10. MOLECULAR GEOMETRY AND CHEMICAL BONDING THEORY
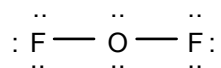
∎ Solutions to Exercises

10.1 a. A Lewis structure of ClO_3^- is

$$\left[\begin{array}{c} \overset{..}{:}\overset{..}{O}: \\ | \\ :\overset{..}{O} - Cl - \overset{..}{O}: \end{array}\right]^{-}$$
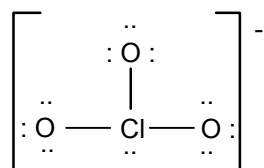
There are four electron pairs in a tetrahedral arrangement about the central atom. Three pairs are bonding, and one pair is nonbonding. The expected geometry is trigonal pyramidal.
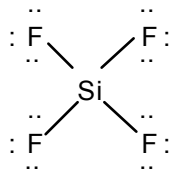
b. The Lewis structure of OF_2 is

$$:\overset{..}{F} - \overset{..}{O} - \overset{..}{F}:$$

There are four electron pairs in a tetrahedral arrangement about the central atom. Two pairs are bonding, and two pairs are nonbonding. The expected geometry is bent.
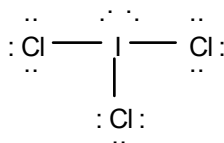
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c. The Lewis structure of SiF_4 is

There are four bonding electron pairs in a tetrahedral arrangement around the central atom. The expected geometry is tetrahedral.

10.2   First, distribute the valence electrons to the bonds and the chlorine atoms. Then, distribute the remaining electrons to iodine.


The five electron pairs around iodine should have a trigonal bipyramidal arrangement with two lone pairs occupying equatorial positions. The molecule is T-shaped.

10.3   Both trigonal pyramidal (b) and T-shaped (c) geometries are consistent with a nonzero dipole moment. In trigonal planar geometry, the Br-F contributions to the dipole moment would cancel.

10.4   On the basis of symmetry, SiF_4 (b) would be expected to have a dipole moment of zero. The bonds are all symmetric about the central atom.

10.5   The Lewis structure for ammonia, NH_3, is
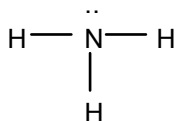
There are four pairs of electrons around the nitrogen atom. According to the VSEPR model, these are arranged tetrahedrally around the nitrogen atom, and you should use sp^3 hybrid orbitals. Each N–H bond is formed by the overlap of a $1s$ orbital of a hydrogen atom with one of the singly occupied sp^3 hybrid orbitals of the nitrogen atom.
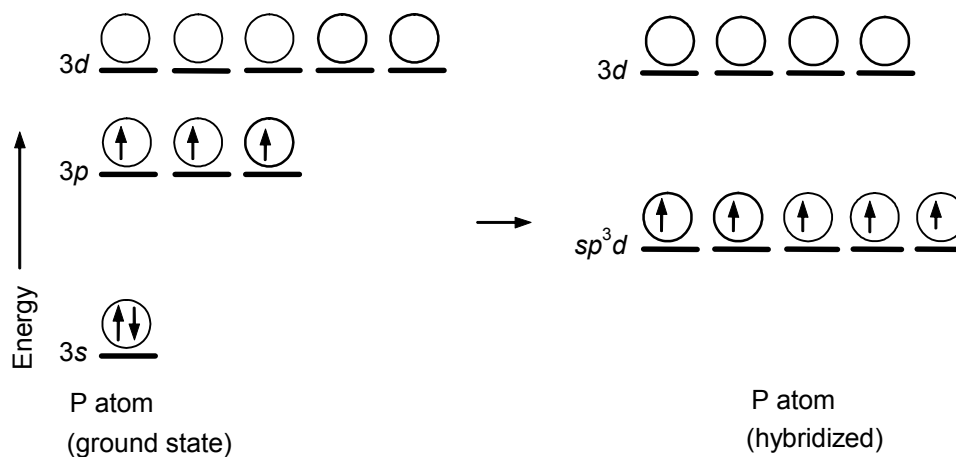
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This gives the following bonding description for NH_3:
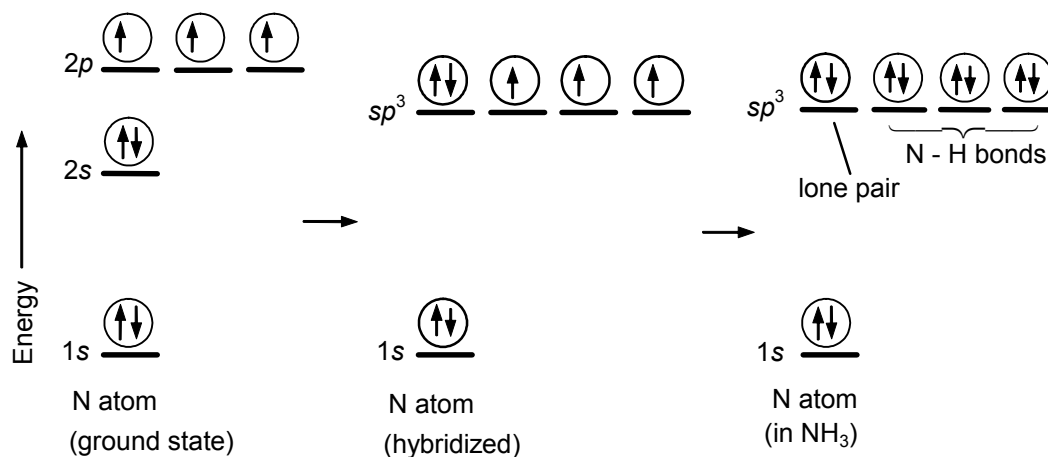
10.6   The Lewis structure for PCl_5 is
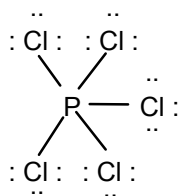
The phosphorus atom has five single bonds and no lone pairs around it. This suggests that you use sp^3d hybrid orbitals on phosphorus. Each chlorine atom (valence shell configuration $3s^23p^5$) has one singly occupied $3p$ orbital. The P–Cl bonds are formed by the overlap of a phosphorus sp^3d hybrid orbital with a singly occupied chlorine $3p$ orbital. The hybridization of phosphorus can be represented as follows:
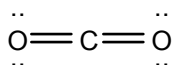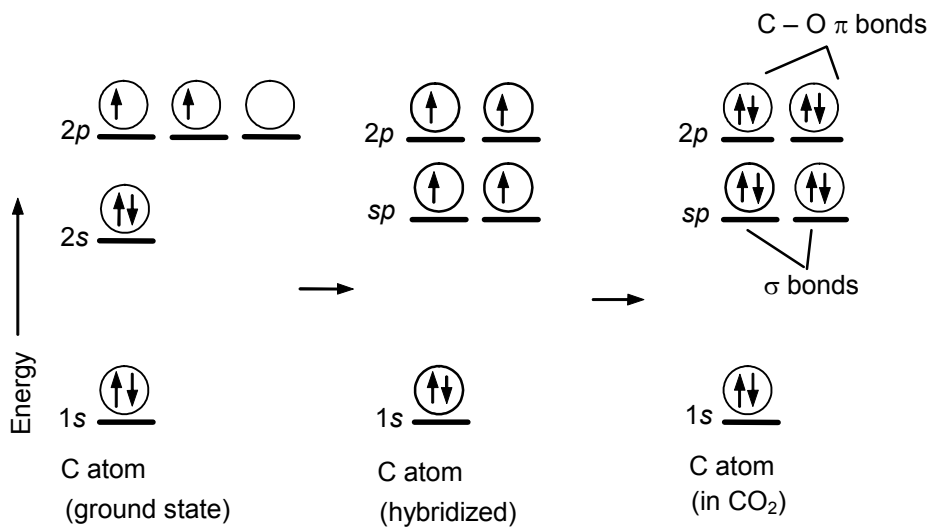
The bonding description of phosphorus in PCl_5 is

3d

P — Cl bonds

sp^3d

P atom
(in PCl_5)
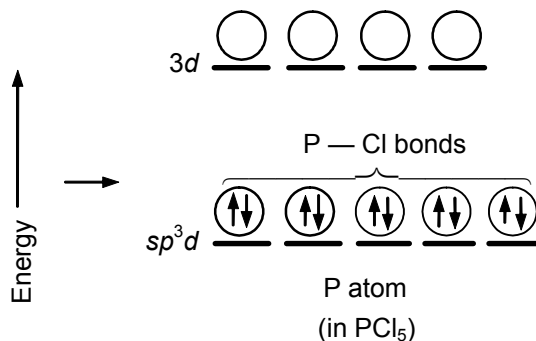
10.7   The Lewis structure of CO_2 is

$$\ddot{O}=C=\ddot{O}$$

The double bonds are each a π bond plus a σ bond. Hybrid orbitals are needed to describe the two σ bonds. This suggests sp hybridization. Each sp hybrid orbital on the carbon atom overlaps with a $2p$ orbital on one of the oxygen atoms to form a σ bond. The π bonds are formed by the overlap of a $2p$ orbital on the carbon atom with a $2p$ orbital on one of the oxygen atoms. Hybridization and bonding of the carbon atom are shown as follows:

C – O π bonds

2p   2p   2p

sp   sp

σ bonds

2s

1s   1s   1s

C atom   C atom   C atom
(ground state)   (hybridized)   (in CO_2)

10.8   The structural formulas for the isomers are as follows:

       cis   *trans*
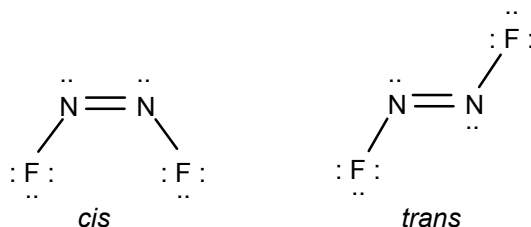
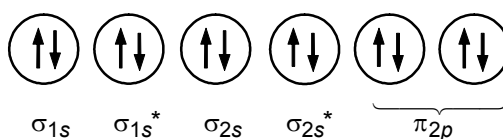These compounds exist as separate isomers with different properties. For these to interconvert, one end of the molecule would have to rotate with respect to the other end. This would require breaking the π bond and expending considerable energy.

10.9   There are 2 x 6 = 12 electrons in C_2. They occupy the orbitals as shown below.

$$\sigma_{1s} \quad \sigma_{1s}^* \quad \sigma_{2s} \quad \sigma_{2s}^* \quad \pi_{2p}$$

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$. There are no unpaired electrons; therefore, C_2 is diamagnetic. There are eight bonding and four antibonding electrons. The bond order is 1/2(8 - 4) = 2.

10.10   There are 6 + 8 = 14 electrons in CO. The orbital diagram is

$$\sigma_{1s} \quad \sigma_{1s}^* \quad \sigma_{2s} \quad \sigma_{2s}^* \quad \pi_{2p} \quad \sigma_{2p}$$
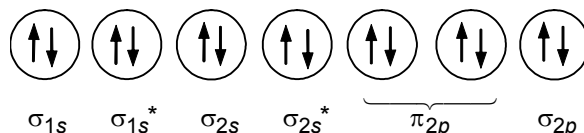
The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$. There are ten bonding and four antibonding electrons. The bond order is 1/2(10 - 4) = 3. There are no unpaired electrons; hence, CO is diamagnetic.

■ Answers to Concept Checks

10.1   The VSEPR model predicts that four electron pairs about any atom in a molecule will distribute themselves to give a tetrahedral arrangement. Any three of these electron pairs would have a trigonal pyramidal arrangement. The geometry of a molecule having a central atom with three atoms bonded to it would be trigonal pyramidal.

10.2   A molecule, AX_3, could have one of three geometries: it could be trigonal planar, trigonal pyramidal, or T-shaped. Assuming the three groups attached to the central atom are alike, as indicated by the formula, the planar geometry should be symmetrical, so even if the A–X bonds are polar, their polarities would cancel to give a nonpolar molecule (dipole moment of zero). This would not be the case in the trigonal pyramidal geometry. In that situation, the bonds all point to one side of the molecule. It is possible for such a molecule to have a lone pair that points away from the bonds and whose polarity might fortuitously cancel the bond polarities, but an exact cancellation is not likely (see Figure 10.19). In general, you should expect the trigonal pyramidal molecule to have a nonzero dipole moment, but a zero dipole is possible. The argument for the T-shaped geometry is similar to that for the trigonal pyramidal geometry. The bonds point in a plane, but toward one side of the molecule. Unless the sum of the bond polarities was fortuitously canceled by the polarities from the lone pairs, this geometry would have a nonzero dipole moment. This means that molecule Y is likely to be trigonal planar, but trigonal pyramidal or T-shaped geometries are possible. Molecule Z cannot have a trigonal planar geometry, but must be either trigonal pyramidal or T-shaped.

10.3   Assuming there are no lone pairs, the atom has four electron pairs and, therefore, an octet of electrons about it. The single bond and the triple bond each require a sigma bond orbital for a total of two such orbitals. This suggests *sp* hybrids on the central atom.

■ Answers to Review Questions

10.1   The VSEPR model is used to predict the geometry of molecules. The electron pairs around an atom are assumed to arrange themselves to reduce electron repulsion. The molecular geometry is determined by the positions of the bonding electron pairs.

10.2   The arrangements are linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral.

10.3   A lone pair is "larger" than a bonding pair; therefore, it will occupy an equatorial position where it encounters less repulsion than if it were in an axial position.

10.4   The bonds could be polar, but if they are arranged symmetrically, the molecule will be nonpolar. The bond dipoles will cancel.

10.5   Nitrogen trifluoride has three N–F bonds arranged to form a trigonal pyramid. These bonds are polar and would give a polar molecule with partial negative charges on the fluorine atoms and a partial positive charge on the nitrogen atom. However, there is also a lone pair of electrons on nitrogen that is directed away from the bonds. The result is that the lone pair nearly cancels the polarity of the bonds and gives a molecule with a very small dipole moment.

10.6   Certain orbitals, such as *p* orbitals and hybrid orbitals, have lobes in given directions. Bonding to these orbitals is directional; that is, the bonding is in preferred directions. This explains why the bonding gives a particular molecular geometry.

10.7   The angle is 109.5°.

10.8   A sigma bond has a cylindrical shape about the bond axis. A *pi* bond has a distribution of electrons above and below the bond axis.

10.9   In ethylene, C_2H_4, the changes on a given carbon atom may be described as follows:
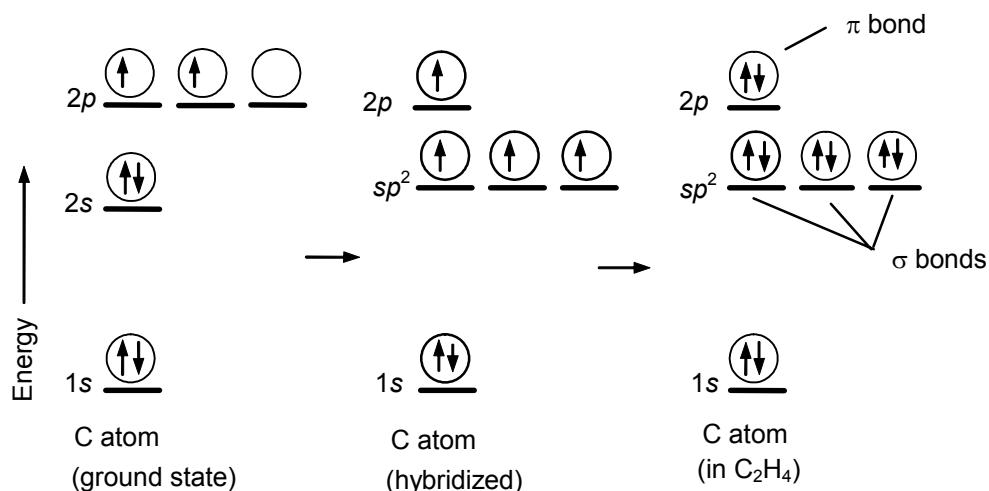
An sp^2 hybrid orbital on one carbon atom overlaps a similar hybrid orbital on the other carbon atom to form a σ bond. The remaining hybrid orbitals on the two carbon atoms overlap 1*s* orbitals from the hydrogen atoms to form four C-H bonds. The unhybridized 2*p* orbital on one carbon atom overlaps the unhybridized 2*p* orbital on the other carbon atom to form a π bond. The σ and π bonds together constitute a double bond.

10.10   Both of the unhybridized 2*p* orbitals, one from each carbon atom, are perpendicular to their CH_2 planes. When these orbitals overlap each other, they fix both planes in the same plane. The two ends of the molecule cannot twist around without breaking the π bond, which requires considerable energy. Therefore, it is possible to have stable molecules with the following structures:
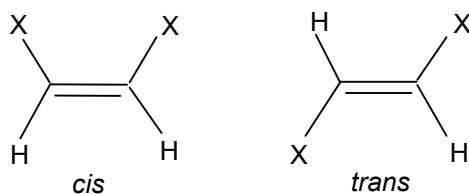
Because these have the same molecular formulas, they are isomers. In this case, they are called *cis-trans* isomers, or geometrical isomers.

10.11 In a bonding orbital, the probability of finding electrons between the two nuclei is high. For this reason, the energy of the bonding orbital is lower than that of the separate atomic orbitals. In an antibonding orbital, the probability of finding electrons between the two nuclei is low. For this reason, the energy of the antibonding orbital is higher than that of the separate atomic orbitals.

10.12 The factors determining the strength of interaction of two atomic orbitals are (1) the energy difference between the interacting orbitals and (2) the magnitude of their overlap.

10.13 When two 2s orbitals overlap, they interact to form a bonding orbital, σ_{2s}, and an antibonding orbital, $\sigma_{2s}{}^*$. The bonding orbital is at lower energy than the antibonding orbital.

10.14 When two 2p orbitals overlap, they interact to form a bonding sigma orbital, σ_{2p}, and an antibonding sigma orbital, $\sigma_{2p}{}^*$. Two bonding pi orbitals, π_{2p} (each having the same energy), and two antibonding pi orbitals, $\pi_{2p}{}^*$ (each having the same energy), are also formed.

10.15 A σ bonding orbital is formed by the overlap of the 1s orbital on the H atom with the 2p orbital on the F atom. This H–F orbital is made up primarily of the fluorine orbital.

10.16 The O_3 molecule consists of a framework of localized orbitals and of delocalized pi molecular orbitals. The localized framework is formed from sp^2 hybrid orbitals on each atom. Thus, an O–O bond is formed by the overlap of a hybrid orbital on the left O atom with a hybrid orbital on the center O atom. Another O–O bond is formed by the overlap of another hybrid orbital on the right O atom with a hybrid orbital on the center O atom. The remaining hybrid orbitals are occupied by lone pairs of electrons. Also, there is one unhybridized p orbital on each of the atoms. These p orbitals are perpendicular to the plane of the molecule and overlap sidewise to give three pi molecular orbitals that are delocalized. The two orbitals of lowest energy are occupied by pairs of electrons.

■ Answers to Conceptual Problems

10.17 In order to solve this problem, draw the Lewis structure for each of the listed molecules. In each case, use your Lewis structure to determine the geometry, and match this geometry with the correct model.

a. SeO_2 is angular and has an AB_2 geometry. This is represented by model (ii).

b. $BeCl_2$ is linear and has an AB_2 geometry. This goes with model (i).

c. PBr_3 is trigonal pyramidal and has an AB_3 geometry. This goes with model (iv).

d. BCl_3 is trigonal planar and has an AB_3 geometry. This is represented by model (iii).

10.18   First, determine the geometry about the central atom, carbon. There is a total of sixteen valence electrons for the molecule. For each atom to obey the octet rule, eight electrons must be shared in bonds. This would require four bonding pairs, a single bond (one pair) between C and Cl, and a triple bond (three pairs) between C and N. The geometry about the central atom is AX_2, which is linear. This is represented by model (a), on the left.

10.19   In a CH_3CH_3 molecule, each C atom has four electron pairs arranged tetrahedrally. Within this molecule, each CH_3 considered as a separate group has a trigonal pyramidal geometry (with three C–H bonding pairs and a fourth pair from the C–C bond around the C atom). The $:CH_3$ molecule retains this trigonal pyramidal geometry, having three bonding pairs and one lone pair around the C atom. The CH_3 molecule, however, has only three electron pairs around the C atom. Initially, as the CH_3 molecule breaks away from the ethane molecule, it has the trigonal pyramidal geometry it had in the ethane molecule. However, the repulsion of the bonding electron pairs on the CH_3 molecule are no longer balanced by the fourth pair (from the C–C bond), so the molecule flattens out to form a trigonal planar geometry.

10.20   The BF_3 molecule starts out in a trigonal planar geometry with three bonding pairs of electrons distributed about the B atom in a plane and 120° apart. After the bond between B and N is formed, the geometry about the B atom is tetrahedral, with 109° bond angles. As the bond begins to form, the lone pair on N approaches the plane of the BF_3 molecule and begins to interact with the bonding pairs. The repulsion between the electron pairs causes the bonding pairs to be pushed downward, forcing them closer together.

10.21   First, determine the geometry of each molecule using VSEPR theory. Then, compare to the orbital pictures for the correct number of bonding and nonbonding orbitals.

   a. BeF_2 is an AX_2 molecule, which has linear geometry. This is depicted by orbital drawing (i).

   b. SiF_4 is an AX_4 molecule, which has tetrahedral geometry. This is depicted by orbital drawing (iii).

   c. SeF_4 is an AX_4E molecule, which has seesaw geometry. This is depicted by orbital drawing (iv).

   d. RnF_4 is an AX_4E_2 molecule, which has square planar geometry. This is depicted by orbital drawing (v).

10.22   The arrangement of electron pairs about this atom suggested by the two bonds and one lone pair is trigonal planar. You would expect sp^2 hybrid orbitals for this atom (a total of three hybrid orbitals). Two of these hybrid orbitals would be used to form the two bonds; the third hybrid orbital would be used for the lone pair.

10.23 The reaction with Br_2 indicates that $C_2H_2Br_2$ has a double bond. There are three possible isomers of $C_2H_2Br_2$ having double bonds:

| I | II | III |
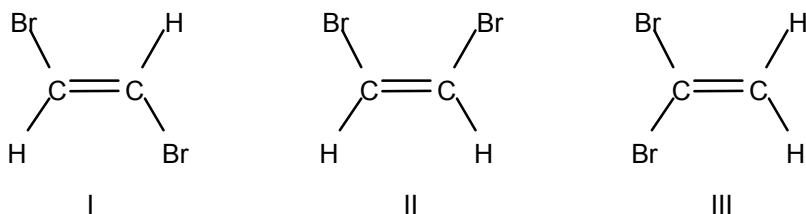
Compounds I and III have dipole moments. The addition of Br_2, with one Br going to each C atom yields the following products:

| IA | IIA | IIIA |
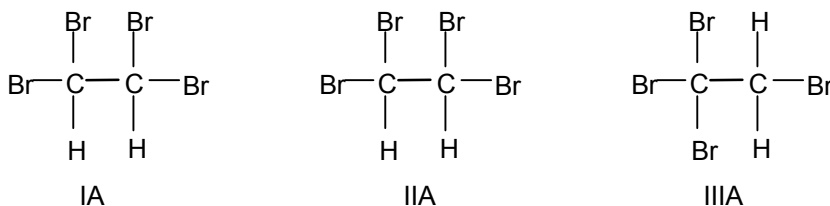
Products IA and IIA are identical and arise from compounds I and II. Thus, the original two compounds, one not having a dipole moment, the other having a dipole moment, but both reacting with bromine to give the same product are compounds I and II, respectively.

10.24 A neutral molecule of the form XF_4 could have either four, five, or six electron pairs around X. With four bonding pairs and no lone pairs, the geometry would be tetrahedral. The molecule would be symmetric and nonpolar. Similarly, with four bonding pairs and two lone pairs, the geometry would be square planar; the molecule would again be symmetric and nonpolar. However, with four bonding pairs and one lone pair, the geometry would be seesaw; the molecule would be nonsymmetric in shape and could be polar. This fits the description of a compound with dipole moment 0.63 D. To identify X, let's look at the total number of valence electrons in XF_4. Each F atom, with its bonding electrons, has an octet (8) of electrons. In addition, there is a lone pair, or two electrons. Thus, the total number of valence electrons is 4 x 8 + 2 = 34. Of these, 4 x 7 = 28 are from the F atoms, leaving 34 - 28 = 6 valence electrons coming from X. So X is a VIA element. X cannot be oxygen because a seesaw geometry would require sp^3d hybrid orbitals, and oxygen does not have d orbitals to hybridize. Thus, X must be sulfur (S), selenium (Se), or tellurium (Te).
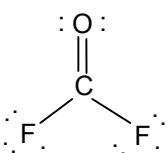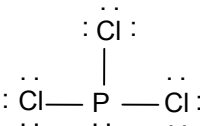
10.25   First, determine the geometry about atoms a, b, and c using VSEPR theory. Then, compare to the geometry in each drawing.

a. The geometry about atom a (carbon) is AX_4, which is tetrahedral geometry. This is depicted by drawing (ii).

b. The geometry about atom b (carbon) is AX_3, which is trigonal planar geometry. This is depicted by drawing (iv).

c. The geometry about atom c (oxygen) is AX_2E_2, which is bent geometry. This is depicted by drawing (i).

10.26   The formate ion, HCO_2^-, is expected to have trigonal planar geometry by the VSEPR model. (Each resonance formula has one C=O bond, one C–O bond, and one C–H bond, giving a total of three groups about the C atom.) The VSEPR model predicts bond angles of 120°. However, a bond between the carbon atom and the oxygen atom has a bond order of 3/2 (resonance between a single and a double bond) and requires more room than a pure single bond. The repulsion between the two C–O bonds would be greater than the repulsion between a C–O bond and the C–H bond. Thus, you would predict that the O–C–O angle is slightly greater than 120°, whereas the O–C–H angle is slightly less than 120°.
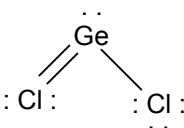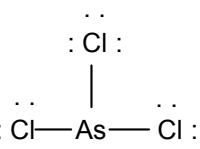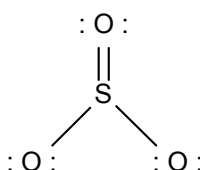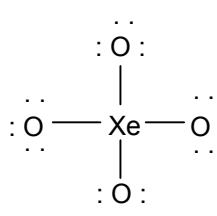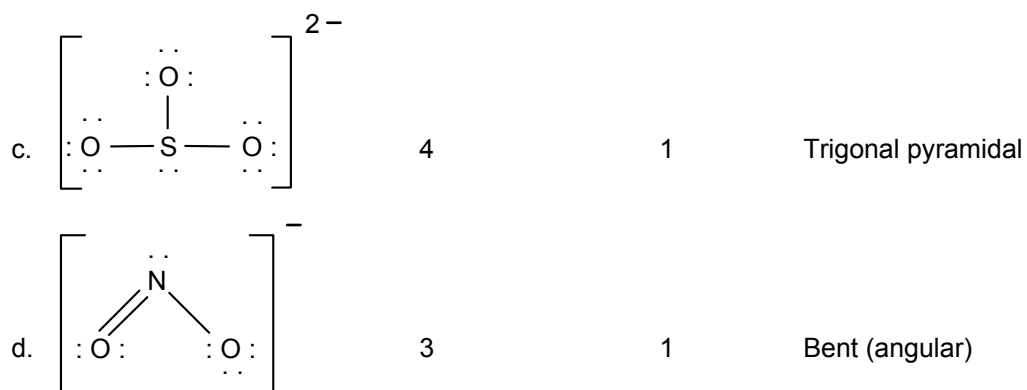
■   Solutions to Practice Problems

10.27   The number of electron pairs, lone pairs and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a.	4	0	Tetrahedral
b.	4	2	Bent

(continued)

c.

$$:O:$$
||
C
:F.   .F:

3   0   Trigonal planar

d.

$$:Cl:$$
|
:Cl— P —Cl:

4   1   Trigonal pyramidal

10.28   The number of electron pairs, lone pairs and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a. Ge :Cl: :Cl:	3	1	Bent (angular)
b. :Cl: :Cl—As—Cl:	4	1	Trigonal pyramidal
c. :O: ‖ S :O: :O:	3	0	Trigonal planar
d. :O: :O—Xe—O: :O:	4	0	Tetrahedral

10.29   The number of electron pairs, lone pairs and geometry are for the central atom.
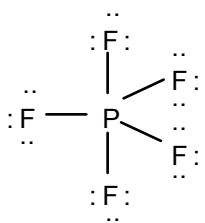
Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a.	4	1	Trigonal pyramidal
b.	4	0	Tetrahedral
c.	2	0	Linear
d.	4	1	Trigonal pyramidal

10.30   The number of electron pairs, lone pairs and geometry are for the central atom.
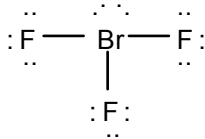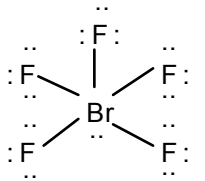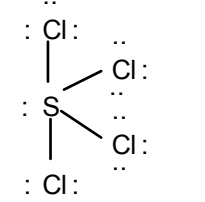
Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a.	2	0	Linear
b.	4	0	Tetrahedral

c.
$$
\left[\begin{array}{c} :\ddot{O}: \\ | \\ :\ddot{O}\!-\!S\!-\!\ddot{O}: \end{array}\right]^{2-}
$$
4   1   Trigonal pyramidal

d.
$$
\left[\begin{array}{c} \ddot{N} \\ :\ddot{O}: \quad\quad :\ddot{O}: \end{array}\right]^{-}
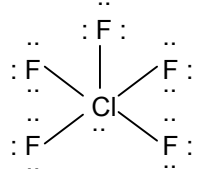$$
3   1   Bent (angular)

10.31 a. CCl_4 is tetrahedral, VSEPR predicts that the bond angles will be 109°, and you would expect them to be this angle.

b. SCl_2 is bent, and VSEPR theory predicts bond angles of 109°, but you would expect the Cl–S–Cl bond angle to be less.

c. $COCl_2$ is trigonal planar. VSEPR theory predicts 120° bond angles. The C–O bond is a double bond, so you would expect the Cl–C–O bond to be more than 120° and the Cl–C–Cl bond to be less than 120°.

d. AsH_3 is trigonal pyramidal, and VSEPR theory predicts bond angles of 109°, but you would expect the H–As–H bond angle to be less.

10.32 a. NCl_3 is trigonal pyramidal, and VSEPR theory predicts bond angles of 109°, but you would expect the Cl–N–Cl bond angle to be less.

b. Both carbon atoms are trigonal planar. VSEPR theory predicts 120° bond angles. The C–C bond is a double bond, so you would expect the F–C–C bond to be more than 120° and the F–C–F bond to be less than 120°.

c. SiF_4 is tetrahedral, VSEPR predicts that the bond angles will be 109°, and you would expect them to be this angle.

d. OF_2 is angular, and VSEPR theory predicts bond angles of 109°, but you would expect the F–O–F bond angle to be less.

10.33   The number of electron pairs, lone pairs and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a. PF_5 structure	5	0	Trigonal bipyramidal
b. BrF_3 structure	5	2	T-shaped
c. BrF_5 structure	6	1	Square pyramidal
d. SCl_4 structure	5	1	Seesaw

10.34   The number of electron pairs, lone pairs and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a. ClF_5 structure	6	1	Square pyramidal

(continued)

	Electron Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
b.	:F—Sb with F's	5	0	Trigonal bipyramidal
c.	:Se with F's	5	1	Seesaw
d.	Te with F's	6	0	Octahedral

10.35   The number of electron pairs, lone pairs and geometry are for the central atom.

	Electron Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a.	[:Cl—Sn with Cl's]⁻	5	0	Trigonal bipyramidal
b.	[P with F's]⁻	6	0	Octahedral

(continued)

|				
c.		5	3	Linear
d.		6	2	Square planar

10.36   The number of electron pairs, lone pairs and geometry are for the central atom.

	Electron Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a.		6	0	Octahedral
b.		5	3	Linear
c.		6	2	Square planar
d.		5	1	Seesaw

10.37 a. Trigonal pyramidal and T-shaped. Trigonal planar would have a dipole moment of zero.

   b. Bent. Linear would have a dipole moment of zero.

10.38 a. Trigonal pyramidal and T-shaped. Trigonal planar would have a dipole moment of zero.

   b. Seesaw. Square planar would have a dipole moment of zero.

10.39 a. CS_2 has a linear geometry and has no dipole moment.

   b. TeF_2 has a bent geometry and has a dipole moment.

   c. $SeCl_4$ has a seesaw geometry and has a dipole moment.

   d. XeF_4 has a square planar geometry and has no dipole moment.

10.40 a. $BeBr_2$ has a linear geometry and has no dipole moment.

   b. H_2Se has a bent, or angular, geometry and has a dipole moment.

   c. AsF_3 has a trigonal pyramidal geometry and has a dipole moment.

   d. SeF_6 has an octahedral geometry and has no dipole moment.

10.41 a. SF_2 is an angular model. The sulfur atom is sp^3 hybridized.

   b. ClO_3^- is a trigonal pyramidal molecule. The chlorine atom is sp^3 hybridized.

10.42 a. $AlCl_3$ is a trigonal planar molecule. The aluminum atom is sp^2 hybridized.

   b. BF_4^- is a tetrahedral ion. The boron atom is sp^3 hybridized.

10.43 a. $SeCl_2$ is a bent molecule. The Se atom is sp^3 hybridized.

   b. NO_2^- is a bent ion. The N atom is sp^2 hybridized.

   c. CO_2 is a linear molecule. The C atom is sp hybridized.

   d. COF_2 is a trigonal planar molecule. The C atom is sp^2 hybridized.

10.44 a. PCl_3 is a trigonal pyramidal molecule. The P atom is sp^3 hybridized.

b. $SiCl_4$ is a tetrahedral molecule. The Si atom is sp^3 hybridized.

c. BeF_2 is a linear molecule. The Be atom is sp hybridized.

d. SO_2 is a bent molecule. The S atom is sp^2 hybridized.

10.45 a. The Lewis structure is

$$: \ddot{Cl} \!\!-\!\! Hg \!\!-\!\! \ddot{Cl} :$$
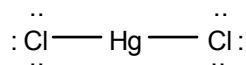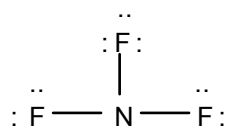
The presence of two single bonds and no lone pairs suggests sp hybridization. Thus, an Hg atom with the configuration $[Xe]4f^{14}5d^{10}6s^2$ is promoted to $[Xe]4f^{14}5d^{10}6s^16p^1$, then hybridized. An Hg–Cl bond is formed by overlapping an Hg hybrid orbital with a $3p$ orbital of Cl.

b. The Lewis structure is

$$\begin{array}{c} : \ddot{Cl} : \\ | \\ : \ddot{Cl} \!\!-\!\! P \!\!-\!\! \ddot{Cl} : \end{array}$$
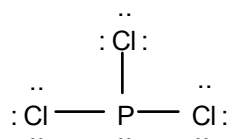
The presence of three single bonds and one lone pair suggests sp^3 hybridization of the P atom. Three hybrid orbitals each overlap a $3p$ orbital of a Cl atom to form a P–Cl bond. The fourth hybrid orbital contains the lone pair.
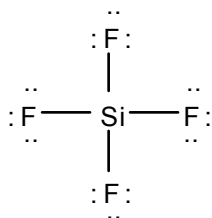
10.46 a. The Lewis structure is

$$\begin{array}{c} : \ddot{F} : \\ | \\ : \ddot{F} \!\!-\!\! N \!\!-\!\! \ddot{F} : \end{array}$$

The presence of three single bonds and one lone pair suggests sp^3 hybridization of the N atom. Three hybrid orbitals each overlap a $2p$ orbital of an F atom to form an N–F bond. The fourth hybrid orbital contains the lone pair.

b. The Lewis structure is

$$\overset{\displaystyle ..}{\underset{\displaystyle ..}{:F:}}$$

The presence of four single bonds and no lone pairs suggests sp^3 hybridization of the Si atom. Each hybrid orbital overlaps a $2p$ orbital of an F atom to form an Si–F bond.

10.47 a. Xenon has eight valence electrons. Each F atom donates one electron to give a total of ten electrons, or five electron pairs, around the Xe atom. The hybridization is sp^3d.

b. Bromine has seven valence electrons. Each F atom donates one electron to give a total of ten electrons, or five electron pairs, around the Br atom. The hybridization is sp^3d.

c. Phosphorus has five valence electrons. The Cl atoms each donate one electron to give a total of ten electrons, or five electron pairs, around the P atom. The hybridization is sp^3d.

d. Chlorine has seven valence electrons, to which may be added one electron from each F atom minus one electron for the charge on the ion. This gives a total of ten electrons, or five electron pairs, around chlorine. The hybridization is sp^3d.

10.48 a. Sulfur has six valence electrons. The F atoms each donate one electron to give a total of ten electrons, or five electron pairs, around the S atom. The hybridization is sp^3d.

b. Arsenic has five valence electrons. Each Cl atom donates one electron to give a total of ten electrons, or five electron pairs, around the As atom. The hybridization is sp^3d.

c. Selenium has six valence electrons. Each F atom donates one electron to give a total of twelve electrons, or six electron pairs, around the Se atom. The hybridization is sp^3d^2.

d. Iodine has seven valence electrons, to which may be added one electron from each of the F atoms and one electron to account for the charge on the ion. This gives a total of twelve electrons, or six electron pairs, around the I atom. The hybridization is sp^3d^2.

10.49 The P atom in PCl_6^- has six single bonds around it and no lone pairs. This suggests sp^3d^2 hybridization. Each bond in this ion is a σ bond formed by overlap of an sp^3d^2 hybrid orbital on P with a $3p$ orbital on Cl.

10.50 The central I atom in I_3^- has two single bonds and three lone pairs around it. This suggests sp^3d hybridization. Each I–I bond is formed by the overlap of an sp^3d hybrid orbital on the central I with a $5p$ orbital from a terminal I.

10.51 a. The structural formula of formaldehyde is

```
        : O :
          ‖
          C
       ⁄     ⁄
     H         H
```
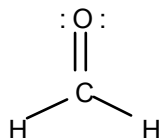
Because the C is bonded to three other atoms, it is assumed to be sp^2 hybridized. One $2p$ orbital remains unhybridized. The carbon-hydrogen bonds are σ bonds formed by the overlap of an sp^2 hybrid orbital on C with a $1s$ orbital on H. The remaining sp^2 hybrid orbital on C overlaps with a $2p$ orbital on O to form a σ bond. The unhybridized $2p$ orbital on C overlaps with a parallel $2p$ orbital on O to form a π bond. Together, the σ and π bonds constitute a double bond.

b. The nitrogen atoms are sp hybridized. A σ bond is formed by the overlap of an sp hybrid orbital from each N. The remaining sp hybrid orbitals contain lone pairs of electrons. The two unhybridized $2p$ orbitals on one N overlap with the parallel unhybridized $2p$ orbitals on the other N to form two π bonds.

10.52 a. Each nitrogen atom is bonded to two other atoms and also has a lone pair of electrons in its valence shell. Therefore, the nitrogen atoms are expected to be sp^2 hybridized. The N–H bonds are σ bonds formed by the overlap of an sp^2 hybrid orbital of an N atom with a $1s$ orbital on an H atom. Each N also contains a lone pair of electrons in an sp^2 hybrid orbital. The remaining sp^2 hybrid orbitals, one on each N, overlap with each other to form a σ bond. The two $2p$ orbitals, one on each N, are oriented parallel to each other so that they may overlap to form a π bond.

b. The carbon atom is bonded to two atoms and has no lone pairs; hence, it is expected to be sp hybridized. The C–H bond is a σ bond formed by the overlap of an sp hybrid orbital on carbon with a $1s$ orbital on hydrogen. The other sp hybrid orbital overlaps with an sp orbital on the nitrogen atom to form a σ bond. The remaining sp hybrid orbital on N contains a lone pair. There remain two unhybridized $2p$ orbitals on the carbon and two $2p$ orbitals on the nitrogen atom. One $2p$ orbital from the C and a parallel $2p$ orbital on the N overlap to form a π bond. The remaining two $2p$ orbitals overlap to form a second π bond between the carbon and nitrogen.

10.53   Each of the N atoms has a lone pair of electrons and is bonded to two atoms. The N atoms are sp^2 hybridized. The two possible arrangements of the O atoms relative to one another are shown below. Because the π bond between the N atoms must be broken to interconvert these two forms, it is to be expected that the hyponitrite ion will exhibit *cis-trans* isomerism.

cis   trans
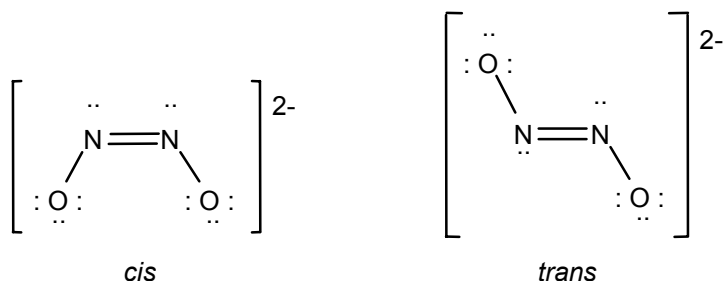
10.54   The C=C bond consists of a σ bond and a π bond. The π bond depends on the parallel orientation of the two *p* orbitals that overlap to form the bond. In order to interconvert the *cis* and *trans* forms, one end of the molecule would have to be rotated relative to the other end, thus changing the orientation of the *p* orbitals and breaking the bond. Because this requires considerable energy, the *cis* and *trans* forms are stable relative to interconversion.
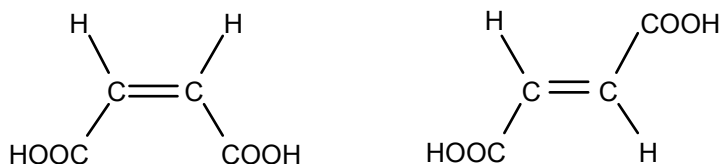
10.55 a. Total electrons = 2 x 5 = 10.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^2$.

Bond order = 1/2 (n_b - n_a) = 1/2 (6 - 4) = 1

The B_2 molecule is stable. It is paramagnetic because the two electrons in the π_{2p} subshell occupy separate orbitals.

b. Total electrons = (2 x 5) - 1 = 9.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^1$.

Bond order = 1/2 (n_b - n_a) = 1/2 (5 - 4) = 1/2

The B_2^+ molecule should be stable and is paramagnetic because there is one unpaired electron in the π_{2p} subshell.

c. Total electrons = (2 x 8) + 1 = 17.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}{}^*)^3$.

Bond order = 1/2 (n_b - n_a) = 1/2 (10 - 7) = 3/2

The $O_2{}^-$ molecule should be stable and is paramagnetic because there is one unpaired electron in the $\pi_{2p}{}^*$ subshell.

10.56 a. Total electrons = (2 x 6) - 1 = 11.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^3$.

Bond order = 1/2 (n_b - n_a) = 1/2 (7 - 4) = 3/2

The $C_2{}^+$ molecule is expected to be stable and paramagnetic.

b. Total electrons = 2 x 10 = 20.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}{}^*)^4(\sigma_{2p}{}^*)^2$.

Bond order = 1/2 (n_b - n_a) = 1/2 (10 - 10) = 0

The Ne_2 molecule is expected to be unstable and diamagnetic.

c. Total electrons = (2 x 6) + 1 = 13.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$.

Bond order = 1/2 (n_b - n_a) = 1/2 (9 - 4) = 5/2

The $C_2{}^-$ molecule is expected to be stable. It is paramagnetic because there is one unpaired electron in the σ_{2p} subshell.

10.57 Total electrons = 6 + 7 + 1 = 14.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$.

Bond order = 1/2 (n_b - n_a) = 1/2 (10 - 4) = 3

The CN^- ion is diamagnetic.

10.58 Total electrons = 5 + 7 = 12.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4$.

Bond order = $1/2\ (n_b - n_a)$ = $1/2\ (8 - 4)$ = 2
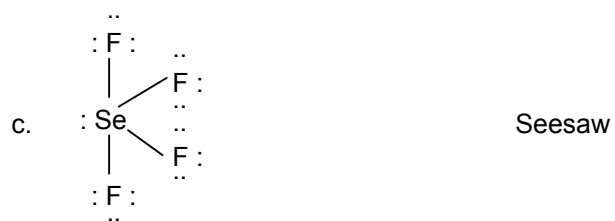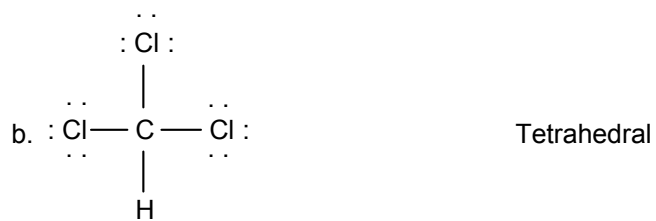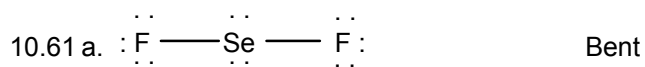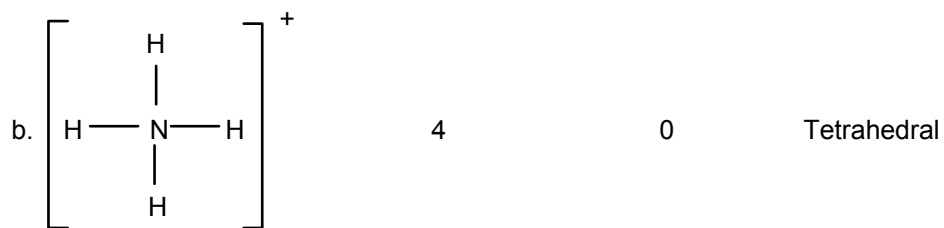
The BN molecule is diamagnetic.

■ Solutions to General Problems

10.59 The number of electron pairs, lone pairs and geometry are for the central atom.

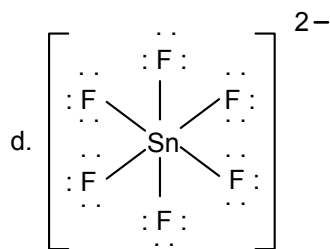| Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a. $:\!Cl\!-\!Sn\!-\!Cl:$	2	1	Bent
b. (O double bonded to C, with two F)	3	0	Trigonal planar
c. $[:\!Cl\!-\!I\!-\!Cl:]^-$	5	3	Linear
d. (P with six Cl, octahedral anion)	6	0	Octahedral

10.60

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
a. $H\!-\!O\!-\!F:$	4	2	Bent, or angular

(continued)

b.

$$\left[\begin{array}{c} H \\ | \\ H - N - H \\ | \\ H \end{array} \right]^+$$

4   0   Tetrahedral

c.

: F :
|
: F — P
F :
F :
: F :

5   0   Trigonal bypyramidal

d.

$$\left[\begin{array}{c} : F : \\ | \\ : Cl \quad F : \\ | \\ : F : \end{array} \quad F : \right]^+$$

5   1   Seesaw

10.61 a.   : F —— Se —— F :   Bent

b.
: Cl :
|
: Cl — C — Cl :
|
H

Tetrahedral

c.
: F :
|
: Se   F :
|
: F :
  F :

Seesaw

(continued)

d.

$$\left[\begin{array}{c} \ddot{F} \\ :F \quad \Big| \quad F: \\ Sn \\ :F \quad \quad F: \\ :F: \end{array} \right]^{2-}$$

Octahedral

10.62 a.

$$\begin{array}{c} :\ddot{Br}: \\ | \\ B \\ :Br \quad \quad Br: \end{array}$$

Trigonal planar

b.

$$\begin{array}{c} H \\ | \\ H - As - H \end{array}$$

Trigonal pyramidal

c.

$$\left[\begin{array}{c} :F \quad \quad F: \\ Cl \\ :F \quad \quad F: \end{array} \right]^{-}$$

Square planar

d.

$$\left[\begin{array}{c} :F: \\ :F \quad | \quad F: \\ Te \\ :F \quad \quad F: \end{array} \right]^{-}$$

Square pyramidal

10.63 a.

$$\begin{array}{c} H \quad \quad H \quad \quad H \\ \diagdown \quad \quad | \quad \quad | \\ C = C - C - O - H \\ \diagup \quad a \quad b \quad | \quad c \\ H \quad \quad \quad \quad H \end{array}$$
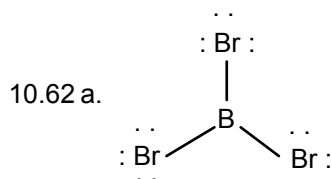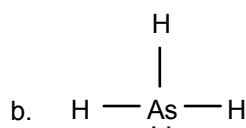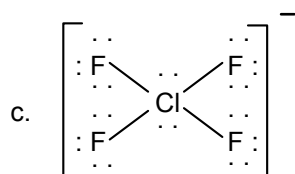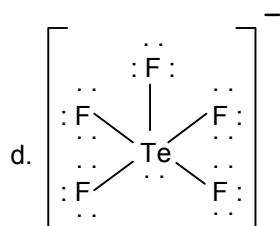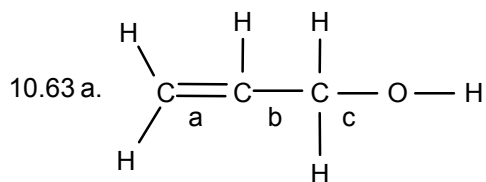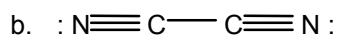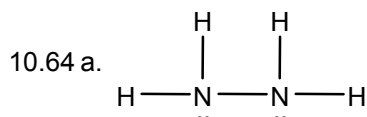
C_a and C_b: Three electron pairs around
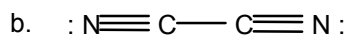They are sp^2 hybridized.

C_c: Four electron pairs around it. It is sp^3
hybridized.

b.   :N≡C — C≡N:

Both C atoms are bonded to two other atoms
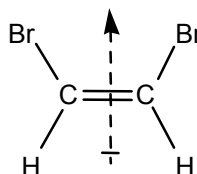and have no lone pairs of electrons. They are
sp hybridized.

10.64 a.

H   H
| |
H—N—N—H
  .. ..

Each N has three atoms and one lone pair electrons. They are *sp* ^{3} hybridized.

b.   : N≡C—C≡N :

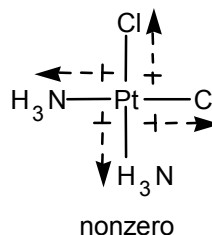Each N has a σ bond to one atom and a lone pair of electrons. They are *sp* hybridized.

10.65

Br   Br
  \   /
   C ═══ C   has a net dipole
  /   \
H   H
   cis

Br   Br
  \   /
   C ═══ C
  /   \
H   H
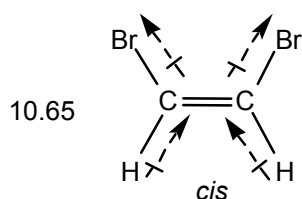
Br   H
  \   /
   C ═══ C   has no net dipole. The two C-Br bond dipoles cancel and
  /   \   the two C-H bond dipoles cancel.
H   Br
   trans

10.66

Cl
|
H₃N—Pt—NH₃
|
Cl

zero
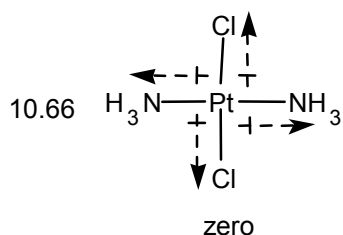
Identical bond dipoles cancel each other.

Cl
|
H₃N—Pt—Cl
|
H₃N

nonzero

Bond dipoles cannot cancel. Dissimilar across from each other.

10.67   All four hydrogen atoms of $H_2C=C=CH_2$ cannot lie in the same plane because the second C=C bond forms perpendicular to the plane of the first C=C bond. By looking at Figure 10.26, you can see how this is so. The second C=C bond forms in the plane of the C–H bonds. Thus, the plane of the C–H bonds on the right side will be perpendicular to the plane of the C–H bonds on the left side. This is shown below using the π orbitals of the two C=C double bonds.
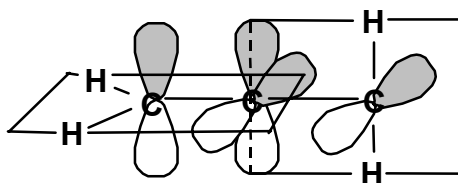
10.68 All four hydrogen atoms of $H_2C=C=C=CH_2$ lie in the same plane because the second C=C bond forms perpendicular to the plane of the first C=C bond, and the third C=C bond forms perpendicular to the plane of the second C=C bond. Thus, the right-hand CH_2 is in the same plane as the left-hand H_2C group.
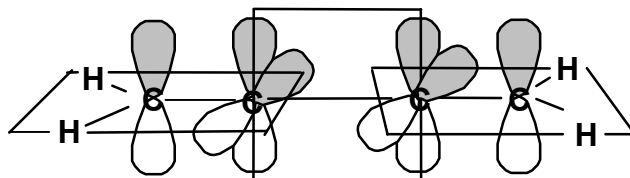
10.69 Total electrons = 2 + 1 - 1 = 2.

The electron configuration is $(\sigma_{1s})^2$.

Bond order = $1/2\ (n_b - n_a)$ = $1/2\ (2)$ = 1

The HeH$^+$ ion is expected to be stable.

10.70 Total electrons = (2 x 2) - 1 = 3.

The electron configuration is $(\sigma_{1s})^2(\sigma_{1s}{}^*)^1$.

Bond order = $1/2\ (n_b - n_a)$ = $1/2\ (2 - 1)$ = 1/2

The He$_2{}^+$ ion is expected to be stable.

10.71 Total electrons = (2 x 6) + 2 = 14.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^+$.

Bond order = $1/2\ (n_b - n_a)$ = $1/2\ (10 - 4)$ = 3

10.72 Total electrons = (2 x 8) + 2 = 18.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}{}^*)^4$.

Bond order = $1/2\ (n_b - n_a)$ = $1/2\ (10 - 8)$ = 1

10.73   The molecular orbital configuration of O_2 is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}{}^*)^2$. $O_2{}^+$ has one electron less than O_2. The difference is in the number of electrons in the $\pi_{2p}{}^*$ antibonding orbital. This means that the bond order is larger for $O_2{}^+$ than for O_2.

O_2: Bond order = 1/2 (n_b - n_a) = 1/2 (10 - 6) = 2

$O_2{}^+$: Bond order = 1/2 (n_b - n_a) = 1/2 (10 - 5) = 5/2

It is expected that the species with the higher bond order, $O_2{}^+$, has the shorter bond length. In $O_2{}^-$, there is one more electron than in O_2. This additional electron occupies a $\pi_{2p}{}^*$ orbital. Increasing the number of electrons in antibonding orbitals decreases the bond order; hence, $O_2{}^-$ should have a longer bond length than O_2.

10.74   The molecular orbital configuration of N_2 is $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$. $N_2{}^+$ has one electron less than N_2. The difference is in the number of electrons in the σ_{2p} bonding orbital. Because $N_2{}^+$ has fewer electrons in bonding orbitals than N_2 and the same number in antibonding orbitals, $N_2{}^+$ has a lower bond order and a longer bond distance. In $N_2{}^-$, there is one more electron than in N_2. This additional electron occupies a $\pi_{2p}{}^*$ antibonding orbital. Because $N_2{}^-$ has more electrons in antibonding orbitals and the same number in bonding orbitals, the bond order is lower; hence, $N_2{}^-$ has a longer bond length than N_2.

10.75   As shown in Figure 10.34, the occupation of molecular orbitals by the N_2 valence electrons is:

$KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}{}^*)^0$
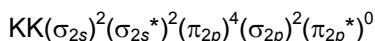
To form the first excited state of N_2, a σ_{2p} electron is promoted to the $\pi_{2p}{}^*$ orbital, giving:

$KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^1(\pi_{2p}{}^*)^1$
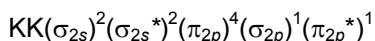
The differences in properties are as follows:

Magnetic character: The ground state is diamagnetic (all electrons paired), and the excited state is paramagnetic.

Bond order: ground state order = 1/2 (8 - 2) = 3
              excited state order = 1/2 (7 - 3) = 2

Bond-dissociation energy: ground state energy = 942 kJ; excited state energy is less than 942 kJ (excited state does not possess a stable triple bond like the ground state)

Bond length: ground state length = 110 pm; excited state length is more than 110 pm.

10.76 For N_2, refer to Figure 10.34. Note that the energy of the highest occupied orbital of atomic nitrogen is greater than the energy of the highest occupied orbital of N_2. Thus the outer electrons of atomic nitrogen are farther from the nucleus and have a smaller ionization energy than that of N_2.

The occupation of the molecular orbitals of O_2 are almost the same as shown in Figure 10.34; the electronic configuration given in Example 10.7 is below with that of atomic oxygen:

O_2: $KK(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}{}^*)^2$

O: $1s^2 2s^2 2p^4$
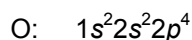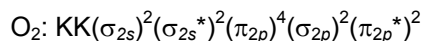
Referring again to Figure 10.34 (after inserting two $\pi_{2p}{}^*$ electrons for O_2), we see that the energy of the highest occupied orbital of O_2 is greater than the energy of the highest occupied orbital of atomic oxygen. Thus, the outer electrons of O_2 are farther from the nucleus and have a smaller ionization energy than that of atomic oxygen.

■ Solutions to Cumulative-Skills Problems

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

10.77 After assuming a 100.0 g sample, convert to moles:

$$60.4 \text{ g Xe} \times \frac{1 \text{ mol Xe}}{131.29 \text{ g Xe}} = 0.46\underline{0}05 \text{ mol Xe}$$

$$22.1 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.3\underline{8}1 \text{ mol O}$$
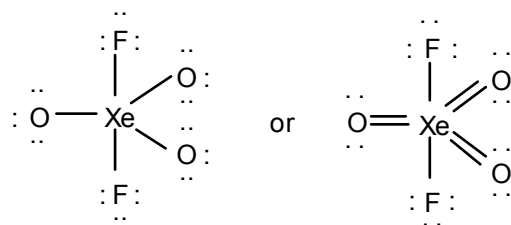
$$17.5 \text{ g F} \times \frac{1 \text{ mol F}}{18.99 \text{ g F}} = 0.92\underline{1}5 \text{ mol F}$$

Divide by 0.460 :

$$\text{Xe: } \frac{0.460}{0.460} = 1; \quad \text{O: } \frac{1.381}{0.460} = 3.00; \quad \text{F: } \frac{0.9215}{0.460} = 2.00$$

(continued)

The simplest formula is XeO_3F_2. This is also the molecular formula. The Lewis formula is

Number of electron pairs = 5, number of lone pairs = 0; hence, the geometry is trigonal bipyramidal. Because xenon has five single bonds, it will require five orbitals to describe the bonding. This suggests sp^3d hybridization.

10.78   After assuming a 100.0 g sample, convert to moles:

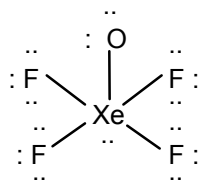$$58.8 \text{ g Xe} \times \frac{1 \text{ mol Xe}}{131.29 \text{ g Xe}} = 0.44\underline{7}8 \text{ mol Xe}$$

$$7.2 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.4\underline{5}00 \text{ mol O}$$

$$34.0 \text{ g F} \times \frac{1 \text{ mol F}}{18.99 \text{ g F}} = 1.7\underline{9}04 \text{ mol F}$$

Divide by 0.4478 :

$$\text{Xe: } \frac{0.4478}{0.4478} = 1; \quad \text{O: } \frac{0.450}{0.4478} = 1.00; \quad \text{F: } \frac{1.7904}{0.4478} = 4.00$$

The simplest formula is $XeOF_4$. This is also the molecular formula. The Lewis formula is
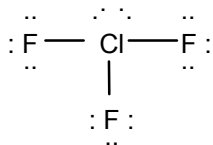

Number of electron pairs = 6, number of lone pairs = 1; hence, the geometry is square pyramidal. Because xenon has six electron pairs, it will require six orbitals to describe the bonding. This suggests sp^3d^2 hybridization.

10.79 $U(s) + ClF_n \rightarrow UF_6 + ClF(g)$
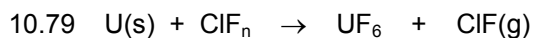
$$\text{mol } UF_6 = 3.53 \text{ g } UF_6 \times \frac{1 \text{ mol } UF_6}{352.07 \text{ g } UF_6} = 0.0100\underline{3} \text{ mol } UF_6$$

$$\text{mol ClF} = n = \frac{PV}{RT} = \frac{2.50 \text{ atm} \times 0.343 \text{ L}}{0.082057 \text{ L} \cdot \text{atm/ (K} \cdot \text{mol)} \times 348K} = 0.300\underline{2} \text{ mol ClF}$$

0.010 mol UF_6 = 0.060 mol F, and 0.030 mol ClF = 0.030 mol F; therefore, the total moles of F from ClF_n = 0.090 mol F. Because mol ClF_n must equal mol ClF, mol ClF_n = 0.030 mol and n = 0.090 mol F ÷ 0.030 mol ClF_n = 3. The Lewis formula is

```
    ..        .· .·        ..
  : F ——— Cl ——— F :
    ..         |         ..
             : F :
               ..
```

Number of electron pairs = 5, number of lone pairs = 2; hence, the geometry is T-shaped. Because chlorine has five electron pairs, it will require five orbitals to describe the bonding. This suggests sp^3d hybridization.

10.80 $Br_2 + \text{excess } F_2 \rightarrow 2BrF_n$

$$\text{mol } Br_2 = n = \frac{PV}{RT} = \frac{(748/ 760) \text{ atm} \times 0.423 \text{ L}}{0.082057 \text{ L} \cdot \text{atm/(K} \cdot \text{mol)} \times 423K}$$

$$= 0.011\underline{99} = 0.0120 \text{ mol } Br_2$$

From the equation, 0.0120 mol Br_2 must produce 0.0240 mol BrF_n.
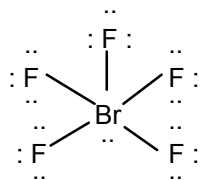
$$\text{Formula wt. } BrF_n = \frac{4.20 \text{ g}}{0.0240 \text{ mol}} = 175 \text{ g/mol}$$

175 g/mol = 79.9 g Br/mol + 19.00 x n g F/mol

$$n = \frac{175 - 79.9}{19.00} = 5.00$$

(continued)

The Lewis formula is

Number of electron pairs = 6, number of lone pairs = 1; hence, the geometry is square pyramidal. Because bromine has six electron pairs, it will require six orbitals to describe the bonding. This suggests sp^3d^2 hybridization.

10.81 N_2:   Triple bond; bond length = 110 pm. Geometry is linear; sp-hybrid orbitals are needed for one lone pair and one σ bond.

N_2F_2:   Double bond; bond length = 122 pm. Geometry is trigonal planar; sp^2-hybrid orbitals are needed for one lone pair and two σ bonds.

N_2H_4:   Single bond; bond length = 145 pm. Geometry is tetrahedral; sp^3-hybrid orbitals are needed for one lone pair and three σ bonds.

10.82   The bond length of C_2 is close to that of C_2H_4, suggesting the same bond order for C_2 as for C_2H_4, which has a C=C bond. Total electrons for C_2 = 2 x 6 = 12. The molecular orbital configuration for C_2 is $KK(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^4(\sigma_{2p})^0$. Bond order = 1/2(8 - 4) = 2. This agrees with the bond-length prediction.
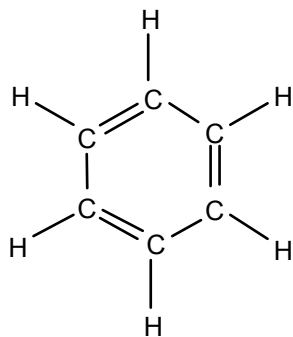
10.83 HNO_3 resonance formulas:
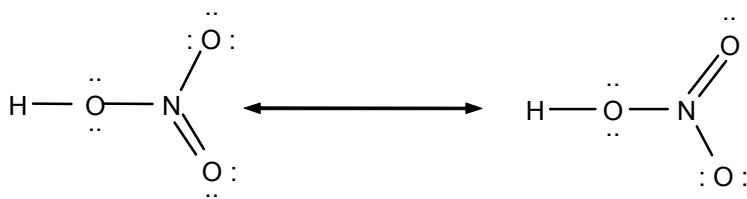
The geometry around the nitrogen is trigonal planar; therefore, the hybridization is sp^2.

Formation reaction: $H_2(g)$ + $3O_2(g)$ + $N_2(g)$ → $2HNO_3(g)$

2 x $\Delta H_f°$ = [BE(H-H) + 3BE(O_2) + BE(N_2)] - [2BE(H-O) + 4BE(N-O) + 2BE(N=O)]

= [(432 + 3 x 494 + 942) - (2 x 459 + 4 x 201 + 2 x 607) kJ/2 mol]

= -80 kJ/2 mol = -40 kJ/mol

Resonance energy = -40 kJ - (-135 kJ) = 95 kJ

10.84   This is the other resonance formula of benzene.

Geometry is trigonal planar; therefore, the hybridization is sp^2.

Formation reaction: $3H_2(g)$ + $6C(graphite)$ → $C_6H_6(g)$ [+ $C(graphite)$ → $C(g)$]

$\Delta H_f°$ =   [3BE(H-H) + 6 x ΔH C(g)] - [6BE(C-H) + 3BE(C-C) + 3BE(C=C)]

= [(3 x 432 + 6 x 715) - (6 x 411 + 3 x 346 + 3 x 602) kJ/mol]

= +276 kJ/mol

Resonance energy = +276 kJ - (-83 kJ) = 359 kJ

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