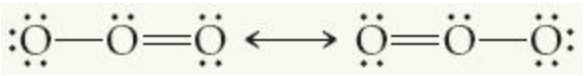
Sample Exercise 9.1 Using the VSEPR Model

Use the VSEPR model to predict the molecular geometry of **(a)** O_3, **(b)** $SnCl_3^-$.

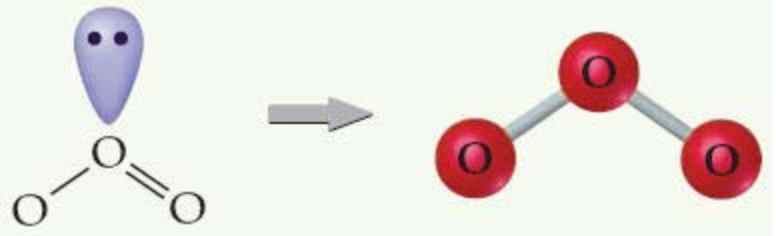
Solution

Analyze: We are given the molecular formulas of a molecule and a polyatomic ion, both conforming to the general formula AB_n and both having a central atom from the *p* block of the periodic table.
Plan: To predict the molecular geometries of these species, we first draw their Lewis structures and then count the number of electron domains around the central atom. The number of electron domains gives the electron-domain geometry. We then obtain the molecular geometry from the arrangement of the domains that are due to bonds.

(a) We can draw two resonance structures for O_3:



Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures the central O atom is bonded to the two outer O atoms and has one nonbonding pair. Thus, there are three electron domains about the central O atoms. (Remember that a double bond counts as a single electron domain.) The arrangement of three electron domains is trigonal planar (Table 9.1). Two of the domains are from bonds, and one is due to a nonbonding pair. So, the molecule has a bent shape with an ideal bond angle of 120° (Table 9.2).

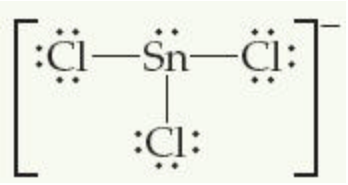


Sample Exercise 9.1 Using the VSEPR Model

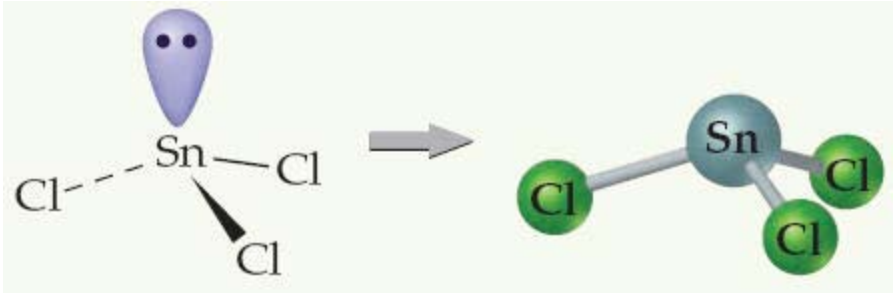
Solution (continued)

As this example illustrates, when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular geometry.

(b) The Lewis structure for the $SnCl_3^-$ ion is



The central Sn atom is bonded to the three Cl atoms and has one nonbonding pair. Therefore, the Sn atom has four electron domains around it. The resulting electron-domain geometry is tetrahedral (Table 9.1) with one of the corners occupied by a nonbonding pair of electrons. The molecular geometry is therefore trigonal pyramidal (Table 9.2), like that of NH_3.



Practice Exercise

Predict the electron-domain geometry and the molecular geometry for **(a)** $SeCl_2$, **(b)** CO_3^{2-}.
Answer: **(a)** tetrahedral, bent; **(b)** trigonal planar, trigonal planar

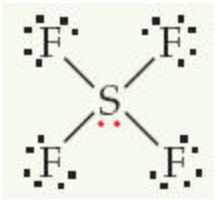
Sample Exercise 9.2 Molecular Geometries of Molecules with Expanded Valance Shells

Use the VSEPR model to predict the molecular geometry of **(a)** SF_4, **(b)** IF_5.

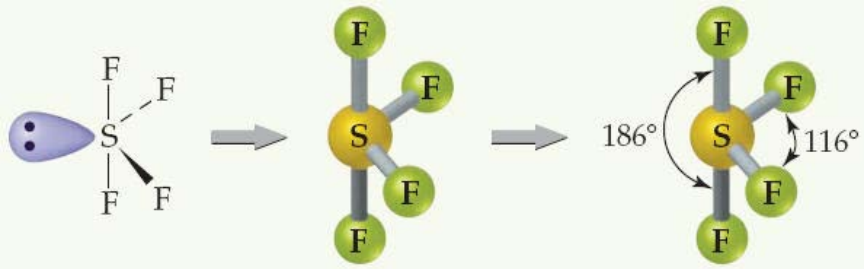
Solution

Analyze: The molecules are of the AB_n type with a central atom from the *p* block of the periodic table.
Plan: We can predict their structures by first drawing Lewis structures and then using the VSEPR model to determine the electron-domain geometry and molecular geometry.

(a) The Lewis structure for SF_4 is



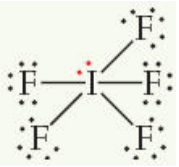
The sulfur has five electron domains around it: four from the S—F bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramid. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions, resulting in a molecular geometry that is described as seesaw-shaped:



Comment: The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial S—F bonds are slightly bent back away from the nonbonding domain, suggesting that the bonding domains are "pushed" by the nonbonding domain, which is larger and has greater repulsion (Figure 9.7).

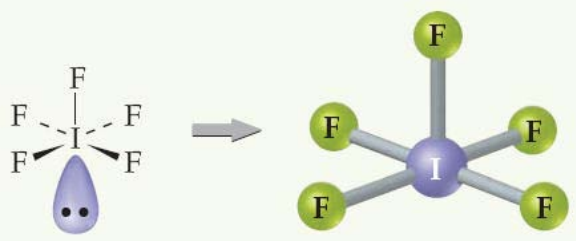
Sample Exercise 9.2 Molecular Geometries of Molecules with Expanded Valance Shells

Solution (continued)



(b) The Lewis structure of IF_5 is

The iodine has six electron domains around it, one of which is from a nonbonding pair. The electron domain geometry is therefore octahedral, with one position occupied by the nonbonding pair. The resulting molecular geometry is therefore *square pyramidal* (Table 9.3):



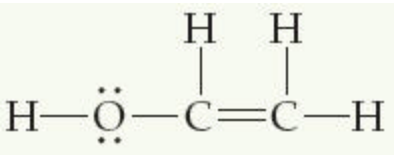
Comment: Because the domain for the nonbonding pair is larger than the other domains, the four F atoms in the base of the pyramid are tipped up slightly toward the F atom on top. Experimentally, we find that the angle between the base and top F atoms is 82°, smaller than the ideal 90°angle of an octahedron.

Practice Exercise

Predict the electron-domain geometry and molecular geometry of **(a)** ClF_3, **(b)** ICl_4^-.
Answer: **(a)** trigonal bipyramidal, T-shaped; **(b)** octahedral, square planar

Sample Exercise 9.3 Predicting Bond Angles

Eyedrops for dry eyes usually contain a water-soluble polymer called *poly(vinyl alcohol)*, which is based on the unstable organic molecule called *vinyl alcohol*:



Predict the approximate values for the H—O—C and O—C—C bond angles in vinyl alcohol.

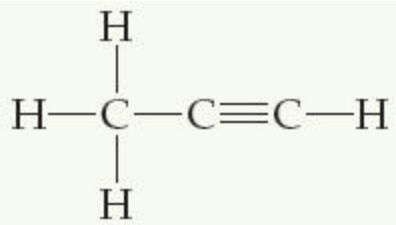
Solution

Analyze: We are given a molecular structure and asked to determine two bond angles in the structure.
Plan: To predict a particular bond angle, we consider the middle atom of the angle and determine the number of electron domains surrounding that atom. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.
Solve: For the H—O—C bond angle, the middle O atom has four electron domains (two bonding and two nonbonding). The electron-domain geometry around O is therefore tetrahedral, which gives an ideal angle of 109.5°. The H—O—C angle will be compressed somewhat by the nonbonding pairs, so we expect this angle to be slightly less than 109.5°.
To predict the O—C—C bond angle, we must examine the leftmost C atom, which is the central atom for this angle. There are three atoms bonded to this C atom and no nonbonding pairs, and so it has three electron domains about it. The predicted electron-domain geometry is trigonal planar, resulting in an ideal bond angle of 120°. Because of the larger size of the C=C domain, however, the O—C—C bond angle should be slightly greater than 120°.

Sample Exercise 9.3 Predicting Bond Angles

Practice Exercise

Predict the H—C—H and C—C—C bond angles in the following molecule, called *propyne*:



Answer: 109.5°, 180°

Sample Exercise 9.4 Polarity of Molecules

Predict whether the following molecules are polar or nonpolar: **(a)** BrCl, **(b)** SO_2, **(c)** SF_6.

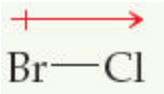
Solution

Analyze: We are given the molecular formulas of several substances and asked to predict whether the molecules are polar.

Plan: If the molecule contains only two atoms, it will be polar if the atoms differ in electronegativity. If the molecule contains three or more atoms, its polarity depends on both its molecular geometry and the polarity of its bonds. Thus, we must draw a Lewis structure for each molecule containing three or more atoms and determine its molecular geometry. We then use the relative electronegativities of the atoms in each bond to determine the direction of the bond dipoles. Finally, we see if the bond dipoles cancel each other to give a nonpolar molecule or reinforce each other to give a polar one.

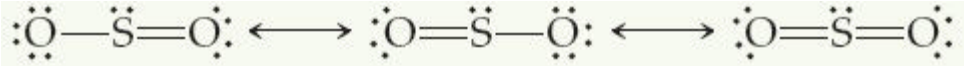
Solve:

(a) Chlorine is more electronegative than bromine. All diatomic molecules with polar bonds are polar molecules. Consequently, BrCl will be polar, with chlorine carrying the partial negative charge:



The actual dipole moment of BrCl, as determined by experimental measurement, is $\mu = 0.57$ D.

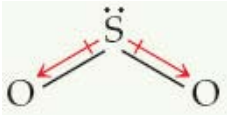
(b) Because oxygen is more electronegative than sulfur, SO_2 has polar bonds. Three resonance forms can be written for SO_2:



Sample Exercise 9.4 Polarity of Molecules

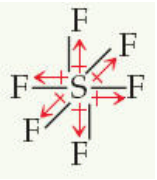
Solution (continued)

For each of these, the VSEPR model predicts a bent geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar:



Experimentally, the dipole moment of SO_2 is $\mu = 1.63$ D.

(c) Fluorine is more electronegative than sulfur, so the bond dipoles point toward fluorine. The six S—F bonds are arranged octahedrally around the central sulfur:



Because the octahedral geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar, meaning that $\mu = 0$.

Practice Exercise

Determine whether the following molecules are polar or nonpolar: **(a)** NF_3, **(b)** BCl_3.

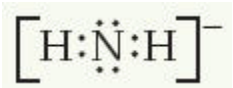
Answer: **(a)** polar because polar bonds are arranged in a trigonal-pyramidal geometry, **(b)** nonpolar because polar bonds are arranged in a trigonal-planar geometry

Sample Exercise 9.5 Hybridization

Indicate the hybridization of orbitals employed by the central atom in **(a)** NH_2^-, **(b)** SF_4 (see Sample Exercise 9.2).

Solution

Analyze: We are given two chemical formulas—one for a polyatomic anion and one for a molecular compound—and asked to describe the type of hybrid orbitals surrounding the central atom in each case.
Plan: To determine the hybrid orbitals used by an atom in bonding, we must know the electron-domain geometry around the atom. Thus, we first draw the Lewis structure to determine the number of electron domains around the central atom. The hybridization conforms to the number and geometry of electron domains around the central atom as predicted by the VSEPR model.
Solve:
(a) The Lewis structure of NH_2^- is



Because there are four electron domains around N, the electron-domain geometry is tetrahedral. The hybridization that gives a tetrahedral electron-domain geometry is sp^3 (Table 9.4). Two of the sp^3 hybrid orbitals contain nonbonding pairs of electrons, and the other two are used to make bonds with the hydrogen atoms.
(b) The Lewis structure and electron-domain geometry of SF_4 are shown in Sample Exercise 9.2. The S atom has five electron domains around it, giving rise to a trigonal-bipyramidal electron-domain geometry. With an expanded octet of ten electrons, a *d* orbital on the sulfur must be used. The trigonal-bipyramidal electron-domain geometry corresponds to sp^3d hybridization (Table 9.4). One of the hybrid orbitals that points in an equatorial direction contains a nonbonding pair of electrons; the other four are used to form the S—F bonds.

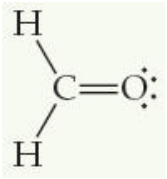
Sample Exercise 9.5 Hybridization

Practice Exercise

Predict the electron-domain geometry and the hybridization of the central atom in **(a)** SO_3^{2-} **(b)** SF_6.
Answer: **(a)** tetrahedral, sp^3; **(b)** octahedral, sp^3d^2

Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Formaldehyde has the Lewis structure



Describe how the bonds in formaldehyde are formed in terms of overlaps of appropriate hybridized and unhybridized orbitals.

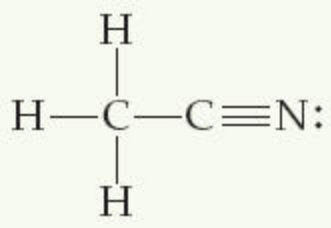
Solution

Analyze: We are asked to describe the bonding in formaldehyde in terms of orbital overlaps.
Plan: Single bonds will be of the type, whereas double bonds will consist of one σ bond and one π bond. The ways in which these bonds form can be deduced from the geometry of the molecule, which we predict using the VSEPR model.
Solve: The C atom has three electron domains around it, which suggests a trigonalplanar geometry with bond angles of about 120°. This geometry implies sp^2 hybrid orbitals on C (Table 9.4). These hybrids are used to make the two C—H and one C—O σ bonds to C. There remains an unhybridized 2*p* orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.
The O atom also has three electron domains around it, and so we will assume that it has sp^2 hybridization as well. One of these hybrids participates in the C—O σ bond, while the other two hybrids hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized 2*p* orbital that is perpendicular to the plane of the molecule. The unhybridized 2*p* orbitals on the C and O atoms overlap to form a C—O π bond, as illustrated in Figure 9.27.

Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Practice Exercise

Consider the acetonitrile molecule:



(a) Predict the bond angles around each carbon atom; **(b)** describe the hybridization at each of the carbon atoms; **(c)** determine the total number of and bonds in the molecule.

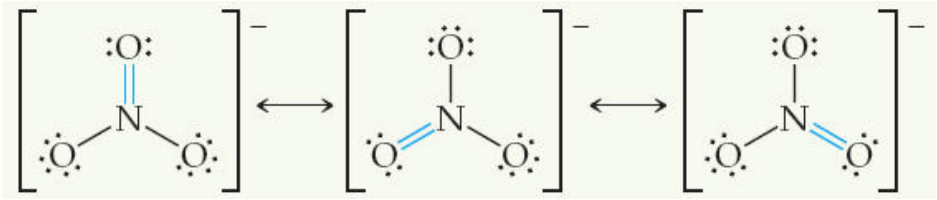
Answer: **(a)** approximately 109° around the left C and 180° on the right C; **(b)** sp^3, sp; **(c)** five σ bonds and two π bonds

Sample Exercise 9.7 Delocalized Bonding

Describe the bonding in the nitrate ion, NO_3^-. Does this ion have delocalized π bonds?

Solution

Analyze: Given the chemical formula for a polyatomic anion, we are asked to describe the bonding and determine whether the ion has delocalized π bonds.
Plan: Our first step in describing the bonding NO_3^- is to construct appropriate Lewis structures. If there are multiple resonance structures that involve the placement of the double bonds in different locations, that suggests that the π component of the double bonds is delocalized.
Solve: In Section 8.6 we saw that NO_3^- has three resonance structures:



In each of these structures the electron-domain geometry at nitrogen is trigonal planar, which implies sp^2 hybridization of the N atom. The sp^2 hybrid orbitals are used to construct the three N—O σ bonds that are present in each of the resonance structures.
The unhybridized 2*p* orbital on the N atom can be used to make π bonds. For any one of the three resonance structures shown, we might imagine a single localized N—O π bond formed by the overlap of the unhybridized 2*p* orbital on N and a 2*p* orbital on one of the O atoms, as shown in Figure 9.30(a). Because each resonance structure contributes equally to the observed structure of NO_3^-, however, we represent the π bonding as spread out, or delocalized, over the three bonds, as shown in Figure 9.30(b).

Sample Exercise 9.7 Delocalized Bonding

Practice Exercise

Which of the following molecules or ions will exhibit delocalized bonding: SO_3, SO_3^{2-}, H_2CO, O_3, NH_4^+?
Answer: SO_3 and O_3, as indicated by the presence of two or more resonance structures involving π bonding for each of these molecules

Sample Exercise 9.8 Bond Order

What is the bond order of the He_2^+ ion? Would you expect this ion to be stable relative to the separated He atom and He^+ ion?

Solution

Analyze: We will determine the bond order for the He_2^+ ion and use it to predict whether the ion is stable.
Plan: To determine the bond order, we must determine the number of electrons in the molecule and how these electrons populate the available MOs. The valence electrons of He are in the 1*s* orbital, and the 1*s* orbitals combine to give an MO diagram like that for H_2 or He_2 (Figure 9.35). If the bond order is greater than 0, we expect a bond to exist, and the ion is stable.
Solve: The energy-level diagram for the He_2^+ ion is shown in Figure 9.36. This ion has three electrons. Two are placed in the bonding orbital, the third in the antibonding orbital. Thus, the bond order is

$$\text{Bond order} = \tfrac{1}{2}(2 - 1) = \tfrac{1}{2}$$

Because the bond order is greater than 0, we predict the He_2^+ ion to be stable relative to the separated He and He^+. Formation of He_2^+ in the gas phase has been demonstrated in laboratory experiments.

Practice Exercise

Determine the bond order of the H_2^- ion.
Answer: $\frac{1}{2}$

Sample Exercise 9.9 Molecular Orbitals of a Second-Row Diatomic Ion

Predict the following properties of O_2^+: **(a)** number of unpaired electrons, **(b)** bond order, **(c)** bond enthalpy and bond length.

Solution

Analyze: Our task is to predict several properties of the cation O_2^+.
Plan: We will use the MO description of O_2^+ to determine the desired properties. We must first determine the number of electrons in O_2^+ and then draw its MO energy diagram. The unpaired electrons are those without a partner of opposite spin. The bond order is one-half the difference between the number of bonding and antibonding electrons. After calculating the bond order, we can use the data in Figure 9.46 to estimate the bond enthalpy and bond length.
Solve:
(a) The O_2^+ ion has 11 valence electrons, one fewer than O_2. The electron removed from O_2 to form O_2^+ is one of the two unpaired π^*_{2p} electrons (see Figure 9.46). Therefore, O_2^+ has just one unpaired electron.
(b) The molecule has eight bonding electrons (the same as O_2) and three antibonding electrons (one fewer than O_2). Thus, its bond order is

$$\tfrac{1}{2}(8 - 3) = 2\tfrac{1}{2}$$

(c) The bond order of O_2^+ is between that for O_2 (bond order 2) and N_2 (bond order 3). Thus, the bond enthalpy and bond length should be about midway between those for O_2 and N_2, approximately 700 kJ/mol and 1.15 Å, respectively. The experimental bond enthalpy and bond length of the ion are 625 kJ/mol and 1.123 Å, respectively.

Practice Exercise

Predict the magnetic properties and bond orders of **(a)** the peroxide ion, O_2^{2-}; **(b)** the acetylide ion, C_2^{2-}.
Answer: **(a)** diamagnetic, 1; **(b)** diamagnetic, 3

Sample Integrative Exercise Putting Concepts Together

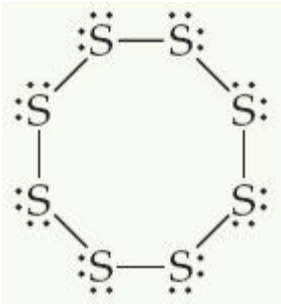
Elemental sulfur is a yellow solid that consists of S_8 molecules. The structure of the S_8 molecule is a puckered, eight-membered ring (Figure 7.34). Heating elemental sulfur to high temperatures produces gaseous S_2 molecules:

$$S_8\,(s) \longrightarrow 4\,S_2\,(g)$$

(a) With respect to electronic structure, which element in the second row of the periodic table is most similar to sulfur? **(b)** Use the VSEPR model to predict the S—S—S bond angles in S_8 and the hybridization at S in S_8. **(c)** Use MO theory to predict the sulfur–sulfur bond order in S_2. Is the molecule expected to be diamagnetic or paramagnetic?
(d) Use average bond enthalpies (Table 8.4) to estimate the enthalpy change for the reaction just described. Is the reaction exothermic or endothermic?

Solution

(a) Sulfur is a group 6A element with an $[Ne]3s^23p^4$ electron configuration. It is expected to be most similar electronically to oxygen (electron configuration, $[He]2s^22p^4$), which is immediately above it in the periodic table. **(b)** The Lewis structure of S_8 is



Sample Exercise 9.9 Molecular Orbitals of a Second-Row Diatomic Ion

Solution (continued)

There is a single bond between each pair of S atoms and two nonbonding electron pairs on each S atom. Thus, we see four electron domains around each S atom, and we would expect a tetrahedral electron-domain geometry corresponding to sp^3 hybridization. (Sections 9.2, 9.5) Because of the nonbonding pairs, we would expect the S—S—S angles to be somewhat less than 109°, the tetrahedral angle. Experimentally, the S—S—S angle in S_8 is 108°, in good agreement with this prediction. Interestingly, if S_8 were a planar ring (like a stop sign), it would have S—S—S angles of 135°. Instead, the S_8 ring puckers to accommodate the smaller angles dictated by *sp*3 hybridization. **(c)** The MOs of S_2 are entirely analogous to those of O_2, although the MOs for S2 are constructed from the 3*s* and 3*p* atomic orbitals of sulfur. Further, S_2 has the same number of valence electrons as O_2. Thus, by analogy to our discussion of O_2, we would expect S_2 to have a bond order of 2 (a double bond) and to be paramagnetic with two unpaired electrons in the π^*_{3p} molecular orbitals of S_2. (Section 9.8) **(d)** We are considering the reaction in which an S_8 molecule falls apart into four S_2 molecules. From parts (b) and (c), we see that S_8 has S—S single bonds and S_2 has S═S double bonds. During the course of the reaction, therefore, we are breaking eight S—S single bonds and forming four S═S double bonds. We can estimate the enthalpy of the reaction by using Equation 8.12 and the average bond enthalpies in Table 8.4:

$$\Delta H_{rxn} = 8\,D(\text{S—S}) - 4\,D(\text{S=S}) = 8(266\text{ kJ}) - 4(418\text{ kJ}) = +456\text{ kJ}$$

Because , $\Delta H_{rxn} > 0$ the reaction is endothermic. (Section 5.4) The very positive value of ΔH_{rxn} suggests that high temperatures are required to cause the reaction to occur.