom would suggest. On the other hand, the two double bonds in structure I still provide a total of four bonds without as much repulsion as that resulting from a triple bond. Structure I also has a -1 formal charge on nitrogen, the second most electronegative of the three atoms. When all of these factors are considered, we are led to the conclusion that structures I and II probably contribute about equally to the true structure.

For CO_2, the structure contains two σ bonds and two π bonds, and it can be shown as

$$\overline{O} = C = \overline{O}$$
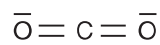
Two σ bonds are an indication of sp hybridization on the central atom, which leaves two p orbitals unhybridized. These orbitals are perpendicular to the molecular axis and can form π bonds with p orbitals on the oxygen atoms.
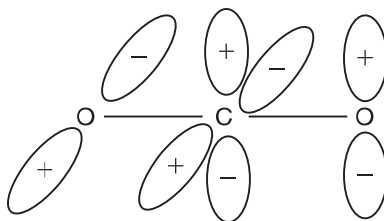

In CO_2, the C=O bond length is 116 pm, which is slightly shorter than the usual length of C=O bonds, which are approximately 120 pm. Note that CO_2, NO_2^+, SCN^-, OCN^-, and N_2O are all triatomic molecules having 16 electrons and all are linear.

There are several important chemical species that consist of four atoms and have a total of 24 valence-shell electrons. Some of the most common isoelectronic species of this type are CO_3^{2-}, NO_3^-, SO_3, and PO_3^- (known as the *meta*phosphate ion). Because four atoms would require a total of 32 electrons for each to have an octet, we conclude that eight electrons must be shared in four bonds. With four bonds to the central atom, there can be no unshared pairs on that atom if the octet rule is to be obeyed. Therefore, we can draw the structure for CO_3^{2-} showing one double C=O bond and two single C–O bonds as
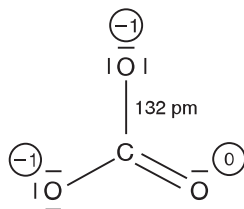
The double bond could also be shown in the other two positions, so the true structure is a resonance hybrid of the three structures. The structure is a trigonal plane that has three identical bonds with each being an average of one double bond and two single bonds. The result is that there is a bond order of 1.33. Because the structure is a trigonal plane, we understand that the hybrid orbital type used by carbon is sp^2. As a result, there is one additional p orbital on the central atom that is perpendicular to the plane, and that orbital is empty. Therefore, a filled p orbital on an oxygen atom can overlap with the empty p orbital on the carbon atom to yield a π bond. This π bond is not restricted to one oxygen atom, because the other two also have filled p orbitals that can be used in π bonding. The result is that the π bond is delocalized over the entire structure:
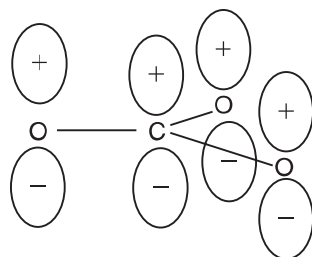
Note that because the carbon atom has a formal charge of 0, there is no necessity to draw structures having more than one double bond. The carbon atom has no valence-shell orbitals other than 2s and 2p orbitals, so only four pairs of electrons can be held in four valence-shell orbitals. The structures of CO, CO_2, and CO_3^{2-} have been described in which the bond orders are 3, 2, and 4/3 and the bond lengths are 112.8, 116 (in CO_2, but ~120 in most C=O bonds), and 132 pm, respectively. As expected, the bond length decreases as the bond order increases. A typical bond length for a C–O single bond is 143 pm, so we have four C–O bond lengths that can be correlated with bond order. Figure 4.2 shows the relationship between the bond order and bond length for these types of C–O bonds.

A relationship such as this is useful in cases where a C–O bond length is known because from it the bond order can be inferred. On this basis, it is also sometimes possible to estimate the contributions
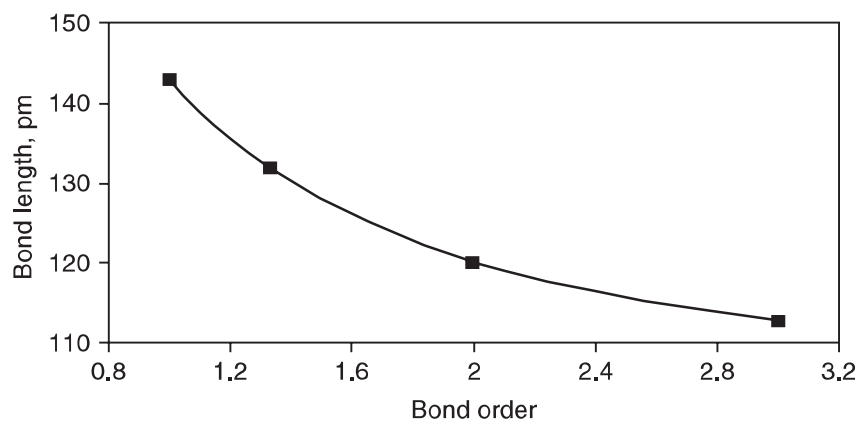

■ **FIGURE 4.2**   The relationship between bond order and bond length for bonds between carbon and oxygen.

of various resonance structures. Pauling proposed an equation relating bond length relative to that of a single bond between the atoms that is written as

$$D_n = D_1 - 71 \log n \tag{4.5}$$

where D_n is the bond length for a bond of order n, D_1 is the length of a single bond, and n is the bond order. Using this equation, calculated bond lengths for C–O bonds having bond orders of 4/3, 2, and 3 are 134, 122, and 106 pm, respectively. The calculated length of a bond of 4/3 order is quite close to that in CO_3^{2-}. In many molecules, the length of a C=O bond is approximately 120 pm, so the agreement is again satisfactory. In the case of the C≡O bond, the molecule that possesses this bond is carbon monoxide, which has some unusual characteristics because of ionic character (see Chapter 3), so the agreement is not as good between the experimental and calculated bond length. However, Eq. (4.5) is useful in many situations to provide approximate bond lengths.

For the SO_3 molecule, the structure we draw first by considering the number of valence shell electrons and the octet rule is
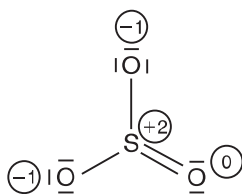

In this case, even with there being one double bond, the formal charge on the sulfur atom is +2, so structures that show two double bonds are possible, which can reduce further the positive formal charge. In order for structures such as
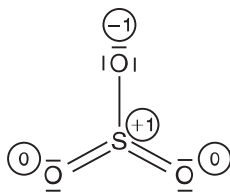

to be drawn, the sulfur atom has 10 electrons around it, which means that the octet rule is not obeyed. However, in addition to the 3s and 3p valence orbitals, the sulfur atom also has empty 3d orbitals that can overlap with filled p orbitals on oxygen atoms. Therefore, unlike the carbon atom in CO_3^{2-}, the sulfur atom in SO_3 can accept additional electron density, and structures showing two double bonds are permissible. The S–O bond length in SO_2 where the bond order is 1.5 is 143 pm. That is almost exactly the S–O bond length in SO_3, which indicates that a bond order of about 1.5 is correct for this molecule. Therefore, there must be some contributions from structures that show two double bonds because the bond order would be 4/3 if only one double bond is present.

The sulfate ion, SO_4^{2-}, exhibits some bonding aspects that deserve special consideration. First, there are five atoms, so 40 electrons would be required to provide an octet of electrons around each atom. However, with only 32 valence-shell electrons (including the two that give the −2 charge), there must

be eight electrons shared. The four bonds will be directed toward the corners of a tetrahedron, which gives the structure
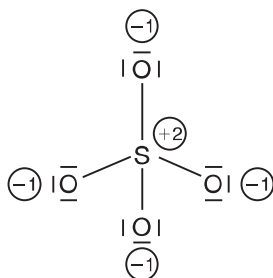

Although this structure agrees with several of our ideas about structure and bonding, there is at least one problem. If we determine the formal charges on the atoms, we find that there is a -1 formal charge on each oxygen atom but a $+2$ formal charge on the sulfur atom. Although sulfur has a lower electronegativity than oxygen, there is disparity in the electron densities on the atoms. This situation can be improved by taking an unshared pair on one of the oxygen atoms and making it a shared pair:
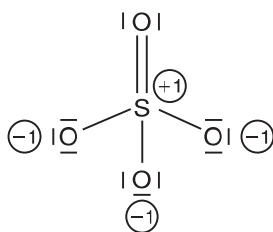

There is no reason that any particular oxygen atom should be chosen, so there are four equivalent structures in which the double bond is shown to a different oxygen atom in each one. The question arises as to how this type of bonding occurs. When an oxygen atom is bonded to the sulfur atom by a single bond, there are three unshared pairs of electrons that reside in p orbitals on the oxygen atom. Although the sulfur atom makes use of sp^3 hybrid orbitals (from $3s$ and $3p$ valence shell orbitals) in forming the four single bonds, the $3d$ orbitals are not greatly higher in energy, and they are empty. The symmetry (mathematical signs) of the filled p orbitals on an oxygen atom matches that of a d orbital. Therefore, electron density is shared between the oxygen and sulfur atoms, but the electrons come from filled orbitals on the oxygen atom. The result is that there is some double bond character to each S–O bond as a result of π bond formation, and the S–O bond lengths are shorter than expected for a single bond between the atoms.

In the H_2SO_4 molecule, there are two oxygen atoms that are bonded to hydrogen atoms and the sulfur atom. These oxygen atoms are unable to participate effectively in π bonding, so the structure of the molecule is
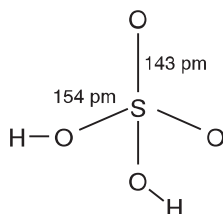
This structure reflects the fact that there is significant multiple bonding to two oxygen atoms, but not to the two others that have hydrogen atoms attached. This behavior is also seen clearly in the structure of HSO_4^-,
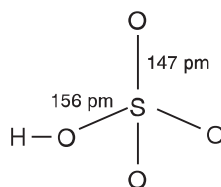

Note that the distance between the sulfur atom and the three oxygen atoms that do not have hydrogen attached is slightly greater than the corresponding distance in H_2SO_4. The reason is that the back donation is now spread over three terminal oxygen atoms rather than only two. The bond order of S–O bonds is slightly greater in H_2SO_4 than in HSO_4^- when only terminal oxygen atoms are considered.

The PO_4^{3-} (known as the *ortho*phosphate ion) and ClO_4^- ions are isoelectronic with SO_4^{2-} ion, and their structures are
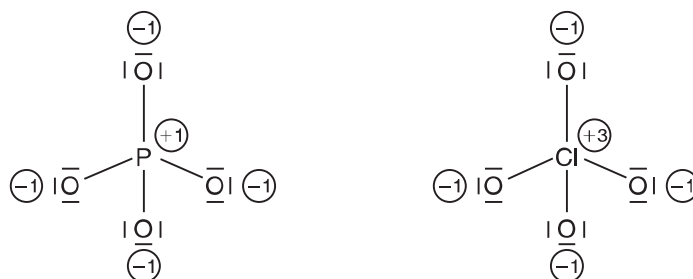

Although the phosphorus atom in PO_4^{3-} has a positive formal charge, it has a significantly lower electronegativity than oxygen. Therefore, there is not as much contribution from structures having double bonds. On the other hand, a $+3$ formal charge on the chlorine atom in ClO_4^- can be partially relieved by shifting some electron density from nonbonding orbitals on oxygen atoms to the empty d orbitals on the chlorine atom:
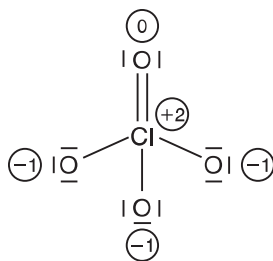

As in the case of the SO_4^{2-} ion, this is accomplished by overlap of filled p orbitals on oxygen atoms with empty d orbitals on the chlorine to give π bonds. The result of the contributions from structures in which there is some double bond character is that the bonds between chlorine and oxygen atoms

are shorter than expected if the bonds were only single bonds. There is no reason why there can not be some double bond character to more than one oxygen atom, which results in structures like
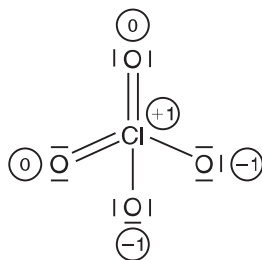

As expected, the extent to which the bonds in ClO_4^- are shortened from the single bond distance is rather large.

The following structure of the H_3PO_4 molecule is similar in many regards to that of H_2SO_4, but there are some significant differences:
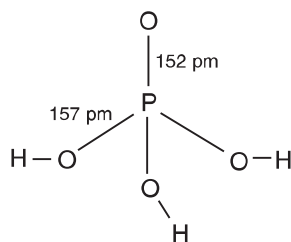

In sulfuric acid, the distance between the sulfur atom and the oxygen atoms without hydrogen atoms attached is 143 pm; the corresponding P O distance in H_3PO_4 is 152 pm. This indicates that there is much less double bond character to the P–O bonds than there is to the S–O bonds. This is to be expected because of the +2 formal charge on sulfur when the structure is drawn showing only single bonds, whereas the phosphorus atom has only a +1 formal charge in a structure for H_3PO_4 showing only single bonds. Moreover, the phosphorus atom has a lower electronegativity than sulfur (2.2 compared to 2.6) so less double bonding to relieve a negative formal charge would be expected. The bond length of the HO–P single bond is 157 pm.

A structure for phosphorous acid, $(HO)_2HPO$, can be drawn as follows:
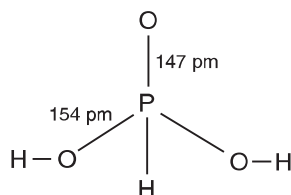
One of the hydrogen atoms is bound directly to the phosphorus atom and is not normally acidic. Note that in this case, the distance between the phosphorus atom and the oxygen atom without a hydrogen atom attached is only 147 pm, indicating more double bond character than there is in the corresponding bond in the H_3PO_4 molecule.

Another interesting structure is that of the dithionite ion, $S_2O_4^{2-}$, which is shown as
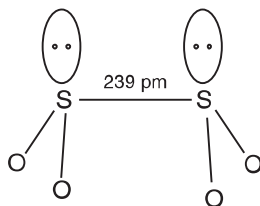
In several compounds that contain S–S single bonds, the bond length is approximately 205 pm. The very long S–S bond in $S_2O_4^{2-}$ is indicative of "loose" bonding, which is illustrated by the fact that when $^{35}SO_2$ is added to a solution containing $S_2O_4^{2-}$, some of the $^{35}SO_2$ is incorporated in $S_2O_4^{2-}$ ions. In contrast, the structure of dithionate, $S_2O_6^{2-}$,
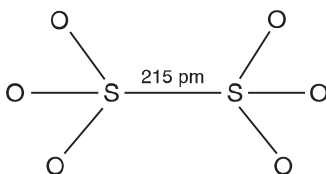

contains an S–S bond of more normal length, and the ion is more stable than is $S_2O_4^{2-}$. In $S_2O_4^{2-}$, the SO bonds are typical of SO bonds that have very little double bond character (151 pm). The fact that the SO bonds in dithionate have substantial double bond character is indicated by the 143 pm bond length, which is equal to that in SO_2.

## 4.3 COMPLEX STRUCTURES—A PREVIEW OF COMING ATTRACTIONS

In addition to the structures discussed so far in this chapter, inorganic chemistry involves many others that can be considered to be chains, rings, or cages. In this section, several of the important structures will be described without resorting to theoretical interpretation. Some of the structures shown occur for several isoelectronic species so they represent structural *types*. In some cases, reactions are shown to illustrate processes that lead to products having such structures. These structures are often the result of an atom bonding to others of its own kind (which is known as *catenation*) or the formation of structures in which there are bridging atoms (especially oxygen, because oxygen normally forms two bonds). An example of the latter type of structure is the pyrosulfate ion, $S_2O_7^{2-}$. This ion can be formed by adding SO_3 to sulfuric acid, or by removing water (as in heating and thus the name *pyro*sulfate) from H_2SO_4 or a bisulfate:

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7 \tag{4.6}$$

$$2\ NaHSO_4 \xrightarrow{\Delta} Na_2S_2O_7 + H_2O \tag{4.7}$$

The structure of the $S_2O_7^{2-}$ ion contains an oxygen bridge,

$$
\begin{array}{ccc}
O & & O \\
\| & & \| \\
O-S-O-S-O \\
\| & & \| \\
O & & O
\end{array}
\quad 2-
$$
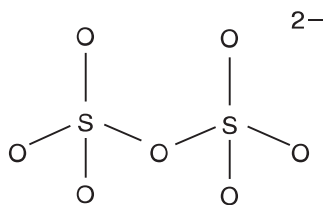
In this structure, as in the case of SO_4^{2-}, there is some double bond character to the bonds between the sulfur atoms and the terminal oxygen atoms. In addition to being the structure of $S_2O_7^{2-}$, this is the structure of the isoelectronic species $P_2O_7^{4-}$ (the *pyro*phosphate ion), $Si_2O_7^{6-}$ (pyrosilicate) and Cl_2O_7 (dichlorine heptoxide). The peroxydisulfate ion, $S_2O_8^{2-}$, has a *peroxide* linkage between the two sulfur atoms:

$$
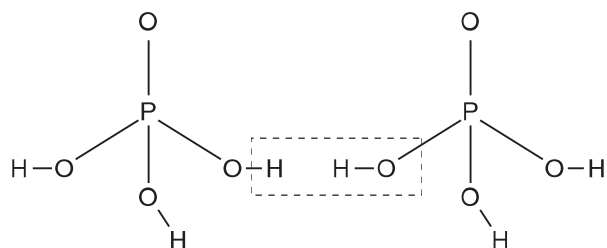\begin{array}{ccc}
O & & O \\
\| & & \| \\
O-S-O-O-S-O \\
\| & & \| \\
O & & O
\end{array}
\quad 2-
$$
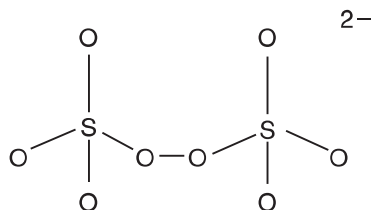
Dichlorine heptoxide, Cl_2O_7, results from the dehydration of $HClO_4$ with a strong dehydrating agent such as P_4O_{10}:

$$12\,HClO_4 + P_4O_{10} \rightarrow 6\,Cl_2O_7 + 4\,H_3PO_4 \tag{4.8}$$

The *di-* or *pyro*phosphate ion results from the partial dehydration of phosphoric acid,

$$2\,H_3PO_4 \rightarrow H_4P_2O_7 + H_2O \tag{4.9}$$

which can be shown as a molecule of water being formed from two H_3PO_4 molecules:

$$
\begin{array}{cccccc}
O & & & & O \\
\| & & & & \| \\
P & & & & P \\
H-O & | & O-H & H-O & | & O-H \\
 & O & & & O \\
 & \backslash & & & \backslash \\
 & H & & & H
\end{array}
$$

The polyphosphoric acids can be considered as arising from the reaction of $H_4P_2O_7$ with additional molecules of H_3PO_4 by the loss of water. In the following process, the product is $H_5P_3O_{10}$, which is

known as tripolyphosphoric acid:

$$H_5P_3O_{10} + H_2O$$
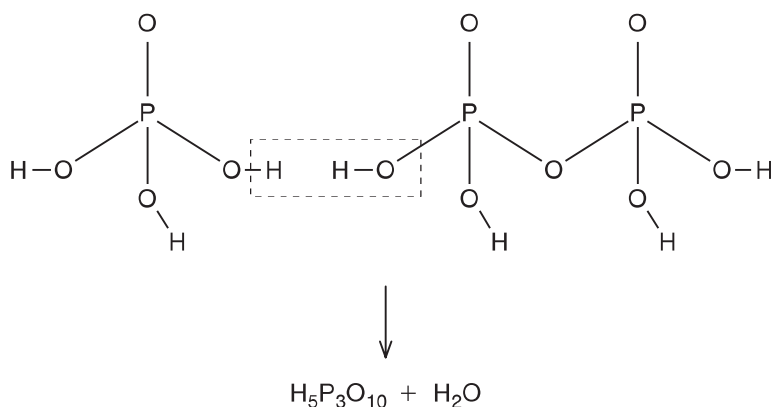
The pyrophosphate ion also results from the dehydration of a salt such as Na_2HPO_4,

$$2\ Na_2HPO_4 \xrightarrow{\Delta} Na_4P_2O_7 + H_2O \tag{4.11}$$

Complete hydration of P_4O_{10} in excess water produces orthophosphoric acid (H_3PO_4),

$$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4 \tag{4.12}$$

but partial hydration of the oxide P_4O_{10} produces $H_4P_2O_7$:

$$P_4O_{10} + 4\ H_2O \rightarrow 2\ H_4P_2O_7 \tag{4.13}$$

Elemental phosphorus is obtained on a large scale by the reduction of calcium phosphate with carbon in an electric furnace at 1200 to 1400°C:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow 6\ CaSiO_3 + 10\ CO + P_4 \tag{4.14}$$
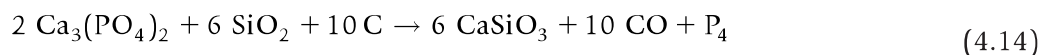
The element has several allotropic forms that are made up of tetrahedral P_4 molecules.
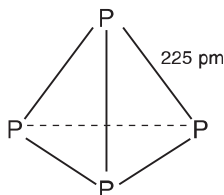

Combustion of phosphorus produces two oxides, P_4O_6 and P_4O_{10}, depending on the relative concentrations of the reactants.

$$P_4 + 3\ O_2 \rightarrow P_4O_6 \tag{4.15}$$

$$P_4 + 5\ O_2 \rightarrow P_4O_{10} \tag{4.16}$$

The structures of both P_4O_6 and P_4O_{10} are based on the P_4 tetrahedron. In the case of P_4O_6, there is an oxygen atom forming a bridge between each pair of phosphorus atoms along the edges of the tetrahedron, resulting a structure which can be shown as

(4.10)
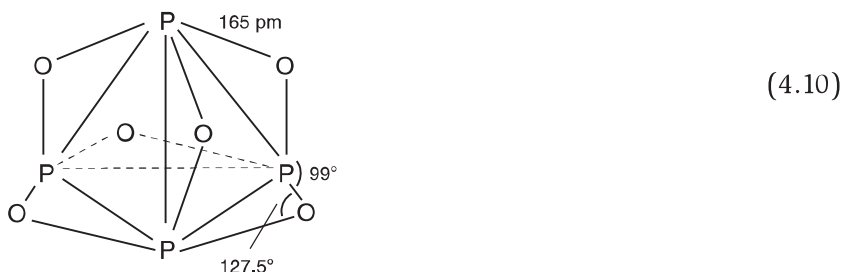
In this structure, the tetrahedron of phosphorus atoms is preserved. In keeping with the fact that when compared to P_4O_6, P_4O_{10} has four additional oxygen atoms, these oxygen atoms are bonded to the phosphorus atoms to give a structure that has not only the six bridging oxygen atoms but also one terminal oxygen atom bonded to each of the phosphorus atoms:
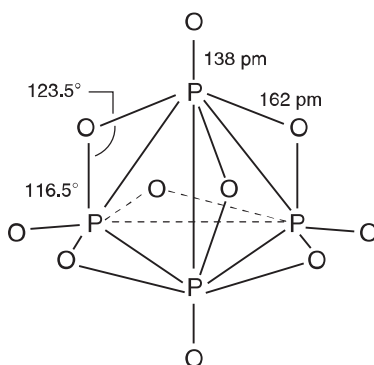

Elemental phosphorus is only one of several elements whose structures are polyatomic species. Another is the structure of elemental sulfur, which consists of puckered S_8 rings:
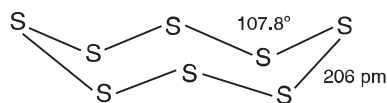

Although this eight-membered ring represents the structure of the molecule in the rhombic crystal phase, it is by no means the only sulfur molecule. Other ring structures have the formulas S_6, S_7, S_9, S_{10}, S_{12}, and S_{20}. Just as gaseous oxygen contains O_2 molecules, sulfur vapor contains S_2 molecules that are paramagnetic. Selenium also exists as Se_8 molecules, but catenation is less pronounced than in the case of sulfur, and tellurium shows even less tendency in this regard. Tellurium resembles metals in its chemistry more than does either sulfur or selenium.

Tetrasulfur tetranitride, S_4N_4, has a structure that can be considered as a hybrid of the following two resonance structures:
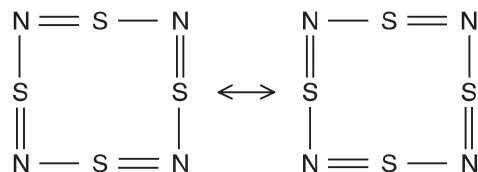

Although these structures show positions of the bonds in the resonance structures, the geometric structure of the molecule is
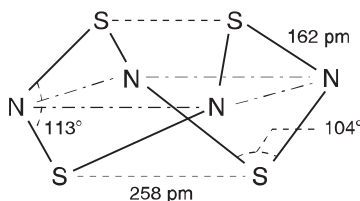

The distance between the sulfur atoms is considerably shorter than expected on the basis of radii of the isolated atoms. Therefore, there is believed to be a long, weak bond between the sulfur atoms. A very large number of derivatives of S_4N_4 are known, and some of them are described in Chapter 15.

Elemental boron exists as an icosahedral B_{12} molecule that has the structure
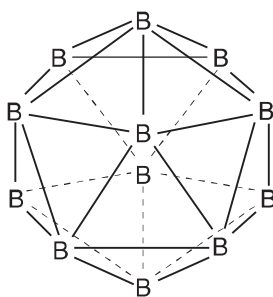

This structure has two staggered planes that contain five boron atoms in each, as well as two boron atoms in apical positions.

No survey of polyatomic elements would be complete without showing the form of carbon that exists as C_{60}. Known as *buckminsterfullerene* (named after R. Buckminster Fuller, the designer of the geodesic dome), C_{60} has a cage structure that has 12 pentagons and 20 hexagons on the surface as shown in Figure 4.3a. Each carbon atom makes use of sp^2 hybrid orbitals and is bonded by three σ bonds and one π bond, with the π bonds being delocalized. A very large number of derivatives of C_{60} are known, and other forms of carbon have general formula C_x ($x \neq 60$). Carbon also exists as diamond and graphite, which have the structures shown in Figure 4.3b and 4.3c.

(a)

(b)

(c)
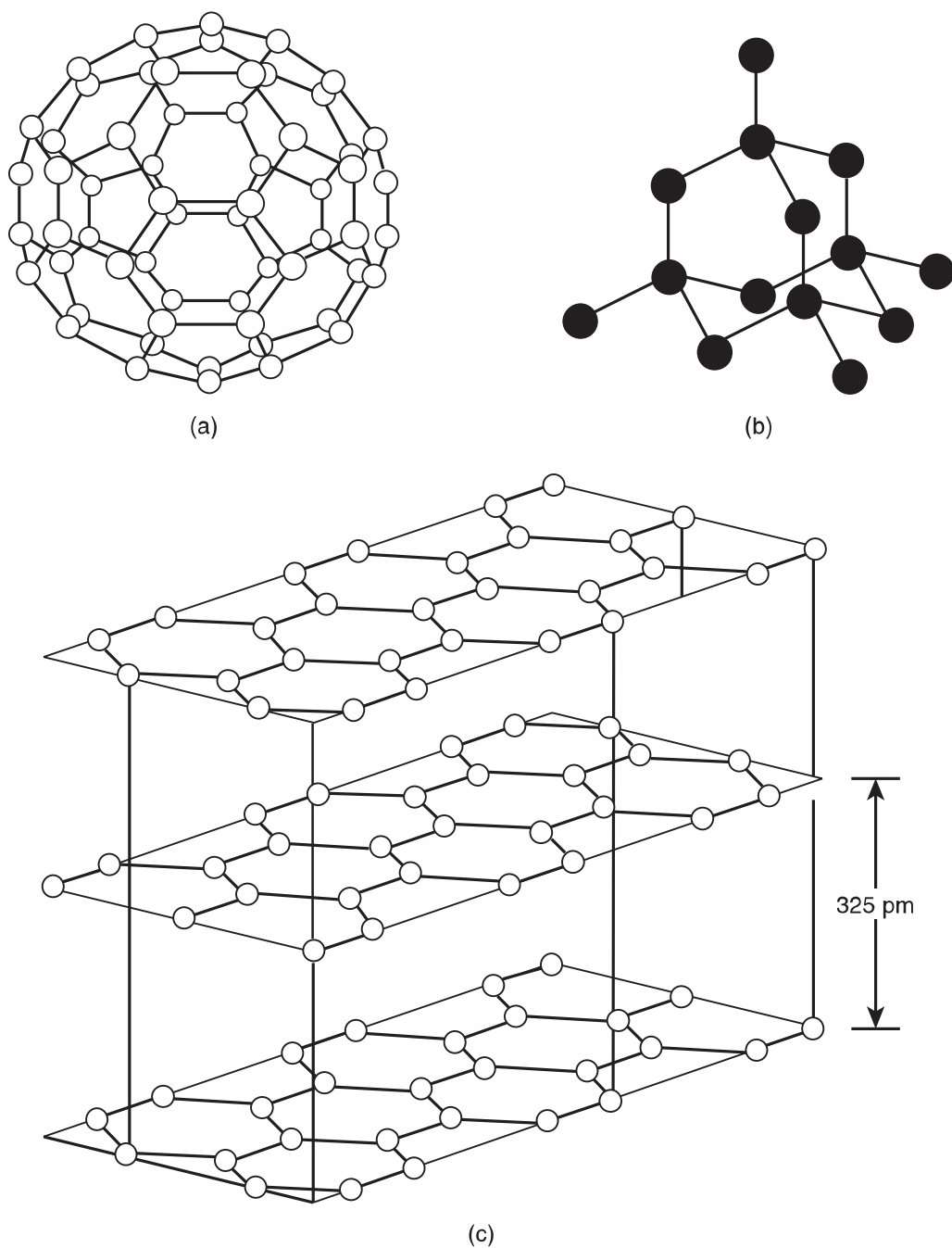
■ **FIGURE 4.3** Some of the structures of elemental carbon (see Chapter 13).

In addition to the structures of these elements, a great deal of structural inorganic chemistry is concerned with the silicates. These materials form a vast array of naturally occurring and synthetic solids whose structures are based on the tetrahedral unit SiO_4. There are structures that contain discrete SiO_4^{4-} ions as well as bridged structures such as $Si_2O_7^{6-}$. Because the Si atom has two fewer valence-shell electrons than the S atom, the SiO_4^{4-} and SO_4^{2-} ions are isoelectronic, as are the $Si_2O_7^{6-}$ and $S_2O_7^{2-}$ ions.
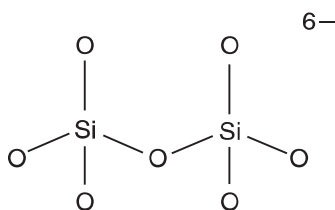
The SiO_4^{4-} ion, known as *ortho*silicate, occurs in minerals such as *zircon*, $ZrSiO_4$, *phenacite*, Be_2SiO_4, and *willemite*, Zn_2SiO_4. The SiO_3^{2-} ion is known as the *meta*silicate ion. Some of the minerals that contain the $Si_2O_7^{6-}$ ion are *thortveitite*, $Sc_2Si_2O_7$, and *hemimorphite*, $Zn_4(OH)_2Si_2O_7$.

Another important silicate structural type is based on a six-membered ring that contains alternating Si and O atoms and has the formula $Si_3O_9^{6-}$.
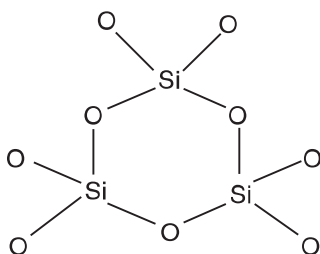
The $P_3O_9^{3-}$ ion (known as the trimetaphosphate ion) and $(SO_3)_3$, a trimer of SO_3, also have this structure. The trimetaphosphate ion can be considered as the anion of the acid $H_3P_3O_9$ (trimetaphosphoric acid), a trimeric form of HPO_3 (metaphosphoric acid). Note that this acid is formally related to $H_5P_3O_{10}$, tripolyphosphoric acid, by the reaction

$$H_3P_3O_9 + H_2O \rightleftharpoons H_5P_3O_{10}$$

(4.17)

A six-membered ring also is present in the anion of $Na_3B_3O_6$. It contains bridging oxygen atoms but has only one terminal oxygen atom on each boron atom:
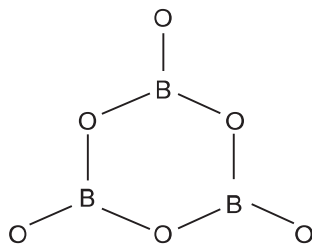
Although the complete description of its structure will not be shown here, boric acid, $B(OH)_3$, has a sheet structure in which each boron atom resides in a trigonal planar environment of oxygen atoms. There is hydrogen bonding between the OH groups in neighboring molecules.

Because there are numerous silicates whose structures are made up of repeating patterns based on the SiO_4 tetrahedron, a type of shorthand notation has been developed for drawing the structures. For example, the SiO_4 unit can be shown as follows.
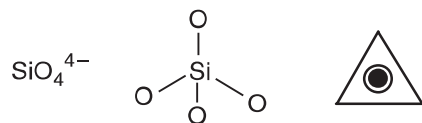
Then, the complex structures shown in Figure 4.4 are built up by combining these units. These structures are based on SiO_4 tetrahedra that share a corner or an edge. In the drawings, the solid circle
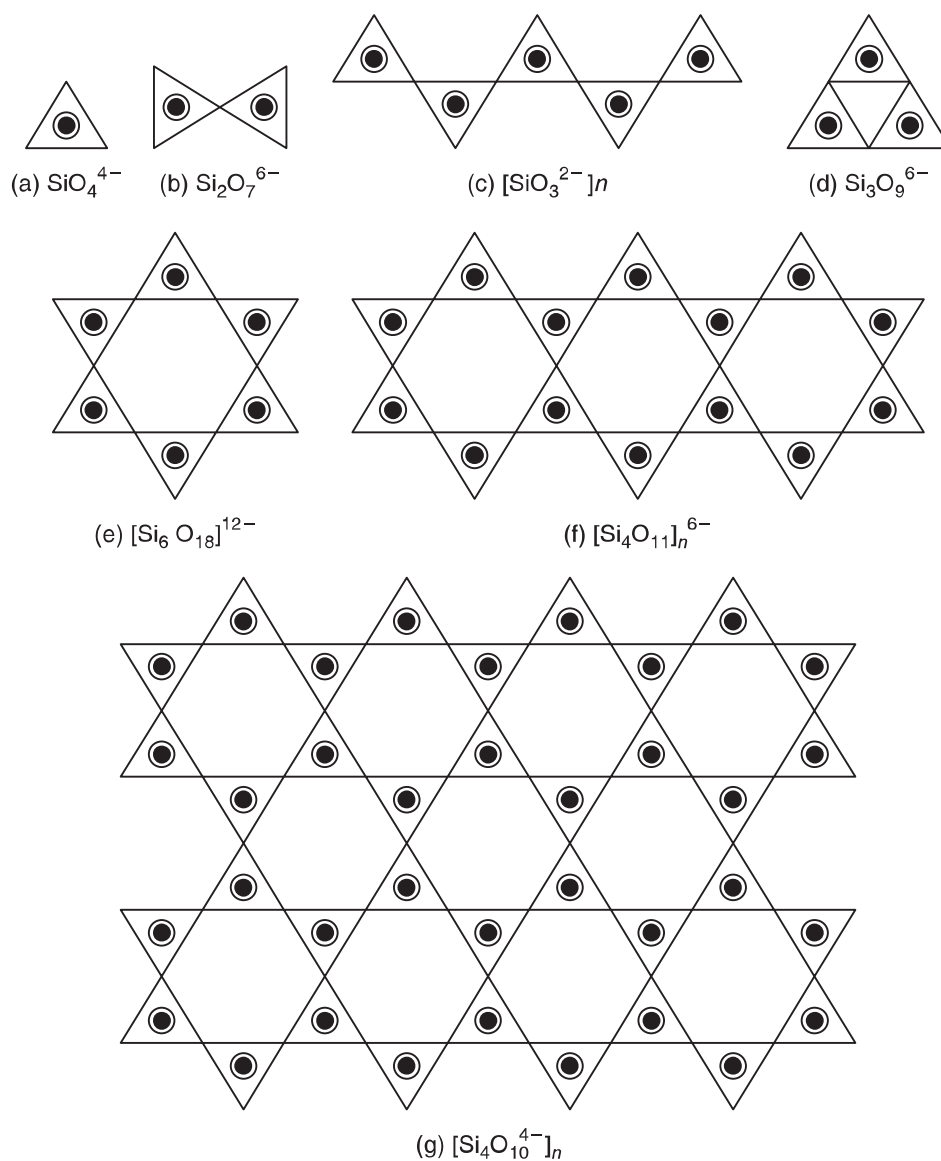
■ **FIGURE 4.4**   Structures of some common silicates.

represents the silicon atom, and the open circle around it represents an oxygen atom that is directed upward out of the page. From combinations of the basic SiO_4 units, a wide range of complex structures results as shown in Figure 4.4.

Although the formula for beryllium chloride is $BeCl_2$, the compound exists in chains in the solid state. The bonding is covalent, and the environment around each Be is essentially tetrahedral with each Cl bridging between two Be atoms separated by 263 pm.
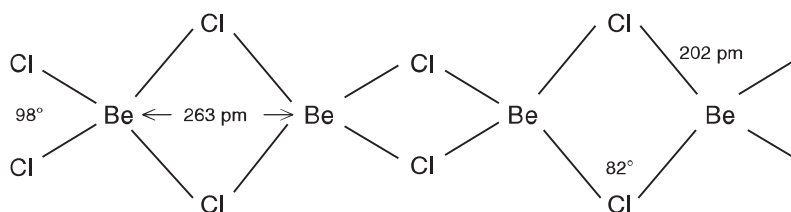
In the $BeCl_2$ monomer, there are only two bonds to Be, which gives only four electrons around the atom. In the bridged structure, unshared pairs of electrons on Cl are donated to complete octets around Be atoms.

In this chapter, procedures for drawing molecular structures have been illustrated, and a brief overview of structural inorganic chemistry has been presented. The structures shown include a variety of types, but many others could have been included. The objective is to provide an introduction and review to the topics of VSEPR, hybrid orbitals, formal charge, and resonance. The principles discussed and types of structures shown will be seen later to apply to the structures of many other species.

## 4.4 ELECTRON-DEFICIENT MOLECULES

In this chapter many of the basic principles related to structure and bonding in molecules have already been illustrated. However, there is another type of compound that is not satisfactorily described by the principles illustrated so far. The simplest molecule of this type is diborane, B_2H_6. The problem is that there are only 10 valence shell electrons available for use in describing the bonding in this molecule.

The BH_3 molecule is not stable as a separate entity. This molecule can be stabilized by combining it with another molecule that can donate a pair of electrons (indicated as :) to the boron atom to complete the octet (see Chapter 9). For example, the reaction between pyridine and B_2H_6 produces $C_5H_5N:BH_3$. Another stable adduct is carbonyl borane, $OC:BH_3$ in which a pair of electrons is donated from carbon monoxide, which stabilizes borane. In CO, the carbon atom has a negative formal charge, so it is the "electron-rich" end of the molecule. Because the stable compound is B_2H_6 rather than BH_3, the bonding in that molecule should be explained.

The *framework* of B_2H_6 can be visualized by considering $B_2H_4^{2-}$, which is isoelectronic with C_2H_4. Starting with $B_2H_4^{2-}$, which would have a π bond like that in C_2H_4, the bonding can be described similarly:
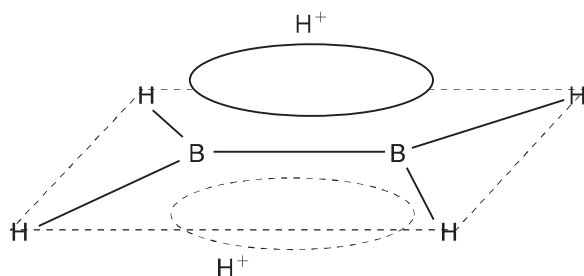
The planar framework has σ bonds as just shown, which involve sp^2 hybrid orbitals on the boron atoms. This leaves one unhybridized p orbital that is perpendicular to the plane. The B_2H_6 *molecule* can be considered being made by adding two H^+ ions to a hypothetical $B_2H_4^{2-}$ ion that is isoelectronic with C_2H_4 because each carbon atom has one more electron than does a boron atom. In the $B_2H_4^{2-}$ *ion*, the two additional electrons reside in a π bond that lies above and below the plane of the structure just shown. When two H^+ ions are added, they become attached to the lobes of the π bond to produce a structure, the details of which can be shown as
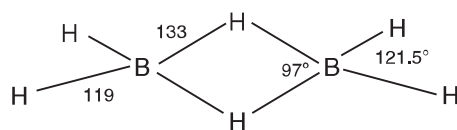
In each of the B–H–B bridges, only two electrons bond the three atoms together by having the orbitals on the boron atoms simultaneously overlap the hydrogen $1s$ orbital. A bond of this type is known as a *two-electron three-center bond*. In terms of molecular orbitals, the bonding can be described as the combination of two boron orbitals and one hydrogen orbital to produce three molecular orbitals, of which only the one of lowest energy is populated:
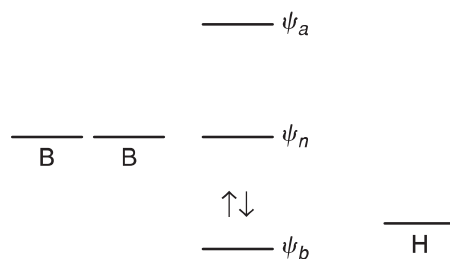
Bonding of this type and other boron hydrides that have three-center two-electron bonds with hydrogen bridges is discussed in Chapter 13.

Aluminum alkyls having the empirical formula AlR_3 are dimerized to give Al_2R_6 structures in which the two-electron three-center bonds involve alkyl groups as the bridging units. For example, $Al_2(CH_3)_6$ has the arrangement and dimensions shown in the following structure:
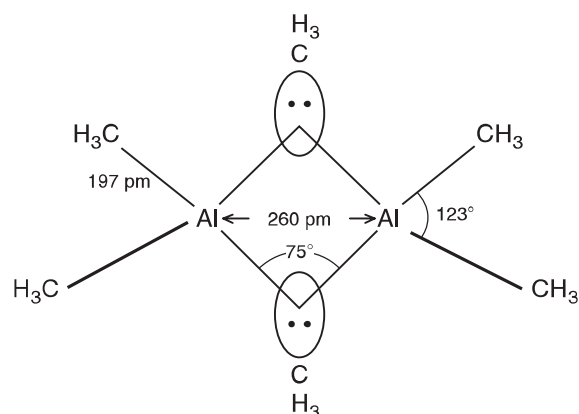
Other aluminum alkyls also exist as dimers as a result of bridging by the alkyl groups. In the structure just shown, there are four CH_3 groups that are nonbridging and only two that are bridging. If an aluminum alkyl is prepared that contains more than one type of alkyl group, it is possible to determine which type of group forms the bridges. One such case is that of $Al_2(CH_3)_2(t\text{-}C_4H_9)_4$. In this case, it is found that the methyl groups are contained in the bridges, but none are found in the more numerous terminal positions. Therefore, we conclude that the methyl group forms stronger bridges between two aluminum atoms than does the *t*-butyl group. When other compounds of this type are prepared so that competition is set up between potential bridging groups, it is found that the strengths of bridges between aluminum atoms varies as $CH_3 > C_2H_5 > t\text{-}C_4H_9$. The associated nature of the aluminum alkyls is discussed in greater detail in Chapter 12. Chloride ions form the bridges in the Al_2Cl_6 dimer. In fact, dimers exist when aluminum is bonded to numerous atoms and groups. The stability of the bridges formed varies in the order $H > Cl > Br > I > CH_3$.

A polymeric structure is exhibited by "beryllium dimethyl," which is actually $[Be(CH_3)_2]_n$ (see the structure of $(BeCl_2)_n$ shown earlier), and $LiCH_3$ exists as a tetramer, $(LiCH_3)_4$. The structure of the tetramer involves a tetrahedron of Li atoms with a methyl group residing above each face of the tetrahedron. An orbital on the CH_3 group forms multicentered bonds to four Li atoms. There are numerous compounds for which the electron-deficient nature of the molecules leads to aggregation.

4.5 STRUCTURES HAVING UNSATURATED RINGS

In addition to the types of structures shown thus far, there are several others that are both interesting and important. One such type of structure contains unsaturated rings. Because $R–C\equiv N$ is called a nitrile, compounds containing the $–P\equiv N$ group were originally called phosphonitriles. An unstable molecule having the formula $:N–PH_2$ is known as phosphazine. Although this molecule is unstable,

polymers containing this monomer unit with chlorine replacing the hydrogen atoms are well known. Heating a solution of PCl_5 and NH_4Cl in C_6H_5Cl or $HCl_2C–CHCl_2$ leads to the reaction

$$nNH_4Cl + nPCl_5 \rightarrow (NPCl_2)_n + 4nHCl \qquad (4.18)$$
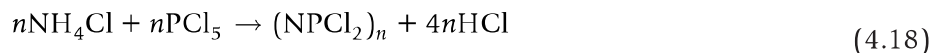
Several materials having the formula $(NPCl_2)_n$ are known, but the most extensively studied of them is the cyclic trimer, $(NPCl_2)_3$, which has the structure
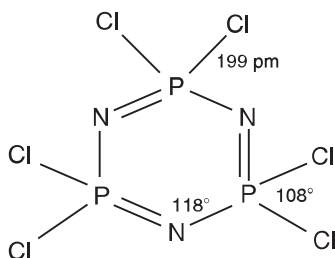
Compounds of this type are known as *phosphazines*, and they have structures that have a planar ring because of π bonding. In $(NPCl_2)_3$, the P–N distance is 158 pm, which is much shorter than the approximately 175 pm that is characteristic of a P–N single bond. Whether or not these compounds are strictly aromatic in character is not certain. The bonding in $(NPCl_2)_3$ is much more complex than that in benzene because, unlike benzene in which the delocalized π orbital arises from overlap of unhybridized p orbitals on the carbon atoms, the P–N bonding involves $p_N - d_P$ (the subscripts show the atoms involved) overlap to give $p_\pi - d_\pi$ bonding. Delocalization does not appear to be as complete in the phosphazines as it is in benzene. Substitution of two groups on the phosphorus atoms in the ring can lead to three types of products. If the substituents are on the same phosphorus atom, the product is known as *geminal*, but if substitution is on different phosphorus atoms, the product may have *cis* or *trans* configuration depending on whether the two groups are on the same or opposite sides of the ring:

Geminal

Cis

Trans
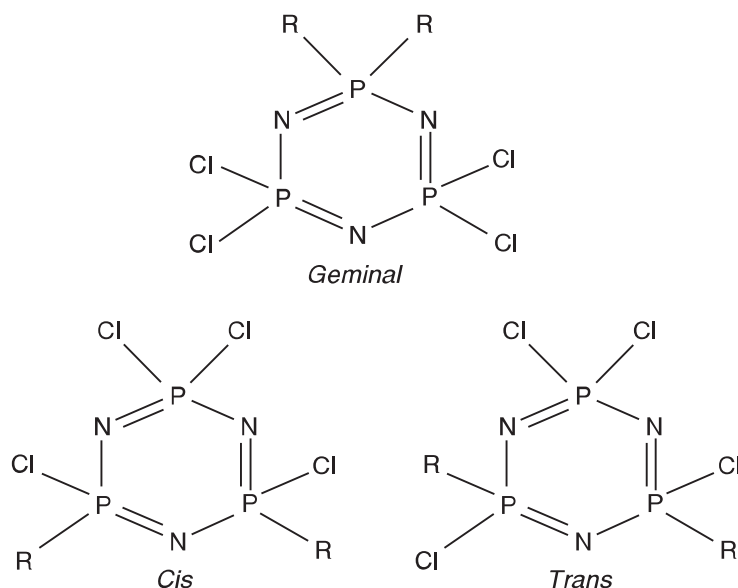
The chemistry of these compounds is discussed in greater detail in Chapter 14.

Carbon atoms have four valence-shell electrons. Because boron and nitrogen atoms have three and five valence-shell electrons, respectively, one boron and one nitrogen atom are formally equivalent to two carbon atoms. Therefore, a compound that contains an even number (n) of carbon atoms, could have an analogous structure that contains $n/2$ atoms of boron and $n/2$ atoms of nitrogen. The most common case of this type is a compound that is analogous to benzene, C_6H_6, which has the formula $B_3N_3H_6$. This compound, sometimes referred to as "inorganic benzene," is actually *borazine*, which has a structure that can be shown using resonance structures analogous to those used to describe benzene:
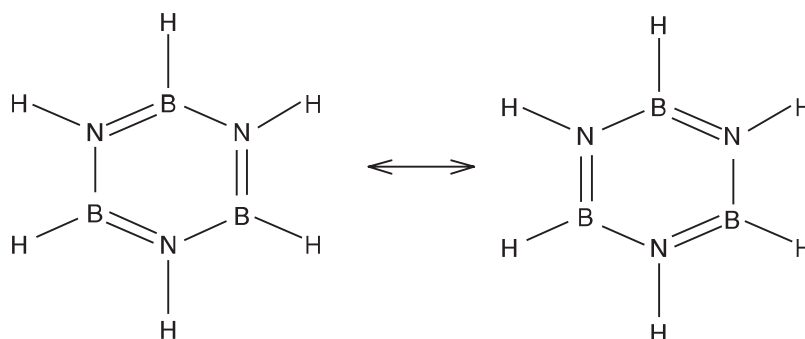
Therefore, the borazine molecule is considered to be aromatic. Borazine has many properties that are similar to those of benzene, although it is more reactive as a result of the B–N bonds being somewhat polar rather than purely covalent.

The trichloro derivative having a chlorine atom bound to each of the boron atoms is known as *B*-trichloroborazine. Borazine can be prepared by several different methods, one of which is the reduction of the trichloro compound:

$$6 \text{ NaBH}_4 + 2 \text{ Cl}_3B_3N_3H_3 \rightarrow 2 \text{ B}_3N_3H_6 + 6 \text{ NaCl} + 3 \text{ B}_2H_6 \tag{4.19}$$
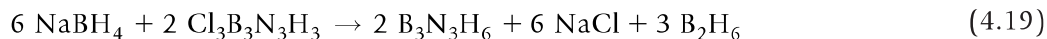
Borazine can also be prepared directly by the reaction of diborane with ammonia.

$$3 \text{ B}_2H_6 + 6 \text{ NH}_3 \rightarrow 2 \text{ B}_3N_3H_6 + 12 \text{ H}_2 \tag{4.20}$$
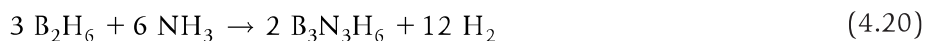
More of the chemistry of this interesting compound is presented in Chapter 13.

4.6 BOND ENERGIES

Closely related to molecular structure are the energies associated with chemical bonds. It is frequently possible to make decisions regarding the stability of alternative structures based on the types of bonds present. However, because SF_4 has four S–F single bonds, it is not possible to determine whether the trigonal pyramidal or irregular tetrahedron is the stable structure because each of them has four bonds. However, for many situations, bond energies provide a useful tool (see Table 4.1).

Table 4.1 Average Bond Energies.

Bond	Energy, kJ mol^{-1}	Bond	Energy, kJ mol^{-1}	Bond	Energy, kJ mol^{-1}
H–H	435	O=S	523	Ge–Ge	188
H–O	459	O–N	201	Ge–H	285
H–F	569	O–P	335	Ge–F	473
H–Cl	431	O–As	331	P–P	209
H–Br	368	O–C	360	P–F	498
H–I	297	O=C	799	P–Cl	331
H–N	389	O≡C	1075	P–Br	268
H–P	326	O–Si	464	P–I	215
H–As	297	O=Si	640	Si–F	598
H–Sb	255	O≡Si	803	Si–Cl	402
H–S	368	O–Ge	360	As–As	180
H–Se	305	S–S	264	As–F	485
H–Te	241	S=S	431	As–Cl	310
H–C	414	S–Cl	272	As–Br	255
H–Si	319	S–Br	212	C–C	347
H–Ge	285	S–C	259	C=C	611
H–Sn	251	N–F	280	C≡C	837
H–Pb	180	N–Cl	188	C–N	305
H–B	389	N–N	159	C–F	490
H–Mg	197	N=N	418	C–Cl	326
H–Li	238	N≡N	946	C–Br	272
H–Na	201	N=O	594	O–F	213
H–K	184	N–Ge	255	O–S	364
H–Rb	167	N–Si	335		
O=O	498	O–Cl	205		
O–O	142	C=N	615		

Consider a compound such as $N(OH)_3$, which we would suspect is not the most stable arrangement for one nitrogen atom, three oxygen atoms, and three hydrogen atoms. Suppose one reaction of such a molecule can be written as
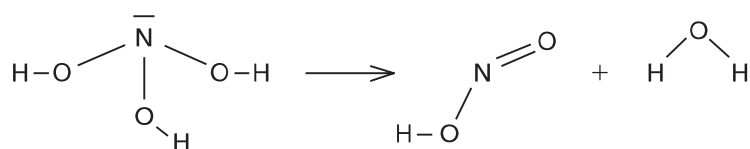
We can consider this reaction as taking place by breaking all the bonds in $N(OH)_3$ and then making all the bonds in HNO_2 (which is actually HONO) and H_2O. Breaking the bonds in $N(OH)_3$ means breaking three N–O bonds (201 kJ each) and three H–O bonds (459 kJ each). The energy required would be $3(201\,kJ) + 3(459\,kJ) = 1980\,kJ$. When the products form, the bonds formed are two H–O bonds in water and one H–O bond, one N–O bond (201 kJ), and one N=O bond (607 kJ) in HNO_2. These bonds give a total of 2185 kJ for the bonds *formed*, which means this is the amount of energy *released*. Therefore, for the entire process the energy change is $(1980\,kJ - 2185\,kJ) = -205\,kJ$, so $N(OH)_3$ should be unstable with respect to the HNO_2 and H_2O products. Such calculations tell us nothing about the *rate* of a process, because the rate depends on the pathway, whereas the thermodynamic stability depends only on the initial and final states. Even reactions that are energetically favorable may take place slowly (or not at all) because there may be no low-energy pathway.

An additional example of the use of bond energies will be considered. Earlier in this chapter, we considered the structure of the cyanate ion, OCN^-. Suppose the structures being considered are

$$\overline{\underline{O}} = C = \overline{\underline{N}} \qquad \overline{\underline{O}} = N = \overline{\underline{C}}$$
$$\text{I} \qquad\qquad \text{II}$$

and we wish to make a prediction regarding the relative stability of the structures. From the discussion presented earlier, we know that structure I is more likely because in structure II there is a positive formal charge on the nitrogen atom. The bond energies that are needed are as follows:

C=O 799 kJ   N=O 594 kJ
C=N 615 kJ

If we start with the atoms (and one additional electron) and form the bonds, structure I would release a total energy of $-1414\,kJ$ while structure II would release $-1209\,kJ$. Therefore, we predict (correctly) that the structure for the ion should be OCN^- rather than ONC^-. However, the structure

$$\overline{\underline{N}} = O = \overline{\underline{C}}$$
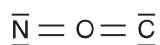
involves one N=O bond (594 kJ) and one C=O bond (799 kJ), so it appears from bond energies to be almost as stable as structure I just shown (1414 kJ versus 1393 kJ). However, this structure places a +2 formal charge on the oxygen atom, which is contrary to the principles of bonding. It is best not to

stretch the bond energy approach too far and to use it in conjunction with other information such as formal charges and electronegativities when trying to decide issues related to stability.

The bond energy approach may not always be adequate because it is the free energy change, ΔG, that is related to equilibrium constants, and the free energy is given by

$$\Delta G = \Delta H - T\Delta S \qquad (4.22)$$

Accordingly, the difference in entropy for the structures in question may also be a factor in some cases. In spite of this, bond energies provide a basis for comparing structures. In order to use this approach, energies for many types of bonds are needed, and they are given in Table 4.1.

It should always be kept in mind that bond energies are usually *average* values based on the energies of bonds in several types of molecules. In a given molecule, a certain bond may have an energy that is somewhat different from the value given in the table. Therefore, in cases where a decision on the difference in stability between two structures is based on bond energies, regard small differences as being inconclusive.

One interesting and highly significant application of bond energies involves the enormous difference in the character of CO_2 and SiO_2. In the case of CO_2, the structure is a monomeric molecule that has two double bonds,

$$\overline{\text{O}} = \text{c} = \overline{\text{O}}$$
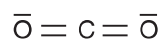
In the case of SiO_2, the structure is a *network* in which oxygen atoms form bridges between silicon atoms, with each Si being surrounded by four oxygen atoms:
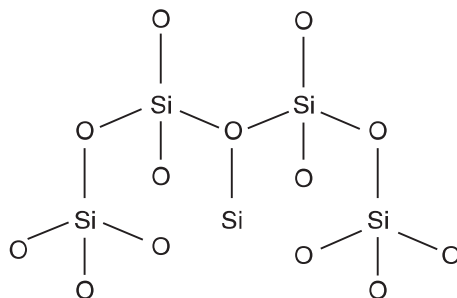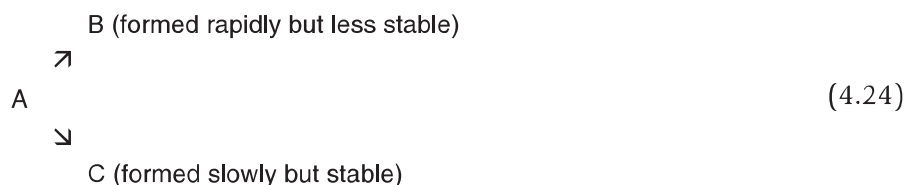

The π bonding in CO_2 results in strong double bonds that actually are stronger than two C–O single bonds (C=O is $745\,\text{kJ mol}^{-1}$, whereas each C–O is $360\,\text{kJ mol}^{-1}$). Between Si and O, π bonding is not as strong because of the difference in size of the orbitals on the two atoms. As a result, a Si–O single bond is $464\,\text{kJ mol}^{-1}$ (which is stronger than a C–O bond because of the greater polarity), whereas a Si=O bond is only $640\,\text{kJ mol}^{-1}$. Therefore, it is energetically more favorable for carbon to form two C=O double bonds, but four Si–O single bonds are more favorable energetically compared to two Si=O bonds. Carbon dioxide is a monomeric gas, whereas SiO_2 (which exists in several forms) is an extended solid that melts at over $1600\,°C$.

A compound that is less stable than some other compound into which it should transform with a release of energy may be locked in the less stable form because of the unfavorable kinetics for its transformation. Suppose the reaction

$$A \rightarrow B \tag{4.23}$$

is thermodynamically favorable. If the pathway for the reaction is such that the rate is very slow, A may not react because of kinetic inertness rather than its thermodynamic stability. Such a situation is known as *kinetic* stability rather than *thermodynamic* stability. A similar situation exists when the following system is considered:

$$
\begin{array}{c}
\text{B (formed rapidly but less stable)} \\
\nearrow \\
A \qquad\qquad\qquad\qquad (4.24) \\
\searrow \\
\text{C (formed slowly but stable)}
\end{array}
$$

In this case, the predominant product of the reaction will be B even though it is less stable than C because of the difference in reaction rates. Sometimes, B is referred to as the *kinetic* product while C is called the *thermodynamic* product.

In this chapter has been presented an elementary discussion of bonding principles that have broad applicability in the study of inorganic chemistry. These topics have been introduced by showing many of the important types of structures that are encountered in the study of inorganic materials. These structures will be revisited in later chapters, but the intent is to show many different types of structures and the relationships between many of them. Resonance, repulsion, electronegativity, and formal charge have been used to explain many of the aspects of bonding and they are useful for understanding structures.

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