Covalent Bonding

7

The Pyramids at dusk (w/c on paper), Lamplough, Augustus Osborne (1877–1930) / Private Collection / © Christopher Wood Gallery, London, UK / The Bridgeman Art Library

These pyramids of ancient Egypt look like tetrahedra but are not. Tetrahedra have three triangular sides and a triangular base. These pyramids have four triangular sides and a square base.

What immortal hand
or eye
Could frame thy
fearful symmetry?

—WILLIAM BLAKE
The Tiger

Earlier we referred to the forces that hold nonmetal atoms to one another, covalent bonds. These bonds consist of an electron pair shared between two atoms. To represent the covalent bond in the H_2 molecule, two structures can be written:

H:H or H—H

These structures can be misleading if they are taken to mean that the two electrons are fixed in position between the two nuclei. A more accurate picture of the electron density in H_2 is shown in Figure 7.1. At a given instant, the two electrons may be located at any of various points about the two nuclei. However, they are more likely to be found between the nuclei than at the far ends of the molecule.

To understand the stability of the electron-pair bond, consider the graph shown in Figure 7.2, where we plot the energy of interaction between two hydrogen atoms as a function of distance. At large distances of separation (far right) the system consists of two isolated H atoms that do not interact with each other. As the atoms come closer together (moving to the left in Figure 7.2), they experience an attraction that leads gradually to an energy minimum. At an internuclear distance of 0.074 nm and an attractive energy of 436 kJ, the system is in its most stable state; we refer to that state as the H_2 molecule. If the atoms are brought closer together, forces of repulsion become increasingly important and the energy curve rises steeply.

The existence of the energy minimum shown in Figure 7.2 is directly responsible for the stability of the H_2 molecule. The attractive forces that bring about this minimum result from two factors:

1. Locating two electrons between the two protons of the H_2 molecule lowers the electrostatic energy of the system. Attractive energies between oppositely charged particles (electron-proton) slightly exceed the repulsive energies between particles of like charge (electron-electron, proton-proton).

2. When two hydrogen atoms come together to form a molecule, the electrons are spread over the entire volume of the molecule instead of being confined to a particular atom. As pointed out in Chapter 6, quantum mechanics tells us that increasing the volume available to an electron decreases its kinetic energy. We often describe this situation by saying that the two 1s orbitals of the hydrogen atom "overlap" to form a

Chapter Outline

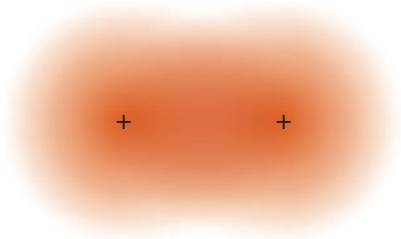


Figure 7.1 Electron density in H_2. The depth of color is proportional to the probability of finding an electron in a particular region.

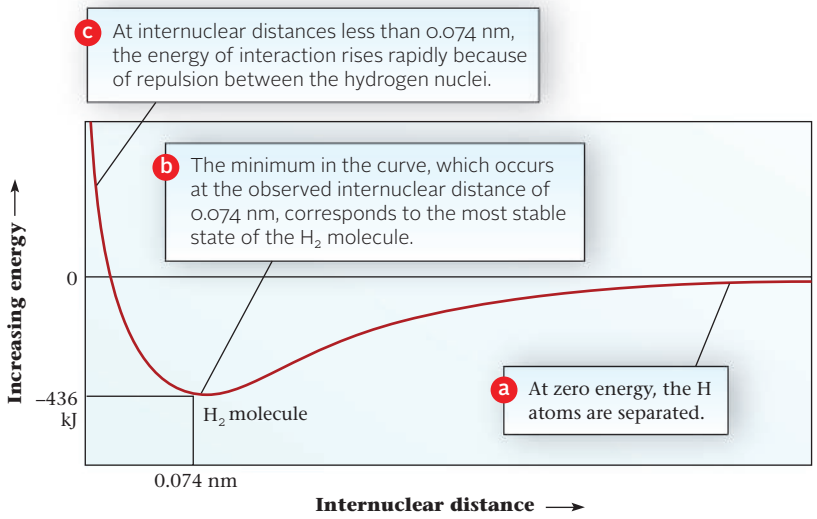


Figure 7.2 Energy of two hydrogen atoms as a function of the distance between their nuclei.

new bonding orbital. At any rate, calculations suggest that this is the principal factor accounting for the stability of the H_2 molecule.

This chapter is devoted to the covalent bond as it exists in molecules and polyatomic ions. We consider

- the distribution of outer level *(valence)* electrons in species in which atoms are joined by covalent bonds. These distributions are most simply described by *Lewis structures* (Section 7-1).
- molecular geometries. The so-called *valence shell electron-pair repulsion (VSEPR) model* can be used to predict the angles between covalent bonds formed by a central atom (Section 7-2).
- the polarity of covalent bonds and the molecules they form (Section 7-3). Most bonds and many molecules are polar in the sense that they have a positive and a negative pole.
- the distribution of valence electrons among *atomic orbitals,* using the valence bond approach (Section 7-4).

7-1 Lewis Structures; The Octet Rule

The idea of the covalent bond was first suggested by the American physical chemist Gilbert Newton Lewis (1875–1946) in 1916. He pointed out that the electron configuration of the noble gases appears to be a particularly stable one. Noble-gas atoms are themselves extremely unreactive. Moreover, as pointed out in Chapter 6, a great many monatomic ions have noble-gas structures. Lewis suggested that ***nonmetal atoms, by sharing electrons to form an electron-pair bond, can acquire a stable noble-gas structure.*** Consider, for example, two hydrogen atoms, each with one electron. The process by which they combine to form an H_2 molecule can be shown as

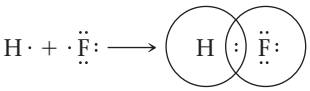
Noble-gas structures are stable in molecules, as they are in atoms and ions.

$$H\cdot + H\cdot \longrightarrow H:H$$

using dots to represent electrons; the circles emphasize that the pair of electrons in the covalent bond can be considered to occupy the 1s orbital of either hydrogen atom. In that sense, each atom in the H_2 molecule has the electronic structure of the noble gas helium, with the electron configuration $1s^2$.

This idea is readily extended to simple molecules of compounds formed by nonmetal atoms. An example is the HF molecule. You will recall that a fluorine atom has the electron configuration $1s^2 2s^2 2p^5$. It has seven electrons in its outermost principal energy level (**n** = 2). These are referred to as **valence electrons,** in contrast to the core electrons filling the principal level, **n** = 1. If the valence electrons are shown as dots around the symbol of the element, the fluorine atom can be represented as

The combination of a hydrogen with a fluorine atom leads to



As you can see, the fluorine atom "owns" six valence electrons outright and shares two others. Putting it another way, the F atom is surrounded by eight valence electrons; its electron configuration has become $1s^2 2s^2 2p^6$, which is that of the noble gas neon. This, according to Lewis, explains why the HF molecule is stable in contrast to species such as H_2F, H_3F, . . . none of which exist.

Any structure like this (without the circles) is referred to as a **Lewis structure.** In writing Lewis structures, only the valence electrons written above are shown, because they are the ones that participate in covalent bonding. For the main-group elements, the only ones dealt with here, the number of valence electrons is equal to the last digit of the group number in the periodic table (Table 7.1). Notice that elements in a given main group all have the same number of valence electrons. This explains why such elements behave similarly when they react to form covalently bonded species.

In the Lewis structure of a molecule or polyatomic ion, valence electrons ordinarily occur in pairs. There are two kinds of electron pairs.

1. A pair of electrons shared between two atoms is a **covalent bond,** ordinarily shown as a straight line between bonded atoms.
2. An **unshared electron pair,** owned entirely by one atom, is shown as a pair of dots on that atom. (An unshared pair is often referred to, more picturesquely, as a *lone pair*.)

The Lewis structures for the species OH^-, H_2O, NH_3, and NH_4^+ are

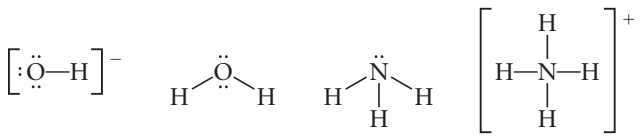


Table 7.1 Lewis Structures of Atoms Commonly Forming Covalent Bonds

Group:	1	2	13	14	15	16	17	18
No. of valence e^-:	1	2	3	4	5	6	7	8
	H·							
		·Be·	·B·	·C·	·N·	·O·	:F·	
				·Si·	·P·	·S·	:Cl·	
				·Ge·	·As·	·Se·	:Br·	:Kr:
					·Sb·	·Te·	:I·	:Xe:

Valence electrons are the ones involved in bonding.

Shared electrons are counted for both atoms.

This is why we put the second digit of the group number in bold type.

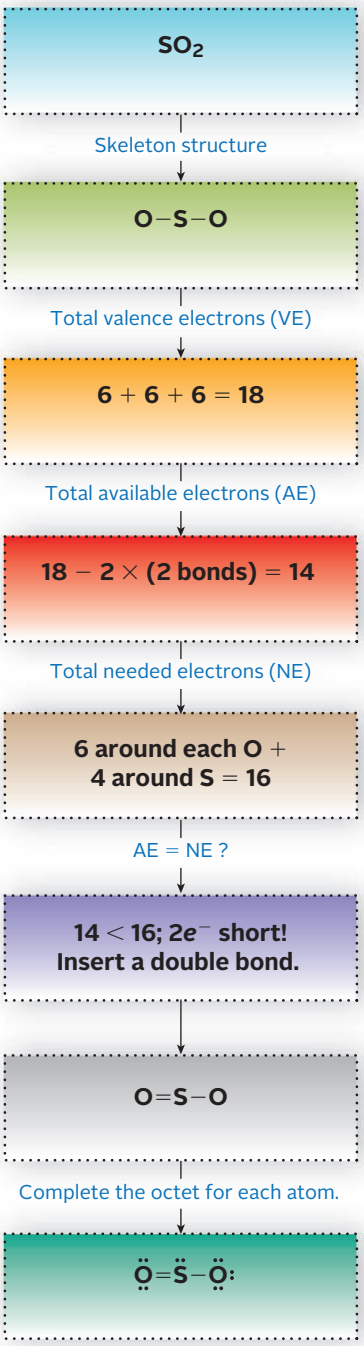
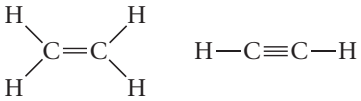


Figure 7.3 Flowchart for writing Lewis structures.

Notice that in each case the oxygen or nitrogen atom is surrounded by eight valence electrons. In each species, a single electron pair is shared between two bonded atoms. Each bond is called a **single bond.** There is one single bond in the OH^- ion, two in the H_2O molecule, three in NH_3, and four in NH_4^+. There are three unshared pairs in the hydroxide ion, two in the water molecule, one in the ammonia molecule, and none in the ammonium ion.

Bonded atoms can share more than one electron pair. A **double bond** occurs when bonded atoms share two electron pairs; in a **triple bond,** three pairs of electrons are shared. In ethylene (C_2H_4) and acetylene (C_2H_2), the carbon atoms are linked by a double bond and triple bond, respectively. Using two parallel lines to represent a double bond and three for a triple bond, we write the structures of these molecules as



ethylene, C_2H_4 acetylene, C_2H_2

Note that each carbon is surrounded by eight valence electrons and each hydrogen by two.

These examples illustrate the principle that atoms in covalently bonded species tend to have noble-gas electronic structures. This generalization is often referred to as the **octet rule.** Nonmetals, except for hydrogen, achieve a noble-gas structure by sharing in an *octet* of electrons (eight). Hydrogen atoms, in molecules or polyatomic ions, are surrounded by a *duet* of electrons (two).

Writing Lewis Structures

For very simple species, Lewis structures can often be written by inspection. Usually, though, you will save time by following these steps:

1. ***Draw a skeleton of the species joining atoms by single bonds***
   Most of the species appearing in this chapter consist of a **central atom** bonded to two or more *terminal atoms*.
   — The central atom is usually written first in the formula.
   — The terminal atoms are most often hydrogen, oxygen, and the halogens.
2. ***Count the number of valence electrons (VE).***
   — For a molecule, add the number of valence electrons of all the atoms present.
   — For a polyatomic anion, add the number of valence electrons of each atom plus one electron for each unit of negative charge (e.g., for SO_4^{2-}, add 2 electrons)
   — For a polyatomic cation, add the number of valence electrons of each atom and subtract one electron for each unit of positive charge (e.g., for NH_4^+, subtract 1 electron)
3. ***Count the number of valence electrons available for distribution (AE).***
   AE = VE − 2(number of bonds in the skeleton)
4. ***Count the number of electrons required to fill out an octet for each atom (except H) in the skeleton (NE).***
   Remember that shared atoms are counted for both atoms.
   (a) If AE = NE, your skeleton is correct. Distribute the available electrons as unshared pairs satisfying the octet rule.
   (b) If AE < NE, modify your skeleton by changing single bonds to double or triple bonds.
   — 2 electrons short: convert one single bond to a double bond.
   — 4 electrons short: convert one single bond to a triple bond, or two single bonds to double bonds.
   Hydrogen and the halogens never form double bonds.

Figure 7.3 shows how to follow these steps for SO_2.

Forming a multiple bond "saves" electrons because bonding pairs are counted for both atoms.

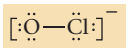
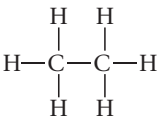
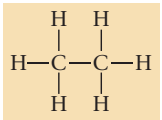
EXAMPLE 7.1

Draw Lewis structures of the hypochlorite ion, OCl^- (Figure 7.4), and the ethane, C_2H_6, molecule.

STRATEGY

1. Follow the steps outlined in Figure 7.3.
2. For ethane, hydrogen must be a terminal atom since it cannot form double bonds. Carbon ordinarily forms four bonds.

SOLUTION

OCl^- skeleton	$[O–Cl]^-$
VE	6 (for O) + 7 (for Cl) + 1(−1 charge) = 14
AE	AE = VE − 2(bonds) = 14 − 2(1 bond) = 12
NE	6 (for O to have an octet) + 6 (for Cl to have an octet) = 12
AE = NE ?	Yes; distribute electrons.
Lewis structure	
C_2H_6 skeleton	
VE	2 × 4 (for C) + 6 × 1 (for H) = 14
AE	AE = VE − 2(bonds) = 14 − 2(7 bonds) = 0
NE	0 : All the H atoms have duets and both C atoms have octets.
AE = NE ?	Yes; distribute electrons.
Lewis structure	

END POINT

After you have written the Lewis structure, it is a good idea to add the number of unshared electron pairs and bonding electrons. This sum must equal the number of valence electrons (VE).

EXAMPLE 7.2

Draw the Lewis structures of NO_2^- and N_2.

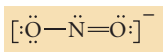
STRATEGY

Follow the steps outlined in Figure 7.3.

SOLUTION

Skeleton for NO_2^-	$[O–N–O]^-$
VE	2(6 (for O)) + 5 (for N) + 1(−1 charge) = 18
AE	AE = VE − 2(bonds) = 18 − 2(2 bonds) = 14
NE	2(6 (for each O)) + 4 (for N) = 16

continued

AE = NE ?	No; 2 electrons short
	Convert a single bond to a double bond.
Lewis structure	
Skeleton for N_2	N–N
VE	2(5 (for each N)) = 10
AE	AE = VE − 2(bonds) = 10 − 2(1 bond) = 8
NE	2 × 6 (for each N to have an octet) = 12
AE = NE ?	No; 4 electrons short
	Convert a single bond to a triple bond.
Lewis structure	

END POINT

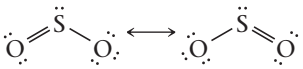
For the Lewis structure of NO_2^-, it does not matter which single bond you convert to a double bond. We will talk about this in more detail when we discuss resonance forms.

Figure 7.4 Hypochlorite ions in action. The OCl^- ion is the active bleaching agent in Clorox™ (see Example 7.1).

Resonance Forms

In certain cases, the Lewis structure does not adequately describe the properties of the ion or molecule that it represents. Consider, for example, the SO_2 structure in Figure 7.3. This structure implies that there are two different kinds of sulfur-to-oxygen bonds in SO_2. One of these appears to be a single bond, the other a double bond. Yet experiment shows that there is only one kind of bond in the molecule.

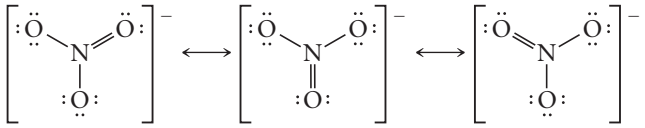
One way to explain this situation is to assume that each of the bonds in SO_2 is intermediate between a single and a double bond. To express this concept, two structures, separated by a double-headed arrow, are written



with the understanding that the true structure is intermediate between them. These are referred to as *resonance forms*. The actual structure is intermediate between the two resonance forms and is called a *resonance hybrid*. It is the only structure that actually exists (Figure 7.5). The individual resonance forms do not exist and are merely a convenient way to describe the real structures. The concept of **resonance** is invoked whenever a single Lewis structure does not adequately reflect the properties of a substance.

The double-headed arrow is used to separate resonance structures.

Another species for which it is necessary to invoke the idea of resonance is the nitrate ion. Here three equivalent structures can be written to explain the experimental observation that the three nitrogen-to-oxygen bonds in the NO_3^- ion are identical in all respects.



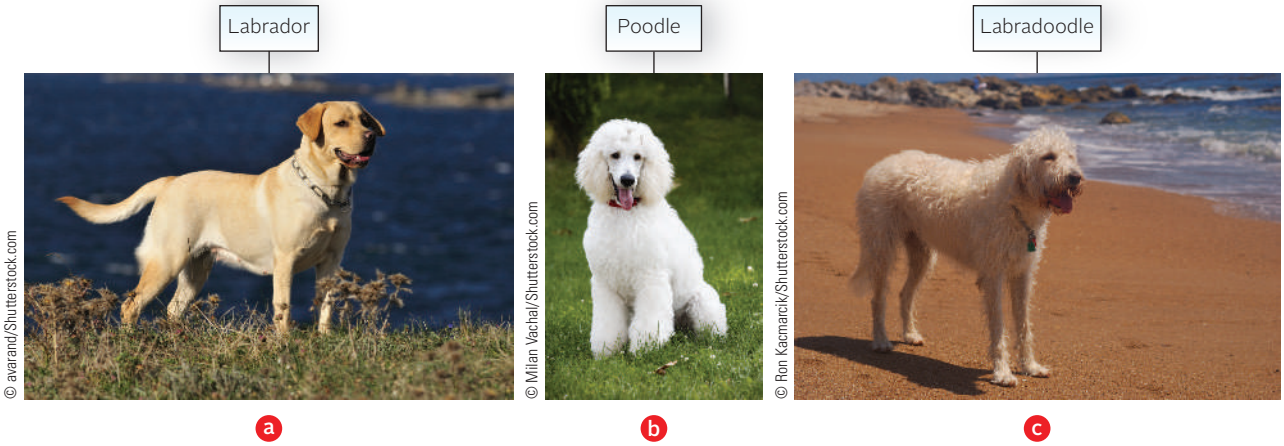
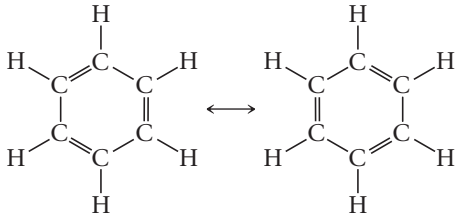
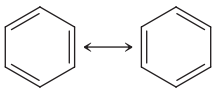


Figure 7.5 The labradoodle (c) is a hybrid of its parents, the labrador (a) and the poodle (b). In similar fashion, a pair of sp hybrid orbitals forms from the parents—an s and a p orbital.

Resonance can also occur with many organic molecules, including benzene, C_6H_6, which is known to have a hexagonal ring structure (Figure 7.6). Benzene can be considered a resonance hybrid of the two forms



These structures are commonly abbreviated as



with the understanding that, at each corner of the hexagon, a carbon is attached to a hydrogen atom.

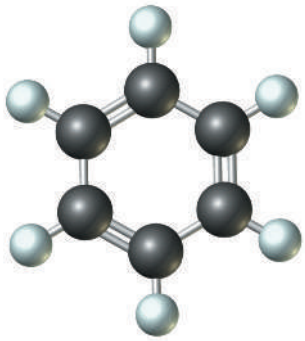


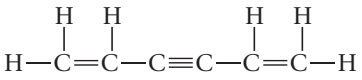
Figure 7.6 Benzene ball-and-stick model, showing double bonds.

We will encounter other examples of molecules and ions whose properties can be interpreted in terms of resonance. In all such species:

1. Resonance forms do not imply different kinds of molecules with electrons shifting eternally between them. There is only one type of SO_2 molecule; its structure is intermediate between those of the two resonance forms drawn for sulfur dioxide.

2. Resonance can be anticipated when it is possible to write two or more Lewis structures that are about equally plausible. In the case of the nitrate ion, the three structures we have written are equivalent. One could, in principle, write many other structures, but none of them would put eight electrons around each atom.

3. Resonance forms differ only in the distribution of electrons, not in the arrangement of atoms. The molecule



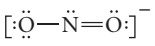
is not a resonance structure of benzene, even though it has the same molecular formula, C_6H_6. Indeed, it is an entirely different substance with different chemical and physical properties.

EXAMPLE 7.3

Write two resonance structures for the NO_2^- ion.

STRATEGY

1. The Lewis structure of NO_2^- is derived in Example 7.2.

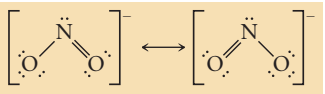


2. Change the position of the multiple bond and one of the unshared electron pairs.

3. Do not change the skeleton.

SOLUTION

The Lewis structures of the two resonance forms are



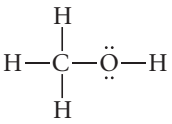
Formal Charge

Often it is possible to write two different Lewis structures for a molecule differing in the arrangement of atoms, that is,

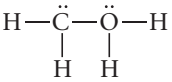
A—A—B or A—B—A

Isomers have the same formula but different properties.

Sometimes both structures represent real compounds that are *isomers* of each other. More often, only one structure exists in nature. For example, methyl alcohol (CH_4O) has the structure



In contrast, the structure



does not correspond to any real compound even though it obeys the octet rule.

There are several ways to choose the more plausible of two structures differing in their arrangement of atoms. As pointed out in Example 7.1, the fact that carbon almost always forms four bonds leads to the correct structure for ethane. Another approach involves a concept called **formal charge,** which can be applied to any atom within a Lewis structure. The formal charge is the difference between the number of valence electrons in the free atom and the number assigned to that atom in the Lewis structure. The assigned electrons include

Formal charge is the charge an atom would have if valence electrons in bonds were distributed evenly.

- all the unshared electrons owned by that atom.
- one half of the bonding electrons shared by that atom.

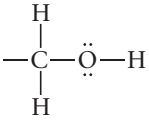
Thus the formal charge can be determined by counting the electrons "owned" by the atom, its valence electrons (VE), the unshared pairs around the atom, and the bonding electrons around the atom. We arrive at the following equation:

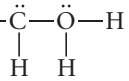
$$C_f = \text{VE} - \text{unshared electrons} - \tfrac{1}{2}(\text{bonding electrons})$$

Since a bond is always made up of two electrons, we can find the formal charge by using the modified equation below:

$$C_f = \text{VE} - \text{unshared electrons} - \text{number of bonds}$$

To show how this works, let's calculate the formal charges of carbon and oxygen in the two structures written above for methyl alcohol:

(1) 

(2) 

For C: VE = 4, unshared e^- = 0, bonds = 4
$C_f = 4 - 0 - 4 = 0$

For C: VE = 4, unshared e^- = 2, bonds = 3
$C_f = 4 - 2 - 3 = -1$

For O: VE = 6, unshared e^- = 4, bonds = 2
$C_f = 6 - 4 - 2 = 0$

For O: VE = 6, unshared e^- = 2, bonds = 3
$C_f = 6 - 2 - 3 = +1$

Ordinarily, the more likely Lewis structure is the one in which

- the formal charges are as close to zero as possible.
- any negative formal charge is located on the most strongly electronegative atom.

Applying these rules, we can see that structure (1) for methyl alcohol is preferred over structure (2). In (1), both carbon and oxygen have formal charges of zero. In (2), a negative charge is assigned to carbon, which is actually less electronegative than oxygen (2.5 versus 3.5).

Formal charge is not an infallible guide to predicting Lewis structures.

The concept of formal charge has a much wider applicability than this short discussion might imply. In particular, it can be used to predict situations in which conventional Lewis structures, written in accordance with the octet rule, may be incorrect (Table 7.2).

Exceptions to the Octet Rule: Electron-Deficient Molecules

Although most of the molecules and polyatomic ions referred to in general chemistry follow the octet rule, there are some familiar species that do not. Among these are molecules containing an odd number of valence electrons. Nitric oxide, NO, and nitrogen dioxide, NO_2, fall in this category:

With an odd number of valence electrons, there's no way they could all be paired.

NO no. of valence electrons = 5 + 6 = 11

NO_2 no. of valence electrons = 5 + 6(2) = 17

For such *odd electron* species (sometimes called free radicals) it is impossible to write Lewis structures in which each atom obeys the octet rule. In the NO

Table 7.2 Possible Structures for BeF_2 and BF_3

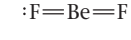
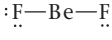
Structure I	C_f	Structure II	C_f
	Be = −2 F = +1		Be = 0 F = 0
	B = −1 F = +1,0,0		B = 0 F = 0

Figure 7.7 Nitrogen dioxide. NO_2, a red-brown gas, has an unpaired electron on the N atom.

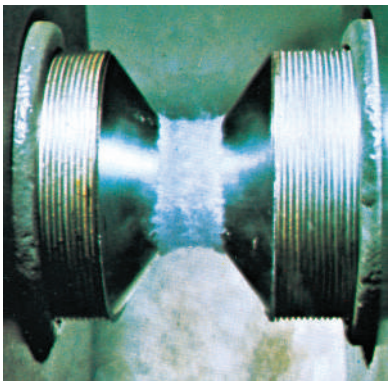
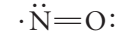
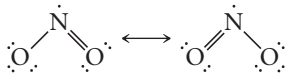


Figure 7.8 Oxygen (O_2) in a magnetic field. The liquid oxygen, which is blue, is attracted into a magnetic field between the poles of an electromagnet. Both the paramagnetism and the blue color are due to the unpaired electrons in the O_2 molecule.

molecule, the unpaired electron is put on the nitrogen atom, giving both atoms a formal charge of zero:

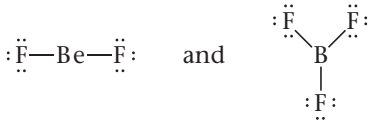


In NO_2 (Figure 7.7), the best structure one can write again puts the unpaired electron on the nitrogen atom:

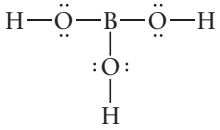


Elementary oxygen, like NO and NO_2, is paramagnetic (Figure 7.8). Experimental evidence suggests that the O_2 molecule contains two unpaired electrons *and* a double bond. It is impossible to write a conventional Lewis structure for O_2 that has these two characteristics. A more sophisticated model of bonding, using molecular orbitals (Appendix 4), is required to explain the properties of oxygen.

There are a few species in which the central atom violates the octet rule in the sense that it is surrounded by two or three electron pairs rather than four. Examples include the fluorides of beryllium and boron, BeF_2 and BF_3. Although one could write multiple bonded structures for these molecules in accordance with the octet rule (Table 7.2), experimental evidence suggests the structures

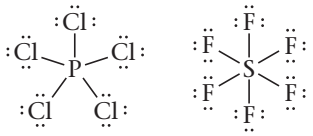


in which the central atom is surrounded by four and six valence electrons, respectively, rather than eight. Another familiar substance in which boron is surrounded by only three pairs of electrons rather than four is boric acid, H_3BO_3, used as an insecticide and fungicide.



Exceptions to the Octet Rule: Expanded Octets

The largest class of molecules to violate the octet rule consists of species in which the central atom is surrounded by more than four pairs of valence electrons. Typical molecules of this type are phosphorus pentachloride, PCl_5, and sulfur hexafluoride, SF_6. The Lewis structures of these molecules are



As you can see, the central atoms in these molecules have **expanded octets.** In PCl_5, the phosphorus atom is surrounded by 10 valence electrons (5 shared pairs); in SF_6, there are 12 valence electrons (6 shared pairs) around the sulfur atom.

In molecules of this type, the terminal atoms are most often halogens (F, Cl, Br, I); in a few molecules, oxygen is a terminal atom. The central atom is a nonmetal in the third, fourth, or fifth period of the periodic table. Most frequently, it is one of the following elements:

	Group 15	Group 16	Group 17	Group 18
3rd period	P	S	Cl	
4th period	As	Se	Br	Kr
5th period	Sb	Te	I	Xe

In most molecules, the central atom is surrounded by 8 electrons. Rarely, it is surrounded by 4 (BeF_2) or 6 (BF_3). Occasionally, the number is 10 (PCl_5) or 12 (SF_6).

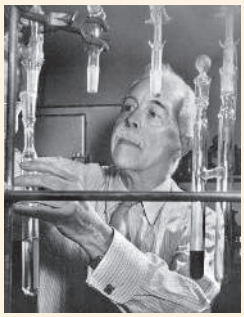
CHEMISTRY THE **HUMAN** SIDE

Born in Massachusetts, G. N. Lewis grew up in Nebraska, then came back East to obtain his B.S. (1896) and Ph.D. (1899) at Harvard. Although he stayed on for a few years as an instructor, Lewis seems never to have been happy at Harvard. A precocious student and an intellectual rebel, he was repelled by the highly traditional atmosphere that prevailed in the chemistry department there in his time. Many years later, he refused an honorary degree from his alma mater.

After leaving Harvard, Lewis made his reputation at MIT, where he was promoted to full professor in only four years. In 1912, he moved across the country to the University of California, Berkeley, as dean of the College of Chemistry and department head. He remained there for the rest of his life. Under his guidance, the chemistry department at Berkeley became perhaps the most prestigious in the country. Among the faculty and graduate students that he attracted were five future Nobel Prize winners: Harold Urey in 1934, William Giauque in 1949, Glenn Seaborg in 1951, Willard Libby in 1960, and Melvin Calvin in 1961.

In administering the chemistry department at Berkeley, Lewis demanded excellence in both research and teaching. Virtually the entire staff was involved in the general chemistry program; at one time eight full professors carried freshman sections.

Lewis's interest in chemical bonding and structure dated from 1902. In attempting to explain "valence" to a class at Harvard, he devised an atomic model to rationalize the octet rule. His model was deficient in many respects; for one thing, Lewis visualized cubic atoms with electrons located at the corners. Perhaps this explains why his ideas of atomic structure were not published until 1916. In that year, Lewis conceived of the electron-pair bond, perhaps his greatest single contribution to chemistry. At that time, it was widely believed that all bonds were ionic; Lewis's ideas were rejected by many well-known organic chemists.



Dr. Glenn Seaborg, University of California, Lawrence Berkeley Laboratories

Gilbert Newton Lewis
(1875–1946)

In 1923, Lewis published a classic book (later reprinted by Dover Publications) titled *Valence and the Structure of Atoms and Molecules*. Here, in Lewis's characteristically lucid style, we find many of the basic principles of covalent bonding discussed in this chapter. Included are electron-dot structures, the octet rule, and the concept of electronegativity. Here too is the Lewis definition of acids and bases (Chapter 13). That same year, Lewis published with Merle Randall a text called *Thermodynamics and the Free Energy of Chemical Substances*. Today, a revised edition of that text is still used in graduate courses in chemistry. (Lewis certainly deserved a Nobel Prize, but he never received one.)

The years from 1923 to 1938 were relatively unproductive for Lewis insofar as his own research was concerned. The applications of the electron-pair bond came largely in the areas of organic and quantum chemistry; in neither of these fields did Lewis feel at home. In the early 1930s, he published a series of relatively minor papers dealing with the properties of deuterium. Then in 1939 he began to publish in the field of photochemistry. Of approximately 20 papers in this area, several were of fundamental importance, comparable in quality to the best work of his early years. Retired officially in 1945, Lewis died a year later while carrying out an experiment on fluorescence.

All these atoms have d orbitals available for bonding (3d, 4d, 5d). These are the orbitals in which the extra pairs of electrons are located in such species as PCl_5 and SF_6. Because there is no 2d sublevel, C, N, and O never form expanded octets.

Sometimes, as with PCl_5 and SF_6, it is clear from the formula that the central atom has an expanded octet. Often, however, it is by no means obvious that this is the case. At first glance, formulas such as ClF_3 or XeF_4 look completely straightforward. However, when you try to draw the Lewis structure it becomes clear that an expanded octet is involved. The number of electrons available after the skeleton is drawn is *greater* than the number required to give each atom an octet. When that happens, ***distribute the extra electrons (two or four) around the central atom as unshared pairs.***

The presence of expanded octets requires modification of the process we delineated in Figure 7.3. Figure 7.9 (page 167) is a modification that includes the possibility of an expanded octet. We use ClF_3 as an example.

EXAMPLE 7.4

Draw Lewis structures of XeF_4.

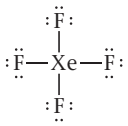
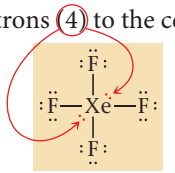
STRATEGY

If AE < NE, follow the process described in Figure 7.3.

If AE = NE, your skeleton is correct; add electrons as unshared pairs to form octets around the atoms.

If AE > NE, follow the process described in Figure 7.9.

SOLUTION

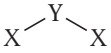
Skeleton	
VE	4(7 (for each F)) + 8 (for Xe) = 36
AE	AE = VE − 2(bonds) = 36 − 2(4 bonds) = 28
NE	4(6 (for each F to have an octet)) + 0 (Xe has an octet) = 24
AE = NE ?	No; AE > NE. There are 4 extra electrons.
Satisfy the octet rule	
Lewis structure	Add extra electrons (4) to the central atom. 

7-2 Molecular Geometry

The geometry of a diatomic molecule such as Cl_2 or HCl can be described very simply. Because two points define a straight line, the molecule must be linear.

Cl—Cl H—Cl

With molecules containing three or more atoms, the geometry is not so obvious. Here, the angle between bonds, called the **bond angle,** must be considered. For example, a molecule of the type YX_2, where Y represents the central atom and X an atom bonded to it, can be

- a **linear molecule,** with a bond angle of 180°: X—Y—X
- a **bent molecule,** with a bond angle less than 180°: 

The major features of **molecular geometry** can be predicted on the basis of a quite simple principle—**electron-pair repulsion.** This principle is the essence of the *valence-shell electron-pair repulsion (VSEPR) model,* first suggested by N. V. Sidgwick (1873–1952) and H. M. Powell (1906–1991) in 1940. It was developed

and expanded later by R. J. Gillespie (1924–) and R. S. Nyholm (1917–1971). According to the **VSEPR model,** ***the valence electron pairs surrounding an atom repel one another. Consequently, the orbitals containing those electron pairs are oriented to be as far apart as possible.***

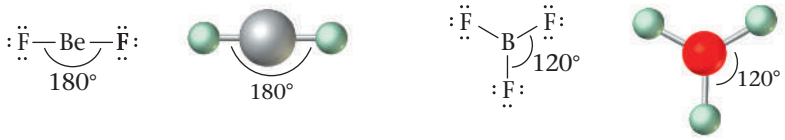
In this section we apply this model to predict the geometry of some rather simple molecules and polyatomic ions. In all these species, a central atom is surrounded by from two to six pairs of electrons.

Ideal Geometries with Two to Six Electron Pairs on the Central Atom

We begin by considering species in which a central atom, A, is surrounded by from two to six electron pairs, all of which are used to form single bonds with terminal atoms, X. These species have the general formulas AX_2, AX_3, . . . , AX_6. It is understood that there are no unshared pairs around atom A.

To see how the bonding orbitals surrounding the central atom are oriented with respect to one another, consider Figure 7.10, which shows the **ideal geometry** positions taken naturally by two to six balloons tied together at the center. The balloons, like the orbitals they represent, arrange themselves to be as far from one another as possible.

Figure 7.11 shows the geometries predicted by the VSEPR model for molecules of the types AX_2 to AX_6. The geometries for two and three electron pairs are those associated with species in which the central atom has less than an octet of electrons. Molecules of this type include BeF_2 (in the gas state) and BF_3, which have the Lewis structures shown below:



Two electron pairs are as far apart as possible when they are directed at 180° to one another. This gives BeF_2 a linear structure. The three electron pairs around the boron atom in BF_3 are directed toward the corners of an equilateral triangle; the bond angles are 120°. We describe this geometry as **trigonal planar.**

In species that follow the octet rule, the central atom is surrounded by four electron pairs. If each of these pairs forms a single bond with a terminal atom, a molecule of the type AX_4 results. The four bonds are directed

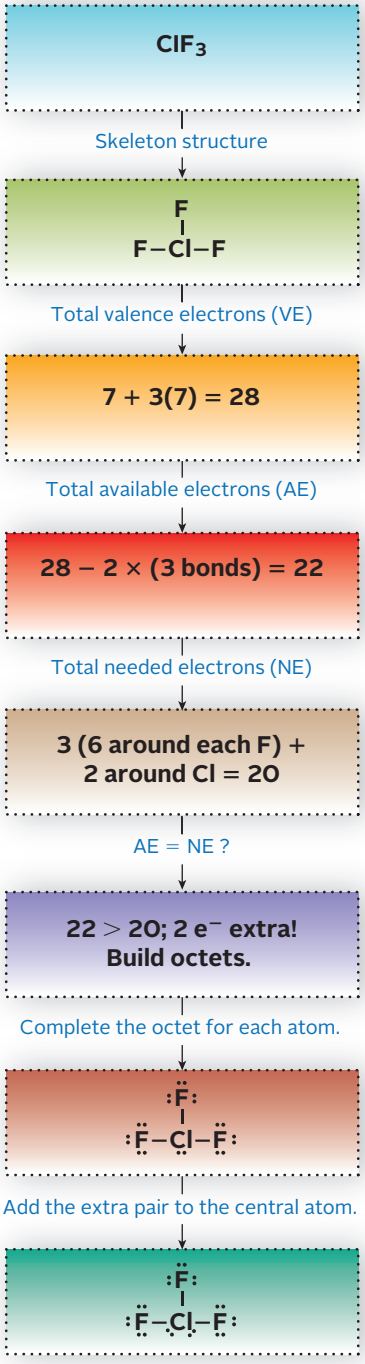
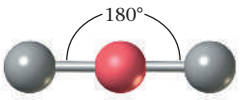
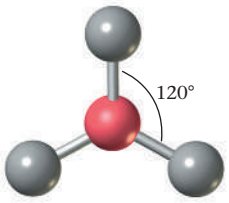
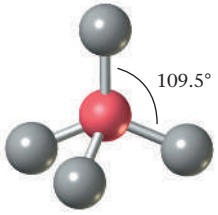
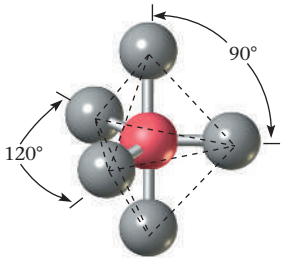
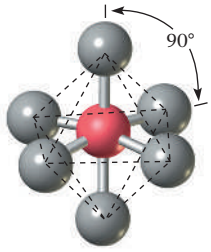


Figure 7.9 Flowchart for Lewis structures with expanded octets.

Figure 7.10 VSEPR electron-pair geometries. The balloons, by staying as far apart as possible, illustrate the geometries (*left to right*) for two to six electron pairs.

Figure 7.11 Molecular geometries for molecules with two to six electron-pair bonds around a central atom (A).

Species type	Orientation of electron pairs	Predicted bond angles	Example	Ball-and-stick model
AX_2	Linear	180°	BeF_2	
AX_3	Trigonal planar	120°	BF_3	
AX_4	Tetrahedron	109.5°	CH_4	
AX_5	Trigonal bipyramid	90° 120° 180°	PF_5	
AX_6	Octahedron	90° 180°	SF_6	

toward the corners of a regular **tetrahedron.** All the bond angles are 109.5°, the tetrahedral angle. This geometry is found in many polyatomic ions such as NH_4^+ and SO_4^{2-} and in a wide variety of organic molecules, the simplest of which is methane, CH_4.

This puts the four electron pairs as far apart as possible.

Molecules of the type AX_5 and AX_6 require the central atom to have an expanded octet. The geometries of these molecules are shown at the bottom of Figure 7.11. In PF_5, the five bonding pairs are directed toward the corners of a **trigonal bipyramid,** a figure formed when two triangular pyramids are fused together, base to base. Three of the fluorine atoms are located at the corners of an equilateral triangle with the phosphorus atom at the center; the other two fluorine atoms are directly above and below the P atom. In SF_6, the six bonds are directed toward the corners of a regular **octahedron,** a figure with eight sides but *six* vertices. An octahedron can be formed by fusing two **square pyramids** base to base. Four of the fluorine atoms in SF_6 are located at the corners of a square with the S atom at the center; one fluorine atom is directly above the *S* atom, another directly below it.

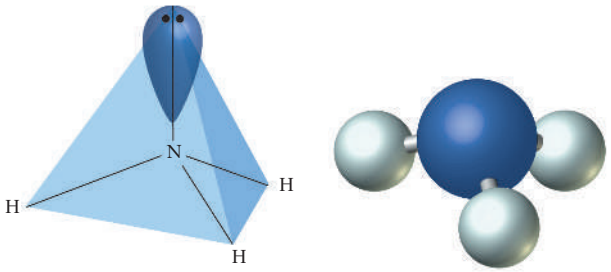


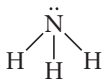
Figure 7.12 Two ways of showing the geometry of the NH_3 molecule. The orientation of the electron pairs, including the unshared pair (black dots), is shown at left. The orientation of the atoms is shown at the right. The nitrogen atom is located directly above the center of the equilateral triangle formed by the three hydrogen atoms. The NH_3 molecule is described as a trigonal pyramid.

Effect of Unshared Pairs on Molecular Geometry

In many molecules and polyatomic ions, one or more of the electron pairs around the central atom are unshared. The VSEPR model is readily extended to predict the geometries of these species. In general

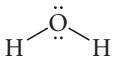
1. The *electron-pair geometry* is approximately the same as that observed when only single bonds are involved. The bond angles are ordinarily a little smaller than the ideal values listed in Figure 7.11.
2. The *molecular geometry* is quite different when one or more unshared pairs are present. In describing molecular geometry, we refer only to the positions of the bonded atoms. These positions can be determined experimentally; positions of unshared pairs cannot be established by experiment. Hence, the locations of unshared pairs are not specified in describing molecular geometry.

With these principles in mind, consider the NH_3 molecule:



The apparent orientation of the four electron pairs around the N atom in NH_3 is shown at the left of Figure 7.12. Notice that, as in CH_4, the four pairs are directed toward the corners of a regular tetrahedron. The diagram at the right of Figure 7.12 shows the positions of the atoms in NH_3. The nitrogen atom is located above the center of an equilateral triangle formed by the three hydrogen atoms. The molecular geometry of the NH_3 molecule is described as a **trigonal pyramid.** The nitrogen atom is at the apex of the pyramid, and the three hydrogen atoms form its triangular base. The molecule is three-dimensional, as the word "pyramid" implies.

The development we have just gone through for NH_3 is readily extended to the water molecule, H_2O. Here the Lewis structure shows that the central oxygen atom is surrounded by two single bonds and two unshared pairs:



The diagram at the left of Figure 7.13 emphasizes that the four electron pairs are oriented tetrahedrally. At the right, the positions of the atoms are shown. Clearly they are not in a straight line; the H_2O molecule is bent.

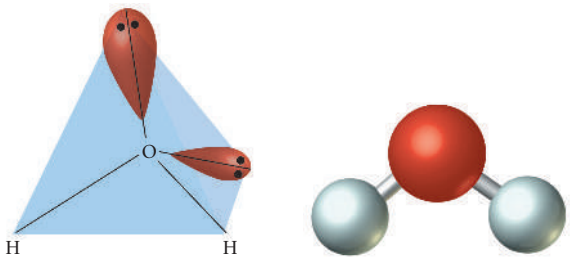


Figure 7.13 Two ways of showing the geometry of the H_2O molecule. At the left, the two unshared pairs are shown. As you can see from the drawing at the right, H_2O is a bent molecule. The bond angle, 105°, is a little smaller than the tetrahedral angle, 109.5°. The unshared pairs spread out over a larger volume than that occupied by the bonding pairs.

Table 7.3 Geometries with Two, Three, or Four Electron Pairs Around a Central Atom

No. of Terminal Atoms (X) + Unshared Pairs (E)	Species Type	Ideal Bond Angles*	Molecular Geometry	Examples
2	AX_2	180°	Linear	BeF_2, CO_2
3	AX_3	120°	Trigonal planar	BF_3, SO_3
	AX_2E	120°*	Bent	GeF_2, SO_2
4	AX_4	109.5°	Tetrahedron	CH_4
	AX_3E	109.5°*	Trigonal pyramid	NH_3
	AX_2E_2	109.5°*	Bent	H_2O

*In these species, the observed bond angle is ordinarily somewhat less than the ideal value.

Unshared pairs reduce bond angles below ideal values.

Experiments show that the bond angles in NH_3 and H_2O are slightly less than the ideal value of 109.5°. In NH_3 (three single bonds, one unshared pair around N), the bond angle is 107°. In H_2O (two single bonds, two unshared pairs around O), the bond angle is about 105°.

These effects can be explained in a rather simple way. An unshared pair is attracted by one nucleus, that of the atom to which it belongs. In contrast, a bonding pair is attracted by two nuclei, those of the two atoms it joins. Hence the electron cloud of an unshared pair is expected to spread out over a larger volume than that of a bonding pair. In NH_3, this tends to force the bonding pairs closer to one another, thereby reducing the bond angle. Where there are two unshared pairs, as in H_2O, this effect is more pronounced. In general, the VSEPR model predicts that unshared electron pairs will occupy slightly more space than bonding pairs.

Table 7.3 summarizes the molecular geometries of species in which a central atom is surrounded by two, three, or four electron pairs. The table is organized in terms of the number of terminal atoms, X, and unshared pairs, E, surrounding the central atom, A.

EXAMPLE 7.5

Predict the geometry of NH_4^+, BF_3, and PCl_3.

STRATEGY

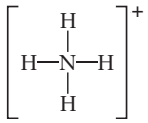
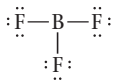
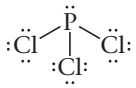
1. Start by writing Lewis structures for each species.
2. Focus on the central atom, then decide what species type (AX_2, AX_3, . . .) the molecule or ion is.

   A represents the central atom.

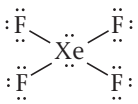
   X represents the terminal atoms.

   E represents the unshared electron pairs.
3. Recall Table 7.3, which matches the species type with the molecular geometry and ideal bond angles for the species.

continued

SOLUTION	
Lewis structure for NH_4^+	
Species type	A = N, X = H (4), no E → AX_4
Geometry	tetrahedral, 109.5° bond angles
Lewis structure for BF_3	
Species type	A = B, X = F (3), no E → AX_3
Geometry	trigonal planar, 120° bond angles
Lewis structure for PCl_3	
Species type	A = P, X = Cl (3), E = 1 → AX_3E
Geometry	trigonal pyramid (The ideal bond angles are 109.5° but actually are 104°.)

In many expanded-octet molecules, one or more of the electron pairs around the central atom are unshared. Recall, for example, the Lewis structure of xenon tetrafluoride, XeF_4 (Example 7.4).



There are six electron pairs around the xenon atom; four of these are covalent bonds to fluorine and the other two pairs are unshared. This molecule is classified as AX_4E_2 (Figure 7.14).

Geometries of molecules such as these can be predicted by the VSEPR model. The results are shown in Figure 7.15. The structures listed include those of all types of molecules having five or six electron pairs around the central atom, one or more of which may be unshared. Note that

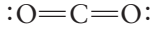
- in molecules of the type AX_4E_2, the two lone pairs occupy opposite rather than adjacent vertices of the octahedron.
- in the molecules AX_4E, AX_3E_2, and AX_2E_3 the lone pairs occupy successive positions in the equilateral triangle at the center of the trigonal bipyramid.

The way the Lewis structure is written does not necessarily imply geometry.

Multiple Bonds

The VSEPR model is readily extended to species in which double or triple bonds are present. A simple principle applies: ***Insofar as molecular geometry is concerned, a multiple bond behaves like a single bond.*** This makes sense. The four electrons in a double bond, or the six electrons in a triple bond, must be located between the two atoms, as are the two electrons in a single bond. This means that the electron pairs in a **multiple bond** must occupy the same region of space as those in a single bond. Hence the "extra" electron pairs in a multiple bond have no effect on geometry.

To illustrate this principle, consider the CO_2 molecule. Its Lewis structure is



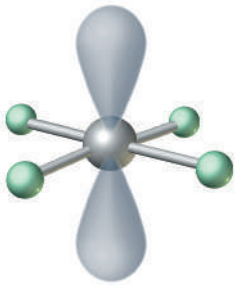
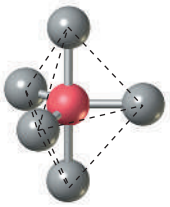
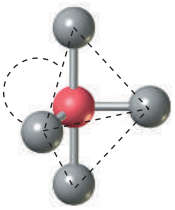
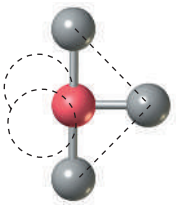
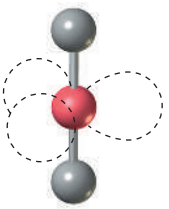


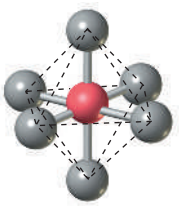
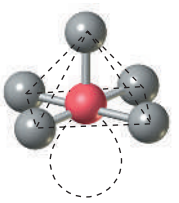
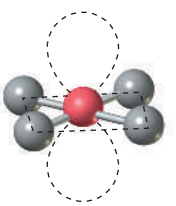
Figure 7.14 Xenon tetrafluoride, an AX_4E_2 molecule.

Figure 7.15 Molecular geometries for molecules with expanded octets and unshared electron pairs. The gray spheres represent terminal atoms (X), and the open ellipses represent unshared electron pairs (E). For example, AX_4E represents a molecule in which the central atom is surrounded by four covalent bonds and one unshared electron pair.

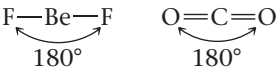
5 ELECTRON PAIRS

Species type	Structure	Description	Example	Bond angles
AX_5		Trigonal bipyramidal	PF_5	90°, 120°, 180°
AX_4E		See-saw	SF_4	90°, 120°, 180°
AX_3E_2		T-shaped	ClF_3	90°, 180°
AX_2E_3		Linear	XeF_2	180°

6 ELECTRON PAIRS

AX_6		Octahedron	SF_6	90°, 180°
AX_5E		Square pyramidal	ClF_5	90°, 180°
AX_4E_2		Square planar	XeF_4	90°, 180°

The central atom, carbon, has two double bonds and no unshared pairs. For purposes of determining molecular geometry, we pretend that the double bonds are single bonds, ignoring the extra bonding pairs. The bonds are directed to be as far apart as possible, giving a 180° O—C—O bond angle. The CO_2 molecule, like BeF_2, is linear:



CO_2, like BeF_2, is an AX_2 molecule with no unshared pairs.

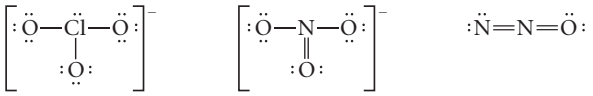
This principle can be restated in a somewhat different way for molecules in which there is a single central atom. The geometry of such a molecule depends only on

- ***the number of terminal atoms, X, bonded to the central atom, irrespective of whether the bonds are single, double, or triple.***
- ***the number of unshared pairs, E, around the central atom.***

This means that Table 7.3 can be used in the usual way to predict the geometry of a species containing multiple bonds.

EXAMPLE 7.6

Predict the geometries of the ClO_3^- ion, the NO_3^- ion, and the N_2O molecule, which have the following Lewis structures, respectively:



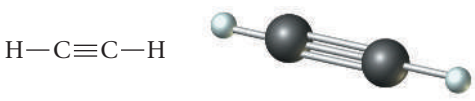
STRATEGY

1. Classify each species as AX_mE_n and use Table 7.3.
2. Multiple bonds count as single bonds. It is the number of terminal atoms (X) that are counted, not the number of bonds.

SOLUTION

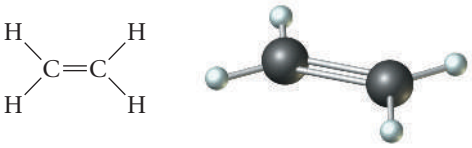
For ClO_3^-:	
Species type	A = Cl, X = O = 3, E = 1 → AX_3E
Geometry	trigonal pyramid, ideal bond angles are 109.5°
For NO_3^-:	
Species type	A = N, X = O = 3, E = 0 → AX_3
Geometry	trigonal planar, ideal bond angles are 120°
For N_2O:	
Species type	A = N, X = N and O = 2, E = 0 → AX_2
Geometry	linear, ideal bond angles are 180°

The VSEPR model applies equally well to molecules in which there is no single central atom. Consider the acetylene molecule, C_2H_2. Recall that here the two carbon atoms are joined by a triple bond:

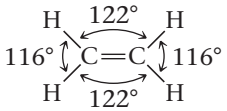


Each carbon atom behaves as if it were surrounded by two electron pairs. Both of the bond angles (H—C≡C and C≡C—H) are 180°. The molecule is linear; the four atoms are in a straight line. The two extra electron pairs in the triple bond do not affect the geometry of the molecule.

In ethylene, C_2H_4, there is a double bond between the two carbon atoms. The molecule has the geometry to be expected if each carbon atom had only three pairs of electrons around it.



The six atoms are located in a plane with bond angles of approximately 120°. Actually, the double bond between the carbon atoms occupies slightly more space than a single bond joining carbon to hydrogen. As a result, the H—C═C angles are slightly larger than 120°, and the H—C—H angles are slightly less.



7-3 Polarity of Molecules

Covalent bonds and molecules held together by such bonds may be—

- *polar*. As a result of an unsymmetrical distribution of electrons, the bond or molecule contains a positive and a negative pole and is therefore a *dipole*.
- *nonpolar*. A symmetrical distribution of electrons leads to a bond or molecule with no positive or negative poles.

Polar and Nonpolar Covalent Bonds

The two electrons in the H_2 molecule are shared equally by the two nuclei. Stated another way, a bonding electron is as likely to be found in the vicinity of one nucleus as another. Bonds of this type are described as nonpolar. A **nonpolar bond** is formed whenever the two atoms joined are identical, as in H_2 and F_2.

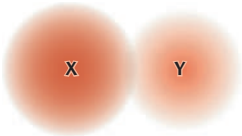


Figure 7.16 Bond polarity. If atom X is more electronegative than atom Y, the electron cloud of the bonding electrons will be concentrated around atom X. Thus the bond is polar.

In the HF molecule, the distribution of the bonding electrons is somewhat different from that in H_2 or F_2. Here the density of the electron cloud is greater about the fluorine atom. The bonding electrons, on the average, are shifted toward fluorine and away from the hydrogen (atom Y in Figure 7.16). A bond in which the electron density is unsymmetrical is referred to as a **polar bond.**

Atoms of two different elements always differ at least slightly in their electronegativity (recall Table 6.7). Hence covalent bonds between unlike atoms are always polar. Consider, for example, the H—F bond. Because fluorine has a higher electronegativity (4.0) than does hydrogen (2.2), bonding electrons are displaced toward the fluorine atom. The H—F bond is polar, with a partial negative charge at the fluorine atom and a partial positive charge at the hydrogen atom.

All molecules, except those of elements, have polar bonds.

The extent of polarity of a covalent bond is related to the difference in electronegativities of the bonded atoms. If this difference is large, as in H—F ($\Delta EN = 1.8$), the bond is strongly polar. Where the difference is small, as in H—C ($\Delta EN = 0.3$), the bond is only slightly polar.

Polar and Nonpolar Molecules

A **polar molecule** is one that contains positive and negative poles. There is a partial positive charge (positive pole) at one point in the molecule and a partial negative charge (negative pole) at a different point. As shown in Figure 7.17, polar molecules orient themselves in the presence of an electric field. The positive pole in the molecule tends to align with the external negative charge, and the negative pole with the

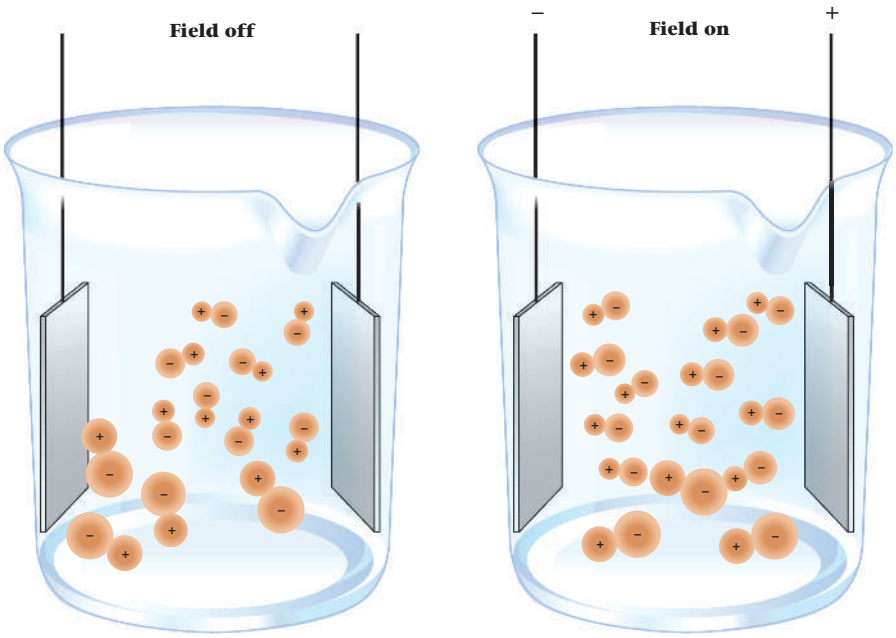


Figure 7.17 Orientation of polar molecules in an electric field. With the field off, polar molecules are randomly oriented. With the field on, polar molecules such as HF align their positive and negative ends toward the negative and positive poles of the field, respectively. Nonpolar molecules such as H_2 do not line up.

external positive charge. In contrast, there are no positive and negative poles in a **nonpolar molecule.** In an electric field, nonpolar molecules, such as H_2, show no preferred orientation.

The extent to which molecules tend to orient themselves in an electrical field is a measure of their *dipole moment*. A polar molecule such as HF has a dipole moment; a nonpolar molecule such as H_2 or F_2 has a dipole moment of zero.

If a molecule is diatomic, it is easy to decide whether it is polar or nonpolar. A diatomic molecule has only one kind of bond; hence the polarity of the molecule is the same as the polarity of the bond. Hydrogen and fluorine (H_2, F_2) are nonpolar because the bonded atoms are identical and the bond is nonpolar. Hydrogen fluoride, HF, on the other hand, has a polar bond, so the molecule is polar. The bonding electrons spend more time near the fluorine atom so that there is a negative pole at that end and a positive pole at the hydrogen end. This is sometimes indicated by writing

$$H \longrightarrow F$$

The arrow points toward the negative end of the polar bond (F atom); the plus sign is at the positive end (H atom). The HF molecule is called a **dipole;** it contains positive and negative poles.

If a molecule contains more than two atoms it is not so easy to decide whether it is polar or nonpolar. In this case, not only bond polarity but also molecular geometry determines the polarity of the molecule. To illustrate what is involved, consider the molecules shown in Figure 7.18.

1. In BeF_2 there are two polar Be—F bonds; in both bonds, the electron density is concentrated around the more electronegative fluorine atom. However, because the BeF_2 molecule is linear, the two Be $\longrightarrow$ F dipoles are in opposite directions and cancel one another. The molecule has no net dipole and hence is nonpolar. From a slightly different point of view, in BeF_2 the centers of positive and negative charge coincide with each other at the Be atom. There is no way that a BeF_2 molecule can line up in an electric field.

2. Because oxygen is more electronegative than hydrogen (3.5 versus 2.2) an O—H bond is polar, with the electron density higher around the oxygen atom. In the bent H_2O molecule, the two H $\longrightarrow$ O dipoles do not cancel each

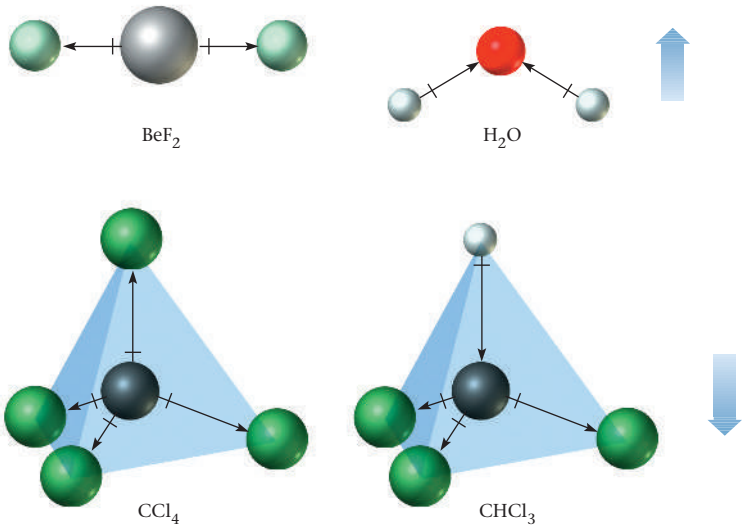


Figure 7.18 Polarity of molecules. All bonds in these molecules are polar, as shown by the ⟷ symbol, in which the arrow points to the more negative end of the bond and the + indicates the more positive end. In BeF_2 and CCl_4 the bond dipoles cancel and the molecules are nonpolar. In H_2O and $CHCl_3$ the molecules are polar, with net dipoles shown by the broad arrows pointing toward the negative poles.

other. Instead, they add to give the H_2O molecule a net dipole. The center of negative charge is located at the O atom; this is the negative pole of the molecule. The center of positive charge is located midway between the two H atoms; the positive pole of the molecule is at that point. The H_2O molecule is polar. It tends to line up in an electric field with the oxygen atom oriented toward the positive electrode.

3. Carbon tetrachloride, CCl_4, is another molecule that, like BeF_2, is nonpolar despite the presence of polar bonds. Each of its four bonds is a dipole, C ⟷ Cl. However, because the four bonds are arranged symmetrically around the carbon atom, they cancel. As a result, the molecule has no net dipole; it is nonpolar. If one of the Cl atoms in CCl_4 is replaced by hydrogen, the situation changes. In the $CHCl_3$ molecule, the H ⟷ C dipole does not cancel with the three C ⟷ Cl dipoles. Hence $CHCl_3$ is polar.

There are two criteria for determining the polarity of a molecule: bond polarity and molecular geometry. ***If the polar A—X bonds in a molecule AX_mE_n are arranged symmetrically around the central atom A, the molecule is nonpolar.***

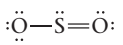
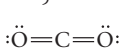
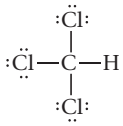
EXAMPLE 7.7

Determine which of the following is polar: SO_2, CO_2, and $CHCl_3$.

STRATEGY

1. Write the Lewis structure.
2. Classify the molecule or ion as AX_mE_n.
3. Decide on the geometry (Table 7.3 or Figure 7.15).
4. Consider the A—X bonds and answer the following questions:
   (a) Are the terminal atoms identical?
   Yes; possibly nonpolar (depends on symmetry). No; polar
   (b) Are the A—X bonds arranged symmetrically around the central atom?
   No; polar, Yes; nonpolar if the answer to (a) is also yes.

continued

SOLUTION	
Lewis structure for SO_2	
Species type	AX_2E
Geometry	bent
Identical terminal atoms?	yes
Symmetric A–X bonds?	no } polar
Lewis structure for CO_2	
Species type	AX_2
Geometry	linear
Identical terminal atoms?	yes
Symmetric A–X bonds?	yes } nonpolar
Lewis structure for $CHCl_3$	
Species type	AX_4
Geometry	tetrahedral
Identical terminal atoms?	no → polar

Generalizing from Example 7.7 and the preceding discussion, we can establish the following rules

- Molecules of the type AX_2 (linear), AX_3 (trigonal planar), and AX_4 (tetrahedral) are nonpolar if the terminal atoms are identical. Examples: CO_2, BF_3, and CCl_4 are nonpolar; $CHCl_3$ is polar.
- Molecules of the type AX_2E (bent), AX_2E_2 (bent), and AX_3E (trigonal pyramid) are polar. Examples: SO_2, H_2O, NH_3

EXAMPLE 7.8 CONCEPTUAL

For each of the species in column A, choose the description in column B that best applies.

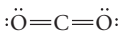
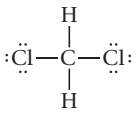
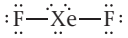
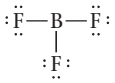
A	B
CO_2	(a) polar, bent
CH_2Cl_2	(b) nonpolar, trigonal planar
XeF_2	(c) nonpolar, linear
BF_3	(d) nonpolar, trigonal pyramid
	(e) polar, tetrahedral
	(f) polar, trigonal pyramid

continued

STRATEGY

1. Note that the descriptions in column B are about geometry and polarity.
2. Draw the Lewis structures of the compounds in column A (Figure 7.3 or 7.9).
3. Determine series type and geometry (Table 7.3 or Figure 7.15).
4. Determine polarity.
5. Match your description with those given in column B.

SOLUTION

2. Lewis structure for CO_2	
3. species type → geometry	AX_2 → linear
4. polarity	nonpolar
5. match	c
2. Lewis structure for CH_2Cl_2	
3. species type → geometry	AX_4 → tetrahedral
4. polarity	polar
5. match	e
2. Lewis structure for XeF_2	
3. species type → geometry	AX_2E_3 → linear
4. polarity	nonpolar
5. match	c
2. Lewis structure for BF_3	
3. species type → geometry	AX_3 → trigonal planar
4. polarity	nonpolar
5. match	b

7-4 Atomic Orbitals; Hybridization

In the 1930s a theoretical treatment of the covalent bond was developed by, among others, Linus Pauling (1901–1994), then at the California Institute of Technology. The *atomic orbital* or **valence bond model** won him the Nobel Prize in chemistry in 1954. Eight years later, Pauling won the Nobel Peace Prize for his efforts to stop nuclear testing.

According to this model, a covalent bond consists of a pair of electrons of opposed spin within an orbital. For example, a hydrogen atom forms a covalent bond by accepting an electron from another atom to complete its 1s orbital. Using orbital diagrams, we could write

	1s
isolated H atom	(↑)
H atom in a stable molecule	(↑↓)

The second electron, shown in blue, is contributed by another atom. This could be another H atom in H_2, an F atom in HF, a C atom in CH_4, and so on.

This simple model is readily extended to other atoms. The fluorine atom (electron configuration $1s^2 2s^2 2p^5$) has a half-filled p orbital:

	1s	2s	2p
isolated F atom	(↑↓)	(↑↓)	(↑↓)(↑↓)(↑)

By accepting an electron from another atom, F can complete this 2p orbital:

	1s	2s	2p
F atom in HF, F_2, . .	(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)

According to this model, it would seem that for an atom to form a covalent bond, it must have an unpaired electron. Indeed, the number of bonds formed by an atom should be determined by its number of unpaired electrons. Because hydrogen has an unpaired electron, an H atom should form one covalent bond, as indeed it does. The same holds for the F atom, which forms only one bond. The noble-gas atoms He and Ne, which have no unpaired electrons, should not form bonds at all; they don't.

When this simple idea is extended beyond hydrogen, the halogens, and the noble gases, problems arise. Consider, for example, the three atoms Be ($Z = 4$), B ($Z = 5$), and C ($Z = 6$):

	1s	2s	2p
Be atom	(↑↓)	(↑↓)	( )( )( )
B atom	(↑↓)	(↑↓)	(↑)( )( )
C atom	(↑↓)	(↑↓)	(↑)(↑)( )

Notice that the beryllium atom has no unpaired electrons, the boron atom has one, and the carbon atom two. Simple valence bond theory would predict that Be, like He, should not form covalent bonds. A boron atom should form one bond, carbon two. Experience tells us that these predictions are wrong. Beryllium forms two bonds in BeF_2; boron forms three bonds in BF_3. Carbon ordinarily forms four bonds, not two.

To explain these and other discrepancies, simple valence bond theory must be modified. It is necessary to invoke a new kind of orbital, called a **hybrid orbital.**

Hybrid Orbitals: sp, sp^2, sp^3, sp^3d, sp^3d^2

The formation of the BeF_2 molecule can be explained by assuming that, as two fluorine atoms approach Be, the atomic orbitals of the beryllium atom undergo a significant change. **Hybridization** occurs when the 2s orbital is mixed or *hybridized* with a 2p orbital to form two new sp hybrid orbitals (Figure 7.19).

one s atomic orbital + one p atomic orbital ⟶ two sp hybrid orbitals

In the BeF_2 molecule, there are two electron-pair bonds. These electron pairs are located in the two sp hybrid orbitals. In each orbital, one electron is a valence electron contributed by beryllium; the other electron comes from the fluorine atom.

A similar argument can be used to explain why boron forms three bonds and carbon forms four. In the case of boron:

one s atomic orbital + two p atomic orbitals ⟶ three sp^2 hybrid orbitals

The number of orbitals is shown by the superscript.

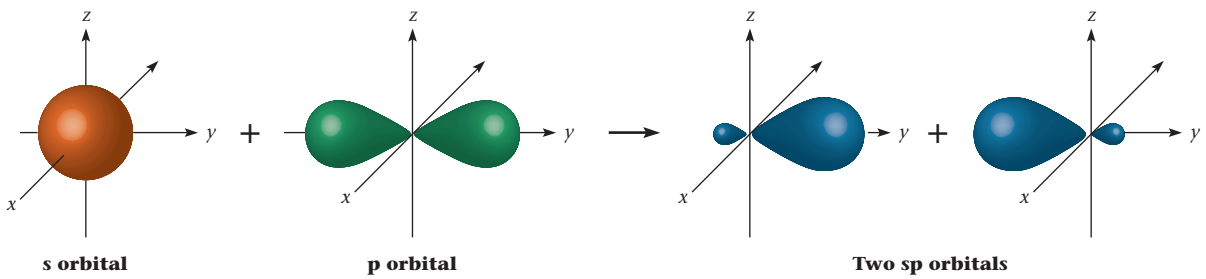


Figure 7.19 Formation of sp hybrid orbitals. The mixing of one s orbital and one p orbital gives two sp hybrid orbitals.

Table 7.4 Hybrid Orbitals and Their Geometries

Number of Electron Pairs	Atomic Orbitals	Hybrid Orbitals	Orientation	Examples
2	s, p	sp	Linear	BeF_2, CO_2
3	s, two p	sp^2	Trigonal planar	BF_3, SO_3
4	s, three p	sp^3	Tetrahedron	CH_4, NH_3, H_2O
5	s, three p, d	sp^3d	Trigonal bipyramid	PCl_5, SF_4, ClF_3
6	s, three p, two d	sp^3d^2	Octahedron	SF_6, ClF_5, XeF_4

With carbon:

one s atomic orbital + three p atomic orbitals ⟶ four sp^3 hybrid orbitals

You will recall that the bond angles in NH_3 and H_2O are very close to that in CH_4. This suggests that the four electron pairs surrounding the central atom in NH_3 and H_2O, like those in CH_4, occupy sp^3 hybrid orbitals. In NH_3, three of these orbitals are filled by bonding electrons, the other by the unshared pair on the nitrogen atom. In H_2O, two of the sp^3 orbitals of the oxygen atom contain bonding electron pairs; the other two contain unshared pairs. The situation in NH_3 and H_2O is not unique. In general, we find that ***unshared as well as shared electron pairs can be located in hybrid orbitals.***

The extra electron pairs in an expanded octet are accommodated by using d orbitals. The phosphorus atom (five valence electrons) in PCl_5 and the sulfur atom (six valence electrons) in SF_6 make use of 3d as well as 3s and 3p orbitals:

With phosphorus:

one s orbital + three p orbitals + one d orbital ⟶ five sp^3d hybrid orbitals

With sulfur:

one s orbital + three p orbitals + two d orbitals ⟶ six sp^3d^2 hybrid orbitals

Hybridization: sp (AX_2), sp^2 (AX_3, AX_2E), sp^3 (AX_4, AX_3E, AX_2E_2).

Table 7.4 summarizes all we have said about hybrid orbitals and also describes their geometry. Note that

- *the number of hybrid orbitals formed is always equal to the number of atomic orbitals mixed.*
- the geometries, as found mathematically by quantum mechanics, are exactly as predicted by VSEPR theory. In each case, the hybrid orbitals are directed to be as far apart as possible.

EXAMPLE 7.9

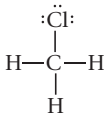
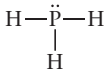
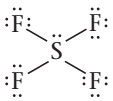
Give the hybridization of carbon in CH_3Cl, phosphorus in PH_3, and sulfur in SF_4.

STRATEGY

1. Draw the Lewis structure of the molecules.
2. Determine the species type: AX_mE_n.
3. Count bonds (m) and unshared pairs (n) around the atom in question.
4. Hybridization:

   m + n = 2 = sp; m + n = 3 = sp^2; m + n = 4 = sp^3; m + n = 5 = sp^3d; m + n = 6 = sp^3d^2

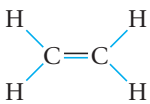
continued

SOLUTION	
1. Lewis structure for CH_3Cl	
2. species type	AX_4
3. m + n	4 + 0 = 4
4. hybridization	m + n = 4 = sp^3
1. Lewis structure for PH_3	
2. species type	AX_3E
3. m + n	3 + 1 = 4
4. hybridization	m + n = 4 = sp^3
1. Lewis structure for SF_4	
2. species type	AX_4E
3. m + n	4 + 1 = 5
4. hybridization	m + n = 5 = sp^3d

Multiple Bonds

In Section 7-2, we saw that insofar as geometry is concerned, a multiple bond acts as if it were a single bond. In other words, the extra electron pairs in a double or triple bond have no effect on the geometry of the molecule. This behavior is related to hybridization. ***The extra electron pairs in a multiple bond (one pair in a double bond, two pairs in a triple bond) are not located in hybrid orbitals.***

To illustrate this rule, consider the ethylene (C_2H_4) and acetylene (C_2H_2) molecules. You will recall that the bond angles in these molecules are 120° for ethylene and 180° for acetylene. This implies sp^2 hybridization in C_2H_4 and sp hybridization in C_2H_2 (see Table 7.4). Using blue lines to represent hybridized electron pairs,



ethylene

acetylene

In both cases, only one of the electron pairs in the multiple bond occupies a hybrid orbital.

EXAMPLE 7.10

State the hybridization of nitrogen in NH_3, NO_2^-, and N_2.

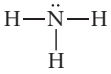
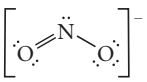
STRATEGY

1. Start by writing a Lewis structure for each species.
2. Determine the species type.

continued

3. The extra electron pairs in a multiple bond are not located in a hybrid orbital. Thus the number of terminal atoms (m) equals the number of bonds in hybrid orbitals.
4. Add m + n.
5. See Example 7.9 for hybridization based on the (m + n) count.

SOLUTION

1. Lewis structure for NH_3	
2. Species type	AX_3E
3. m + n	3 + 1 = 4
4. hybridization	m + n = 4 = sp^3
1. Lewis structure for NO_2^-	
2. Species type	AX_2E
3. m + n	2 + 1 = 3
4. hybridization	m + n = 3 = sp^2
1. Lewis structure for N_2	:N≡N:
2. Species type	AXE
3. m + n	1 + 1 = 2
4. hybridization	m + n = 2 = sp

Sigma and Pi Bonds

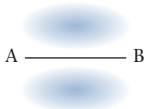
We have noted that the extra electron pairs in a multiple bond are not hybridized and have no effect on molecular geometry. At this point, you may well wonder what happened to those electrons. Where are they in molecules like C_2H_4 and C_2H_2?

To answer this question, it is necessary to consider the shape or spatial distribution of the orbitals filled by bonding electrons in molecules. From this point of view, we can distinguish between two types of bonding orbitals. The first of these, and by far the more common, is called a *sigma* bonding orbital. It consists of a single lobe:

in which the electron density is concentrated in the region directly between the two bonded atoms, A and B. A **sigma bond** (σ) consists of an electron pair occupying a sigma bonding orbital.

The unhybridized electron pairs associated with multiple bonds occupy orbitals of a quite different shape, called *pi bonding orbitals*. Such an orbital consists of two lobes, one above the bond axis, the other below it.

Sigma and pi orbitals, like s and p, differ in shape; each orbital can hold $2e^-$.



Along the bond axis itself, the electron density is zero. The electron pair of a **pi bond** (π) occupies a pi bonding orbital. There is one π bond in the C_2H_4 molecule, two in

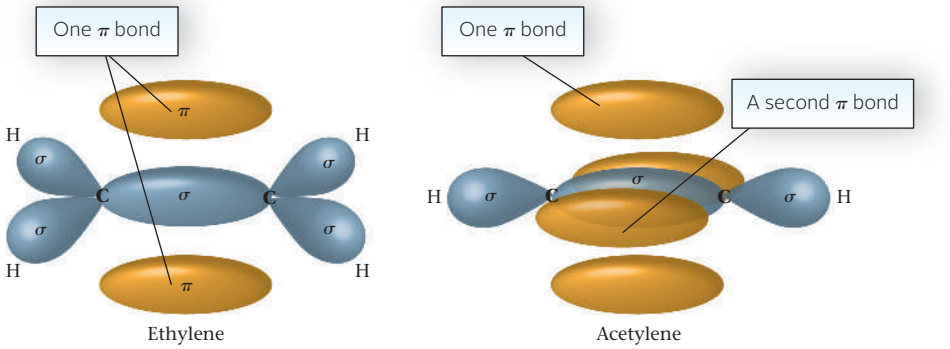


Figure 7.20 Bonding orbitals in ethylene ($CH_2{=}CH_2$) and acetylene ($CH{\equiv}CH$). The sigma bond backbones are shown in blue. The pi bonds (one in ethylene and two in acetylene) are shown in red. Note that a pi bonding orbital consists of two lobes.

C_2H_2. The geometries of the bonding orbitals in ethylene and acetylene are shown in Figure 7.20.

In general, to find the number of σ and π bonds in a species, remember that

- all single bonds are sigma bonds.
- one of the electron pairs in a multiple bond is a sigma bond; the others are pi bonds.

EXAMPLE 7.11

Give the number of pi and sigma bonds in NH_3, NO_2^-, and N_2.

STRATEGY

1. The Lewis structures for these species are given in Example 7.10.
2. Determine the species type. The number of sigma bonds is m.
3. Count total bonds in the Lewis structure.
4. pi bonds = total bonds − m

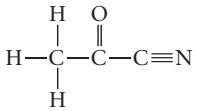
SOLUTION

For NH_3	
2. species type	AX_3; m = 3 → 3 sigma (σ) bonds
3. number of bonds	3
4. number of pi (π) bonds	3 − m = 3 − 3 = 0 → no pi (π) bonds
For NO_2^-	
2. species type	AX_2E; m = 2 → 2 sigma (σ) bonds
3. number of bonds	3
4. number of pi (π) bonds	3 − m = 3 − 2 = 1 → 1 pi (π) bond
For N_2	
2. species type	AXE; m = 1 → 1 sigma (σ) bond
3. number of bonds	3
4. number of pi (π) bonds	3 − m = 3 − 1 = 2 → 2 pi (π) bonds

continued

END POINT

If the molecule does not have a defined central atom but instead has a long chain as in



Count all single bonds (in this case: 5), and all multiple bonds (here, 1 double bond and 1 triple bond).

The multiple bonds each contribute a sigma bond. The rest of the multiple bonds are pi bonds. Thus this molecule has

sigma bonds: 5 + 1 (from the double bond) + 1 (from the triple bond) = 7

pi bonds: 1 (from the double bond) + 2 (from the triple bond) = 3

CHEMISTRY **BEYOND** THE CLASSROOM

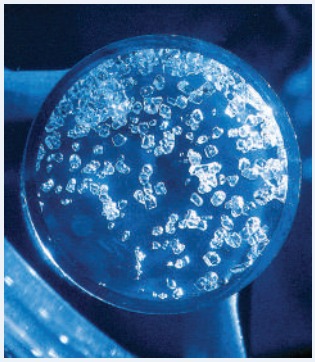
The Noble Gases

The modern periodic table contains six relatively unreactive gases that were unknown to Mendeleev: the noble gases that make up Group **18** at the far right of the table. The first of these elements to be isolated was argon, which makes up about 0.9% of air. The physicist Lord Rayleigh (1842–1919) found that the density of atmospheric nitrogen, obtained by removing O_2, CO_2, and H_2O from air, was slightly greater than that of chemically pure N_2 (MM = 28.02 g/mol). Following up on that observation, Sir William Ramsay (1852–1916) separated argon (MM = 39.95 g/mol) from air. Over a three-year period between 1895 and 1898, this remarkable Scotsman, who never took a formal course in chemistry, isolated three more noble gases: Ne, Kr, and Xe. In effect, Ramsay added a whole new group to the periodic table.

Helium, the first member of the group, was detected in the spectrum of the Sun in 1868. Because of its low density ($\frac{1}{7}$ that of air), helium is used in all kinds of balloons and in synthetic atmospheres to make breathing easier for people suffering from emphysema.

Research laboratories use helium as a liquid coolant to achieve very low temperatures (bp He = −269°C). Argon and, more recently, krypton are used to provide an inert atmosphere in lightbulbs, thereby extending the life of the tungsten filament. In neon signs, a high voltage is passed through a glass tube containing neon at very low pressures. The red glow emitted corresponds to an intense line at 640 nm in the neon spectrum.

Until about 40 years ago, these elements were referred to as "inert gases"; they were believed to be entirely unreactive toward other substances. In 1962 Neil Bartlett (1932–2008), a 29-year-old chemist at the University of British Columbia, shook up the world of chemistry by preparing the first noble-gas compound. In the course of his research on platinum-fluorine compounds, he isolated a reddish solid that he showed to be $O_2^+(PtF_6^-)$. Bartlett realized that the ionization energy of Xe (1170 kJ/mol) is virtually identical to that of the O_2 molecule (1165 kJ/mol). This encouraged him to attempt to make the analogous compound $XePtF_6$. His success opened up a new era in noble-gas chemistry.



Argonne National Laboratory

Figure A Crystals of xenon tetrafluoride (XeF_4).

The most stable binary compounds of xenon are the three fluorides, XeF_2, XeF_4, and XeF_6. Xenon difluoride can be prepared quite simply by exposing a 1:1 mol mixture of xenon and fluorine to ultraviolet light; colorless crystals of XeF_2 (mp = 129°C) form slowly.

$$Xe(g) + F_2(g) \longrightarrow XeF_2(s)$$

The higher fluorides are prepared using excess fluorine (Figure A). All these compounds are stable in dry air at room temperature. However, they react with water to form compounds in which one or more of the fluorine atoms has been replaced by oxygen. Thus xenon hexafluoride reacts rapidly with water to give the trioxide

$$XeF_6(s) + 3H_2O(l) \longrightarrow XeO_3(s) + 6HF(g)$$

Xenon trioxide is highly unstable; it detonates if warmed above room temperature.

In the past 40 years, compounds have been isolated in which xenon is bonded to several nonmetals (N, C, and Cl) in addition to fluorine and oxygen. In the year 2000, it was reported (*Science,* Volume 290, page 117) that a compound had

been isolated in which a metal atom was bonded to xenon. This compound is a dark red solid stable at temperatures below −40°C; it is believed to contain the $[AuXe_4]^{2+}$ cation.

The chemistry of xenon is much more extensive than that of any other noble gas. A group in Finland synthesized HArF, the first known compound of argon. Only one binary compound of krypton, KrF_2, has been prepared. It is a colorless solid that decomposes at room temperature. The chemistry of radon is difficult to study because all its isotopes are radioactive. Indeed, the radiation given off is so intense that it decomposes any reagent added to radon in an attempt to bring about a reaction.

Key Concepts

1. Draw Lewis structures for molecules and polyatomic ions.
   (Examples 7.1, 7.2, 7.4; Problems 1–20, 67, 68)
2. Write resonance forms.
   (Example 7.3; Problems 21–26, 29, 30)
3. Use Table 7.3 and Figure 7.15, applying the VSEPR, to predict molecular geometry.
   (Examples 7.5, 7.6, 7.8; Problems 31–42)
4. Knowing the geometry of a species, predict whether it will be polar.
   (Examples 7.7, 7.8; Problems 43–48)
5. State the hybridization of an atom in a bonded species.
   (Examples 7.9, 7.10; Problems 49–62)
6. State the number of sigma and pi bonds in a species.
   (Example 7.11; Problems 63–66)

Key Terms

bent molecule
bond
—bond angle
—covalent bond
—double bond
—nonpolar bond
—pi bond
—polar bond
—sigma bond
—single bond
—triple bond
dipole
electron-pair repulsion
expanded octets
formal charge
hybrid orbital
Lewis structure
linear molecule
molecular geometry
nonpolar molecule
octahedron
octet rule
polar molecule
resonance
tetrahedron
trigonal bipyramid
trigonal planar
trigonal pyramid
unshared electron pair
valence electrons
VSEPR model

Summary Problem

Consider the species SO_2, XeO_3, RnO_4, and XeF_2.

(a) Draw the Lewis structures of these species.

(b) Draw the resonance structures for SO_2.

(c) Describe the geometries of these species, including bond angles.

(d) Which species are nonpolar?

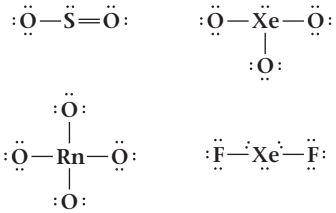
(e) What is the hybridization of the central atom for each species?

(f) How many sigma and pi bonds are in each species?

(g) SO_2 can have two Lewis structures. One has an expanded octet and two double bonds. The other has an octet with one double bond. Draw both Lewis structures, calculate the formal charges, and state which is the more likely structure based on formal charge alone.

Answers

(a)



(b)

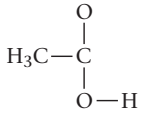
(c) SO_2: bent, 120°
XeO_3: trigonal pyramid, 109.5°
RnO_4: tetrahedron, 109.5°
XeF_2: linear, 180°
(d) RnO_4, XeF_2
(e) sp^2 in SO_2; sp^3 in XeO_3; sp^3 in RnO_4; sp^3d^2 in XeF_2
(f) SO_2: 2σ, 1π XeO_3: 3σ, RnO_4: 4σ XeF_2: 4σ
(g)
The structure on the left is more likely based on formal charge alone.

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

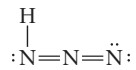
7-1 Lewis Structures; The Octet Rule

Lewis Structures

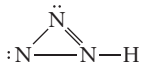
1. Write the Lewis structures for the following molecules and polyatomic ions. In each case, the first atom is the central atom.
(a) CCl_4 (b) NCl_3 (c) $COCl_2$ (d) SO_3^{2-}
2. Follow the directions of Question 1 for
(a) NH_3 (b) KrF_2 (c) NO^+ (d) BrO_2^-
3. Follow the directions of Question 1 for
(a) IO_2^- (b) SiF_4 (c) BrI_3 (d) CN^-
4. Follow the directions of Question 1 for
(a) ClF_4^- (b) PF_6^- (c) CNS^- (d) $SnCl_5^-$
5. Follow the directions of Question 1 for
(a) OCl_2 (b) PF_3 (c) $SbCl_6^-$ (d) ICl_4^-
6. Follow the directions of Question 1 for
(a) C_2^{2-} (b) NFO (c) BrF_4^+ (d) NI_3
7. Oxalic acid, $H_2C_2O_4$, is a poisonous compound found in rhubarb leaves. Draw the Lewis structure for oxalic acid. There is a single bond between the two carbon atoms, each hydrogen atom is bonded to an oxygen atom, and each carbon is bonded to two oxygen atoms.
8. Radio astronomers have detected the isoformyl ion, HOC^+, in outer space. Write the Lewis structure for this ion.
9. Draw Lewis structures for the following species. (The skeleton is indicated by the way the molecule is written.)
(a) Cl_2CO (b) $H_3C—CN$ (c) $H_2C—CH_2$
10. Follow the directions of Question 9 for the following species:
(a)  (b) Br_2C-CF_2 (c) H_3C-NH_2
11. Dinitrogen pentoxide, N_2O_5, when bubbled into water can form nitric acid. Its skeleton structure has no N—N or O—O bonds. Write its Lewis structure.
12. Formic acid is the irritating substance that gets on your skin when an ant bites. Its formula is HCOOH. Carbon is the central atom, and it has no O—O bonds. Draw its Lewis structure.
13. Two different molecules have the formula $C_2H_2Cl_2$. Draw a Lewis structure for each molecule. (All the H and Cl atoms are bonded to carbon. The two carbon atoms are bonded to each other.)
14. Two different molecules have the formula C_2H_6O. One of the molecules has the oxygen atom bonded to both carbon atoms. The other molecule has the oxygen atom bonded to only one carbon atom while both carbon atoms are bonded to each other. Write Lewis structures for both of these compounds.
15. Give the formula of a polyatomic ion that you would expect to have the same Lewis structure as
(a) Cl_2 (b) H_2SO_4 (c) CH_4 (d) $GeCl_4$
16. Give the formula for a molecule that you would expect to have the same Lewis structure as
(a) BrO^- (b) NH_4^+ (c) CN^- (d) SO_4^{2-}
17. Write a Lewis structure for
(a) XeF_3^+ (b) PCl_4^+
(c) BrF_5 (d) HPO_4^{2-} (no P—H or O—O bonds)
18. Write a Lewis structure for
(a) BCl_4 (b) ClO^- (c) $S_2O_3^{2-}$ (d) $NFCl_2$
19. Write reasonable Lewis structures for the following species, none of which follow the octet rule.
(a) BF_3 (b) NO (c) CO^+ (d) ClO_3
20. Write reasonable Lewis structures for the following species, none of which follow the octet rule.
(a) $BeCl_2$ (b) SeO_2^- (c) ClO_3 (d) CH_3

Resonance Forms and Formal Charge

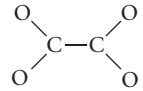
21. Draw possible resonance structures for
(a) Cl—NO_2 (b) H_2C—N—N (c) SO_3
22. Draw resonance structures for
(a) SeO_3 (b) CS_3^{2-} (c) CNO^-
23. The Lewis structure for hydrazoic acid may be written as



(a) Draw two other possible resonance forms for this molecule.
(b) Is

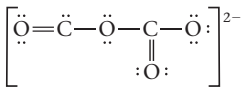


another form of hydrazoic acid? Explain.
24. The oxalate ion, $C_2O_4^{2-}$, has the skeleton structure



(a) Complete the Lewis structure of this ion.
(b) Draw three possible resonance forms for $C_2O_4^{2-}$, equivalent to the Lewis structure drawn in (a).

(c) Is

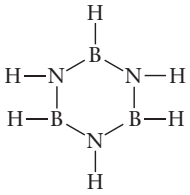


a resonance form of the oxalate ion?

25. The skeleton structure for disulfur dinitride, S_2N_2, is

Draw possible resonance forms of this molecule.

26. Borazine, $B_3N_3H_6$, has the skeleton



Draw the resonance forms of the molecule.

27. What is the formal charge on the indicated atom in each of the following species?

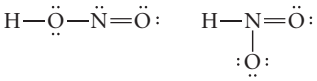
(a) sulfur in SO_2
(b) nitrogen in N_2H_4
(c) each oxygen atom in ozone, O_3

28. Follow the directions in Question 27 for

(a) oxygen in HOF (b) nitrogen in NO_2^-
(c) phosphorus in PCl_3

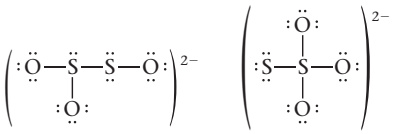
29. Below are two different Lewis structures for nitrous acid (HNO_2). Which is the better Lewis structure based only on formal charge?

Structure I Structure II



30. Below are two different Lewis structures for the thiosulfate ion ($S_2O_3^{2-}$). Which is the better Lewis structure based only on formal charge?

Structure I Structure II



7-2 Molecular Geometry

31. Predict the geometry of the following species:
(a) SO_2 (b) BeF_2 (c) $SeCl_4$ (d) PCl_5

32. Predict the geometry of the following species:
(a) O_3 (b) OCl_2 (c) $SnCl_3^-$ (d) CS_2

33. Predict the geometry of the following species:
(a) $SeOF_2$ (b) TeF_5^- (c) ICl_4^- (d) RnF_2

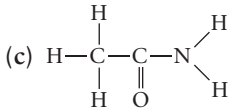
34. Predict the geometry of the following species:
(a) NNO (b) ONCl (c) NH_4^+ (d) O_3

35. Predict the geometry of the following species:
(a) ClF_2^- (b) SeF_5Br (c) SO_3^{2-} (d) BrO_2^-

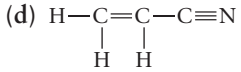
36. Predict the geometry of the following species:
(a) ClF_5 (b) XeF_4 (c) SiF_6^{2-} (d) PCl_5

37. Give all the ideal bond angles (109.5°, 120°, or 180°) in the following molecules and ions. (The skeleton does not imply geometry.)

(a) Cl—S—Cl
(b) F—Xe—F



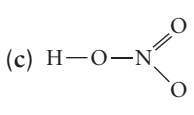
(c)



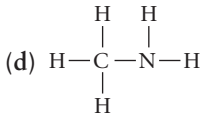
(d)

38. Follow the instructions in Question 37 for

(a) NO_2^- (b) BF_3

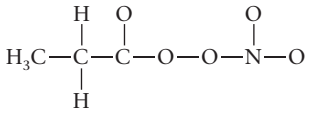


(c)



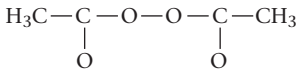
(d)

39. Peroxypropionyl nitrate (PPN) is an eye irritant found in smog. Its skeleton structure is



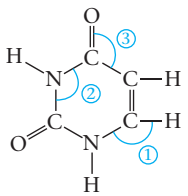
(a) Draw the Lewis structure of PPN.
(b) Indicate all the bond angles.

40. An objectionable component of smog is acetyl peroxide, which has the following skeleton structure.

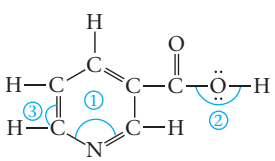


(a) Draw the Lewis structure of this compound.
(b) Write the bond angles indicated by the numbered angles.

41. The uracil molecule is one of the bases in DNA. Estimate the approximate values of the indicated bond angles. Its skeleton (not its Lewis structure) is given below.

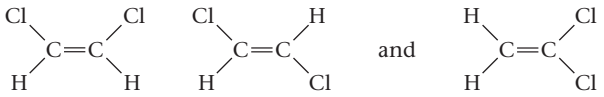


42. Niacin is one of the B vitamins (B_3). Estimate the approximate values of the indicated bond angles. Its skeleton (not its Lewis structure) is given below.

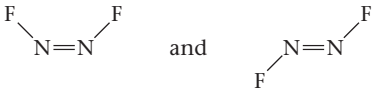


7-3 Polarity of Molecules

43. Which of the species with octets in Question 31 are dipoles?
44. Which of the species with octets in Question 32 are dipoles?
45. Which of the species with octets in Question 33 are dipoles?
46. Which of the species with octets in Question 34 are dipoles?
47. There are three compounds with the formula $C_2H_2Cl_2$:



Which of these molecules are polar?
48. There are two different molecules with the formula N_2F_2:

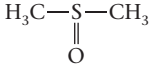


Is either molecule polar? Explain.

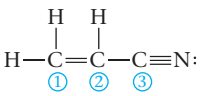
7-4 Atomic Orbitals; Hybridization

Hybridization

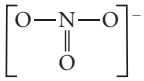
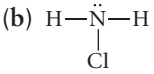
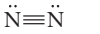
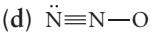
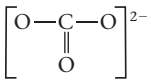
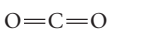
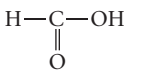
49. Give the hybridization of the central atom in each species in Question 31.
50. Give the hybridization of the central atom in each species in Question 32.
51. Give the hybridization of the central atom in each species in Question 33.
52. Give the hybridization of the central atom in each species in Question 34.
53. Give the hybridization of the central atom in each species in Question 35.
54. Give the hybridization of the central atom in each species in Question 36.
55. In each of the following polyatomic ions, the central atom has an expanded octet. Determine the number of electron pairs around the central atom and the hybridization in
(**a**) SF_2^{2-} (**b**) $AsCl_6^-$ (**c**) SCl_4^{2-}
56. Follow the directions of Question 55 for the following polyatomic ions.
(**a**) ClF_4^- (**b**) $GeCl_6^{2-}$ (**c**) $SbCl_4^-$
57. Give the hybridization of each atom (except H) in the solvent dimethylsulfoxide. (Unshared electron pairs are not shown.)



58. Acrylonitrile, C_3H_3N, is the building block of the polymer Orlon. Its Lewis structure is



What is the hybridization of nitrogen and of the three numbered carbon atoms?

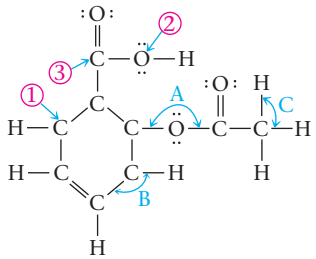
59. What is the hybridization of nitrogen in
(**a**)  (**b**) 
(**c**)  (**d**) 
60. What is the hybridization of carbon in
(**a**) CH_3Cl (**b**) 
(**c**)  (**d**) 
61. Give the hybridization of the central atom (underlined in red).
(**a**) $\underline{C}OCl_2$ (**b**) $H\underline{N}O_2$ (**c**) $(CH_3)_2\underline{C}HCH_3$
62. Give the hybridization of the central atom (underlined in red).
(**a**) $HO\underline{Br}O_3$ (**b**) $Cl_2\underline{O}$ (**c**) $O\underline{P}Br_3$

Sigma and Pi Bonds

63. Give the number of sigma and pi bonds in the molecule in Question 57.
64. Give the number of sigma and pi bonds in the molecule in Question 58.
65. Give the number of sigma and pi bonds in each species in Question 59.
66. Give the number of sigma and pi bonds in each species in Question 60.

Unclassified

67. In which of the following molecules does the sulfur have an expanded octet? For those that do, write the Lewis structure.
(**a**) SO_2 (**b**) SF_4 (**c**) SO_2Cl_2 (**d**) SF_6
68. Consider the pyrosulfate ion, $S_2O_7^{2-}$. It has no sulfur–sulfur nor oxygen–oxygen bonds.
(**a**) Write a Lewis structure for the pyrosulfate ion using only single bonds.
(**b**) What is the formal charge on the sulfur atoms for the Lewis structure you drew in part (a)?
(**c**) Write another Lewis structure using six S=O bonds and two O—S bonds.
(**d**) What is the formal charge on each atom for the structure you drew in part (c)?
69. Consider acetyl salicylic acid, better known as aspirin. Its structure is



(**a**) How many sigma and pi bonds are there in aspirin?
(**b**) What are the approximate values of the angles marked (in blue) A, B, and C?
(**c**) What is the hybridization of each atom marked (in red) 1, 2, and 3?
70. Complete the table on next page.

Species	Atoms Around Central Atom A	Unshared Pairs Around A	Geometry	Hybridization	Polarity (Assume all X atoms the same)
AX_2E_2	_____	_____	_____	_____	_____
_____	3	0	_____	_____	_____
AX_4E_2	_____	_____	_____	_____	_____
_____	_____	_____	trigonal bipyramid	_____	_____

Conceptual Questions

71. Given the following electronegativities

C = 2.5 N = 3.0 S = 2.6

what is the central atom in CNS^-?

72. Based on the concept of formal charge, what is the central atom in

(**a**) HCN (do not include H as a possibility)?

(**b**) NOCl (Cl is always a terminal atom)?

73. Describe the geometry of the species in which there are, around the central atom,

(**a**) four single bonds, two unshared pairs of electrons.

(**b**) five single bonds.

(**c**) two single bonds, one unshared pair of electrons.

(**d**) three single bonds, two unshared pairs of electrons.

(**e**) two single bonds, two unshared pairs of electrons.

(**f**) five single bonds, one unshared pair of electrons.

74. Consider the following molecules: SiH_4, PH_3, H_2S. In each case, a central atom is surrounded by four electron pairs. In which of these molecules would you expect the bond angle to be less than 109.5°? Explain your reasoning.

75. Give the formula of an ion or molecule in which an atom of

(**a**) N forms three bonds using sp^3 hybrid orbitals.

(**b**) N forms two pi bonds and one sigma bond.

(**c**) O forms one sigma and one pi bond.

(**d**) C forms four bonds in three of which it uses sp^2 hybrid orbitals.

(**e**) Xe forms two bonds using sp^3d^2 hybrid orbitals.

76. In each of the following molecules, a central atom is surrounded by a total of three atoms or unshared electron pairs: $SnCl_2$, BCl_3, SO_2. In which of these molecules would you expect the bond angle to be less than 120°? Explain your reasoning.

77. Explain the meaning of the following terms.

(**a**) expanded octet (**b**) resonance

(**c**) unshared electron pair (**d**) odd-electron species

Challenge Problems

78. A compound of chlorine and fluorine, ClF_x, reacts at about 75°C with uranium to produce uranium hexafluoride and chlorine fluoride, ClF. A certain amount of uranium produced 5.63 g of uranium hexafluoride and 457 mL of chlorine fluoride at 75°C and 3.00 atm. What is *x*? Describe the geometry, polarity, and bond angles of the compound and the hybridization of chlorine. How many sigma and pi bonds are there?

79. Draw the Lewis structure and describe the geometry of the hydrazine molecule, N_2H_4. Would you expect this molecule to be polar?

80. Consider the polyatomic ion IO_6^{5-}. How many pairs of electrons are around the central iodine atom? What is its hybridization? Describe the geometry of the ion.

81. It is possible to write a simple Lewis structure for the SO_4^{2-} ion, involving only single bonds, which follows the octet rule. However, Linus Pauling and others have suggested an alternative structure, involving double bonds, in which the sulfur atom is surrounded by six electron pairs.

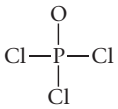
(**a**) Draw the two Lewis structures.

(**b**) What geometries are predicted for the two structures?

(**c**) What is the hybridization of sulfur in each case?

(**d**) What are the formal charges of the atoms in the two structures?

82. Phosphoryl chloride, $POCl_3$, has the skeleton structure



Write

(**a**) a Lewis structure for $POCl_3$ following the octet rule. Calculate the formal charges in this structure.

(**b**) a Lewis structure in which all the formal charges are zero. (The octet rule need not be followed.)