CHAPTER 11 THEORIES OF COVALENT BONDING

11.1 Table 11.1 describes the types of shapes that form from a given set of hybrid orbitals.
   a) trigonal planar: three electron groups - three hybrid orbitals: \( sp^2 \)
   b) octahedral: six electron groups - six hybrid orbitals: \( sp^3 d^2 \)
   c) linear: two electron groups - two hybrid orbitals: \( sp \)
   d) tetrahedral: four electron groups - four hybrid orbitals: \( sp^3 \)
   e) trigonal bipyramidal: five electron groups - five hybrid orbitals: \( sp^3 d \)

11.2 a) \( sp^2 \) b) \( sp^3 \) c) \( sp^3 d \) d) \( sp^3 d^2 \)

11.3 Carbon and silicon have the same number of valence electrons, but the outer level of electrons is
   \( n = 2 \) for carbon and \( n = 3 \) for silicon. Thus, silicon has \( 3d \) orbitals in addition to \( 3s \) and \( 3p \) orbitals
   available for bonding in its outer level, to form up to 6 hybrid orbitals, whereas carbon has only \( 2s \) and
   \( 2p \) orbitals available in its outer level to form up to 4 hybrid orbitals.

11.4 **Four.** The same number of hybrid orbitals will form as the initial number of atomic orbitals
   mixed.

11.5 The **number** of orbitals remains the same as the number of orbitals before hybridization. The **type**
   depends on the orbitals mixed.
   a) There are six unhybridized orbitals, and therefore **six** hybrid orbitals result. The type is \( sp^3 d^2 \).
   b) **Four** \( sp^3 \) hybrid orbitals form from three \( p \) and one \( s \) atomic orbitals.

11.6 a) **two** \( sp \) **orbitals** b) **five** \( sp^3 d \) **orbitals**

11.7 To determine hybridization, draw the Lewis structure and count the number of electron groups.
   Hybridize that number of orbitals. Single, double and triple bonds all count as one electron group.
   An unshared pair of electrons or one unshared electron also counts as one electron group.
   a) The three electron groups (one double bond, one lone pair and one unpaired electron) around
      nitrogen require three hybrid orbitals. The hybridization is \( sp^2 \).
      \[
      \cdot\text{N}==\cdot\text{O}
      \]
   b) The nitrogen has three electron groups (one single bond, one double bond and one unpaired
      electron), requiring three hybrid orbitals so hybridization is \( sp^3 \).
      \[
      \cdot\cdot\text{N}\cdot\cdot\text{O}=\cdot\cdot\cdot\cdot
      \]
   c) The nitrogen has three electron groups (one single bond, one double bond and one lone pair so
      hybridization is \( sp^3 \).
      \[
      \cdot\cdot\cdot\cdot\cdot\text{N}\cdot\cdot\cdot\cdot\text{O}
      \]
11.8  a) $sp^2$

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\end{array}
\]

b) $sp^3$

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{O}
\end{array}
\end{array}
\]

c) $sp$

\[
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{O}
\end{array}
\end{array}
\]

11.9  To determine hybridization, draw the Lewis structure and count the number of electron groups. Hybridize that number of orbitals. Single, double and triple bonds all count as one electron group. An unshared pair of electrons or one unshared electron also counts as one electron group.

a) $sp^3$  The Cl has four electron groups (1 lone pair, 1 lone electron, and 2 double bonds) and therefore four hybrid orbitals are required; the hybridization is $sp^3$. Note that in ClO\textsubscript{2}, the $\pi$ bond is formed by the overlap of $d$-orbitals from chlorine with $p$-orbitals from oxygen.

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{Cl} \\
\text{O}
\end{array}
\end{array}
\]

b) $sp^3$  The Cl has four electron groups (1 lone pair and 3 bonds) and therefore four hybrid orbitals are required; the hybridization is $sp^3$.

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{Cl} \\
\text{O}
\end{array}
\end{array}
\]

c) $sp^3$  The Cl has four electron groups (4 bonds) and therefore four hybrid orbitals are required; the hybridization is $sp^3$.

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{Cl} \\
\text{O}
\end{array}
\end{array}
\]

11.10  a) $sp^3d$

\[
\begin{array}{c}
\begin{array}{c}
\text{F} \\
\text{Br} \\
\text{F}
\end{array}
\end{array}
\]
11.11  

a) Silicon has four electron groups (four bonds) requiring four hybrid orbitals; four $sp^3$ hybrid orbitals are made from one $s$ and three $p$ atomic orbitals.

\[
\text{Cl} \quad \text{Si} \quad \text{H} \\
\text{H} 
\]

b) Carbon has two electron groups (two double bonds) requiring two hybrid orbitals; two $sp$ hybrid orbitals are made from one $s$ and one $p$ orbital.

\[
\text{S} \quad \text{C} \quad \text{S} 
\]

c) Sulfur is surrounded by 5 electron groups (4 bonding pairs, 1 lone pair) requiring five hybrid orbitals; five $sp^3d$ hybrid orbitals are formed from one $s$ orbital, three $p$ orbitals, and one $d$ orbital.

\[
\text{F} \quad \text{Cl} \quad \text{S} \\
\text{Cl} 
\]

d) Nitrogen is surrounded by 4 electron groups (3 bonding pairs, 1 lone pair) requiring four hybrid orbitals; four $sp^3$ hybrid orbitals are formed from one $s$ orbital and three $p$ orbitals.

\[
\text{F} \quad \text{N} \quad \text{F} \\
\text{F} 
\]

11.12  

a) $sp^3 \leftarrow s + 3p$

\[
\text{Cl} \quad \text{O} \quad \text{Cl} \\
\text{Cl} 
\]

b) $sp^3d \leftarrow s + 3p + d$

\[
\text{Cl} \quad \text{Br} \quad \text{Cl} 
\]
c) $sp^3d \leftarrow s + 3p + d$

\[ \begin{array}{c}
\text{F} \\
\text{F} \\
\text{P} \\
\text{F}
\end{array} \]

\[ \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{O}
\end{array} \]

\[ \begin{array}{c}
\text{O} \\
\text{S} \\
\text{O}
\end{array} \]_{2-}

11.13 a) The P in PH$_3$ has four electron groups (1 lone pair and 3 bonds) and therefore four hybrid orbitals are required; the hybridization is $sp^3$. The P in the product also has four electron groups (4 bonds) and again four hybrid orbitals are required. The hybridization of P remains $sp^3$. There is no change in hybridization. Illustration B best shows the hybridization of P during the reaction as $sp^3 \rightarrow sp^3$.

b) The B in BH$_3$ has three electron groups (3 bonds) and therefore three hybrid orbitals are required; the hybridization is $sp^2$. The B in the product has four electron groups (4 bonds) and four hybrid orbitals are required. The hybridization of B is now $sp^3$. The hybridization of B changes from $sp^2$ to $sp^3$; this is best shown by illustration A.

\[ \begin{array}{c}
\text{H} \\
\text{H} \\
\text{P} \\
\text{H} \\
\text{H}
\end{array} \] + \[ \begin{array}{c}
\text{H} \\
\text{H} \\
\text{B} \\
\text{H} \\
\text{H}
\end{array} \] \[ \rightarrow \]

\[ \begin{array}{c}
\text{H} \\
\text{H} \\
\text{P} \\
\text{B} \\
\text{H}
\end{array} \]

11.14 a) The Te in TeF$_6$ has six electron groups (6 bonds) and therefore six hybrid orbitals are required; the hybridization is $sp^3d^2$. Te in TeF$_5$ also has six electron groups (5 bonds and one unshared pair) and again six hybrid orbitals are required. The hybridization of Te remains $sp^3d^2$. There is no change in hybridization. Illustration A best shows the hybridization of Te when TeF$_6$ forms TeF$_5$: $sp^3d^2 \rightarrow sp^3d^2$.

\[ \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{Te} \\
\text{F}
\end{array} \] \[ \rightarrow \]

\[ \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{Te} \\
\text{F}
\end{array} \]
b) The Te in TeF₄ has five electron groups (4 bonds and 1 unshared pair) and therefore five hybrid orbitals are required; the hybridization is $sp^3d$. Te in TeF₆ has six electron groups (6 bonds) and therefore six hybrid orbitals are required; the hybridization is $sp^3d^2$. Illustration C best shows the change in hybridization of Te from $sp^3d$ to $sp^3d^2$.

11.15 a) Germanium is the central atom in GeCl₄. Ge has four electron groups (four bonds), requiring four hybrid orbitals. Hybridization is $sp^3$ around Ge.

a) Boron is the central atom in BCl₃. B has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is $sp^2$ around B.
b) Carbon is the central atom in \( \text{CH}_3^+ \). C has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is \( sp^2 \) around C.

\[
\begin{array}{c}
H \\
H \quad C \\
H \\
\end{array}
\]

Isolated C atom

\[
\begin{array}{c}
H \\
p \\
\end{array}
\quad \rightarrow \quad
\begin{array}{c}
H \\
sp^2 \\
p \\
\end{array}
\quad + \quad e^-
\]

Hybridized C atom

11.16 a) 

\[
\begin{array}{c}
s \quad p \\
\end{array}
\quad \rightarrow \quad
\begin{array}{c}
sp^3 \\
\end{array}
\quad + \quad 3e^-
\]

b) 

\[
\begin{array}{c}
s \quad p \\
\end{array}
\quad \rightarrow \quad
\begin{array}{c}
sp^3 \\
\end{array}
\quad + \quad 3e^-
\]

11.17 a) In \( \text{SeCl}_2 \), Se is the central atom and has four electron groups (two single bonds and two lone pairs), requiring four hybrid orbitals. Se is \( sp^3 \) hybridized. Two \( sp^3 \) orbitals are filled with lone electron pairs and two \( sp^3 \) orbitals bond with the chlorine atoms.

\[
\begin{array}{c}
\text{Cl} - \text{Se} - \text{Cl}
\end{array}
\]

b) In \( \text{H}_3\text{O}^+ \), O is the central atom and has four electron groups (three single bonds and one lone pair, requiring four hybrid orbitals. O is \( sp^3 \) hybridized. One \( sp^3 \) orbital is filled with a lone electron pair and three \( sp^3 \) orbitals bond with the hydrogen atoms.

\[
\begin{array}{c}
\text{H} \\
\text{H} - \text{O} - \text{H}
\end{array}
\quad +
\]
c) I is the central atom in IF₄⁻ with 6 electron groups (four single bonds and two lone pairs) surrounding it. Six hybrid orbitals are required and I has sp³d² hybrid orbitals. The sp³d² hybrid orbitals are composed of one s orbital, three p-orbitals, and two d-orbitals. Two sp³d² orbitals are filled with a lone pair and four sp³d² orbitals bond with the fluorine atoms.

11.18

a)

b)

c)
11.19

\[
\text{H} \quad \text{N} \quad \text{C} \quad \text{O} \\
\text{sp}^3 \quad \text{sp}^2 \quad \text{sp}
\]

11.20  

a) False, a double bond is one sigma (\(\sigma\)) and one pi (\(\pi\)) bond. 
b) False, a triple bond consists of one sigma (\(\sigma\)) and two pi (\(\pi\)) bonds. 
c) True 
d) True 
e) False, a pi bond consists of one pair of electrons; it occurs after a \(\sigma\) bond has been previously formed. 
f) False, end-to-end overlap results in a bond with electron density along the bond axis.

11.21  
a) Nitrogen is the central atom in NO\(_3^–\). Nitrogen has 3 surrounding electron groups (two single bonds and one double bond), so it is \(sp^2\) hybridized. Nitrogen forms three \(\sigma\) bonds (one each for the N–O bonds) and one \(\pi\) bond (part of the N=O double bond).

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\end{array}
\]

b) Carbon is the central atom in CS\(_2\). Carbon has 2 surrounding electron groups (two double bonds), so it is \(sp\) hybridized. Carbon forms two \(\sigma\) bonds (one each for the C–S bonds) and two \(\pi\) bonds (part of the two C=S double bonds).

\[
\begin{array}{c}
\text{S} \\
\text{C} \\
\text{S} \\
\end{array}
\]

c) Carbon is the central atom in CH\(_2\)O. Carbon has 3 surrounding electron groups (two single bonds and one double bond), so it is \(sp^2\) hybridized. Carbon forms three \(\sigma\) bonds (one each for the two C–H bonds and one C–O bond) and one \(\pi\) bond (part of the C=O double bond).

11.22  
a) \(sp^2\) 2 \(\sigma\) and 1 \(\pi\) bonds

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}
\]

b) \(sp^3d\) 2 \(\sigma\) bonds

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]

c) \(sp^2\) 3 \(\sigma\) and 1 \(\pi\) bonds

\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{O} \\
\text{Cl} \\
\end{array}
\]
11.23 a) Examine the Lewis structure. Three electron groups (one lone pair, one single bond and one double bond) surround the central N atom. Hybridization is \(sp^2\) around nitrogen. One sigma bond exists between F and N, and one sigma and one pi bond exist between N and O. Nitrogen participates in a total of 2 \(\sigma\) and 1 \(\pi\) bonds.

\[ \text{FN} \quad \text{O} \]

b) Examine the Lewis structure. Each carbon has three electron groups (two single bonds and one double bond) with \(sp^2\) hybridization. The bonds between C and F are sigma bonds. The C–C bond consists of one sigma and one pi bond. Each carbon participates in a total of 3 \(\sigma\) and 1 \(\pi\) bonds.

\[ \text{c} \quad \text{c} \quad \text{N} \]

c) Examine the Lewis structure. Each carbon has two electron groups (1 single bond and one triple bond) and is \(sp\) hybridized with a sigma bond between the two carbons and a sigma and two pi bonds comprising each C–N triple bond. Each carbon participates in a total of 2 \(\sigma\) and 2 \(\pi\) bonds.

\[ \text{N} \quad \equiv \quad \text{C} \quad \equiv \quad \text{C} \quad \equiv \quad \text{N} \]

11.24 a) \(sp^3d\) 3 \(\sigma\) bonds

\[ \text{F} : \quad \text{F} : \quad \text{Br} : \quad \text{F} : \]

b) \(sp^3\) (CH₃) \(sp\) (both other C’s) 6 \(\sigma\) and 2 \(\pi\) bonds

\[ \text{H} \quad \text{C} \quad \text{C} \quad \equiv \quad \text{C} \quad \equiv \quad \text{H} \]

c) \(sp^2\) 2 \(\sigma\) and 2 \(\pi\) bonds

\[ \text{\textellipsis} \quad \text{\textellipsis} \quad \text{\textellipsis} \]

11.25 The double bond in 2-butene restricts rotation of the molecule, so that \textit{cis} and \textit{trans} structures result. The two structures are shown below:

\[ \text{cis} \quad \text{trans} \]

11-9
The carbons participating in the double bond each have three surrounding groups, so they are $sp^2$ hybridized. The $=C-H$ $\sigma$ bonds result from the head-on overlap of a C $sp^2$ orbital and a H $s$ orbital. The C-CH$_3$ bonds are also $\sigma$ bonds, resulting from the head-on overlap of an $sp^2$ orbital and an $sp^3$ orbital. The C=C bond contains 1 $\sigma$ bond (head on overlap of two $sp^2$ orbitals) and 1 $\pi$ bond (sideways overlap of unhybridized $p$ orbitals). Finally, C-H bonds in the methyl (-CH$_3$) groups are $\sigma$ bonds resulting from the overlap of C’s $sp^3$ orbital with H’s $s$ orbital.

11.26 Four molecular orbitals form from the four $p$ atomic orbitals. In forming molecular orbitals, the total number of molecular orbitals must equal the number of atomic orbitals. Two of the four molecular orbitals formed are bonding orbitals and two are antibonding.

11.27 Two $p_x$ atomic orbitals were used to form a sigma bonding MO (lower energy) and a sigma antibonding MO (higher energy). The bonding MO does not have a node separating the two halves of the orbital.

11.28 a) Bonding MO’s have lower energy than antibonding MO’s. The bonding MO’s lower energy, even lower than its constituent atomic orbitals, accounts for the stability of a molecule in relation to its individual atoms. However, the sum of energy of the MO’s must equal the sum of energy of the AO’s.

b) The node is the region of an orbital where the probability of finding the electron is zero, so the nodal plane is the plane that bisects the node perpendicular to the bond axis. There is no node along the bond axis (probability is positive between the two nuclei) for the bonding MO. The antibonding MO does have a nodal plane.

11.29 A bonding MO may contain a nodal plane lying along the internuclear axis, as in $\pi$ bonding. In an antibonding MO, the nodal plane is perpendicular to the bond axis, between the atoms.

11.30 a) **Two** electrons are required to fill a $\sigma$-bonding molecular orbital. Each molecular orbital requires two electrons.

b) **Two** electrons are required to fill a $\pi$-antibonding molecular orbital. There are two $\pi$-antibonding orbitals, each holding a maximum of two electrons.

c) **Four** electrons are required to fill the two $\sigma$ molecular orbitals (two electrons to fill the $\sigma$-bonding and two to fill the $\sigma$-antibonding) formed from two $1s$ atomic orbitals.

11.31 a) **twelve**  b) **two**  c) **four**

11.32 a) A is the $\pi_{2p}^*$ molecular orbital; B is the $\sigma_{2p}$ molecular orbital; C is the $\pi_{2p}$ molecular orbital; D is the $\sigma_{2p}^*$ molecular orbital.

b) The $\pi_{2p}^*$ molecular orbital, A, $\sigma_{2p}$ molecular orbital, B, and $\pi_{2p}$ molecular orbitals, C, are all occupied by at least one electron. The $\sigma_{2p}^*$ molecular orbital is unoccupied.

c) A $\pi_{2p}^*$ molecular orbital, A, has only one electron.
11.33  a) A is the $\pi^*_{2p}$ molecular orbital; B is the $\sigma_{2p}$ molecular orbital; C is the $\pi_{2p}$ molecular orbital; D is the $\sigma^*_{2p}$ molecular orbital; E is the $\sigma_{3s}$ molecular orbital; F is the $\sigma^*_{2s}$ molecular orbital.

b) The $\sigma^*_{2p}$ molecular orbital, D, is the highest in energy.

c) The $\sigma_{3s}$, molecular orbital, E, is the lowest in energy.

d) $\sigma_{2s} < \sigma^*_{2s} < \pi_{2p} < \sigma_{2p} < \pi^*_{2p} < \sigma^*_{2p}$

11.34  a) The molecular orbital configuration for $\text{Be}_2^+$ with a total of 7 electrons

The sequence of MO’s for C$_2$ is shown in Figure 11.21 (the ($\sigma_{1s}$)$^2$ and ($\sigma_{1s}$)$^2$ MO’s are not shown for convenience). For each species, determine the total number of electrons, the valence molecular electron configuration and bond order. Bond order = $\frac{1}{2}$ (number of electrons in bonding MO – number of electrons in antibonding MO)

b) No, the ion has one unpaired electron in the $\sigma^*_{2s}$ MO, so it is paramagnetic, not diamagnetic.

c) Valence electrons would be those in the molecular orbitals at the $n = 2$ level, so the valence electron configuration is ($\sigma_{2s}$)$^2$($\sigma^*_{2s}$)$^1$.

11.35  a) The molecular orbital configuration for $\text{O}_2^-$ with a total of 17 electrons

b) $\text{O}_2^-$ is paramagnetic with an unpaired electron in the $\pi^*_{2p}$ MO.

c) ($\sigma_{2s}$)$^2$($\sigma^*_{2s}$)$^1$($\pi_{2p}$)$^2$($\pi^*_{2p}$)$^1$

11.36  The sequence of MO’s for C$_2$ is shown in Figure 11.21 (the ($\sigma_{1s}$)$^2$ and ($\sigma_{1s}$)$^2$ MO’s are not shown for convenience). For each species, determine the total number of electrons, the valence molecular electron configuration and bond order. Bond order = $\frac{1}{2}$ (number of electrons in bonding MO – number of electrons in antibonding MO)

11.37  Bond Order

11.38  a) BrO$_3^-$  AX$_3$E  trigonal pyramidal  $sp^3$ hybrid AO  109.5°  $\leq$ 109.5°

b) AsCl$_4^-$  AX$_4$E  see–saw  $sp^3d$ hybrid AO  120°, 90°  $\leq$ 120°, <90°

c) SeO$_4^{2-}$  AX$_4$  tetrahedral  $sp^3$ hybrid AO  109.5°  none

d) BiF$_5^{2-}$  AX$_5$E  square pyramidal  $sp^3d^2$ hybrid AO  90°  $\leq$ 90°
e) SbF$_4^+$ AX$_4$ \textbf{tetrahedral} \\
$sp^3$ hybrid AO \\
109.5° none

f) AlF$_6^{3-}$ AX$_6$ \textbf{octahedral} \\
$sp^3d^2$ hybrid AO \\
90° none

g) IF$_4^+$ AX$_E$ \textbf{see-saw} \\
$sp^3d$ hybrid AO \\
120°, 90° <120°, <90°

Lewis structures:

11.39 a) There are 9 σ and 2 π bonds. Each of the six C–H bonds are sigma bonds. The C–C bond contains a sigma bond. The double bonds between the carbons consist of a pi bond in addition to the sigma bond.

b) No, cis/trans structural arrangements are not possible because one of the carbons in each double bond has two hydrogens bonded to it. Cis/trans structural arrangements only occur when both carbons in the double bond are bonded to two groups that are not identical.

11.40 a) Each of the six C atoms in the ring has three electron groups (two single bonds and a double bond) and has \textit{sp}³ hybridization; all of the other C atoms have four electron groups (four single bond) and have \textit{sp}³ hybridization; all of the O atoms have four electron groups (two single bonds and two lone pairs and have \textit{sp}³ hybridization; the N atom has four electron groups (three single bonds and a lone pair) and has \textit{sp}³ hybridization.
b) Each of the single bonds is a sigma bond; each of the double bonds has one sigma bond for a total of \textbf{26 sigma bonds.}

c) The ring has three double bonds each of which is composed of one sigma bond and one pi bond; so there are three pi bonds each with 2 electrons for a total of \textbf{6 pi electrons.}

11.41

a) 

\begin{array}{c}
\text{s} \\
\text{p} \\
\text{d} \\
\text{+ e}^- \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\text{sp}^3 d \\
\text{d}^4 \\
\end{array}

b) 

\begin{array}{c}
\text{s} \\
\text{p} \\
\text{d} \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\text{sp}^3 d \\
\text{d}^4 \\
\end{array}

c) 

\begin{array}{c}
\text{s} \\
\text{p} \\
\text{d} \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\text{sp}^3 d^2 \\
\text{d}^3 \\
\end{array}

d) 

\begin{array}{c}
\text{s} \\
\text{p} \\
\end{array}

\begin{array}{c}
\uparrow \\
\uparrow \\
\end{array}

\begin{array}{c}
\text{sp}^2 \\
\end{array}

\begin{array}{c}
\text{p} \\
\end{array}

11.42

a) Every single bond is a sigma bond. There is one sigma bond in each double bond as well. There are \textbf{17} \(\sigma\) bonds in isoniazid. Every atom-to-atom connection contains a \(\sigma\) bond.

b) All carbons have three surrounding electron groups (two single and one double bond), so their hybridization is \textbf{sp}^2. The ring N also has three surrounding electron groups (one single bond, one double bond and one lone pair), so its hybridization is also \textbf{sp}^2. The other two N’s have four surrounding electron groups (three single bonds and one lone pair) and are \textbf{sp}^3 hybridized.
11.43 a) Hydrazine
\[ \text{H} \overline{\text{N}} \text{H} \]
\[ \text{H} \overline{\text{N}} \text{H} \]
Carbon disulfide
\[ \text{N} \overline{\text{S}} \text{N} \]
\[ \text{S} \overline{\text{S}} \]
b) The electron-group arrangement around each nitrogen changes from tetrahedral to trigonal planar. The molecular shape changes from trigonal pyramidal to bent and the hybridization changes from sp\(^3\) to sp\(^2\).
c) The electron-group arrangement and molecular shape around carbon change from linear to trigonal planar. The hybridization changes from sp to sp\(^2\).

11.44 a) B changes from sp\(^2\) → sp\(^3\). Boron in BF\(_3\) has three electron groups with sp\(^2\) hybridization. In BF\(_4^–\), 4 electron groups surround B with sp\(^3\) hybridization.

\[ \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{B} \\
\text{F}
\end{array} \rightarrow \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{B} \\
\text{F}
\end{array} \]

b) P changes from sp\(^3\) → sp\(^3\)\(^d\). Phosphorus in PCl\(_3\) is surrounded by 4 electron groups (3 bonds to Cl and 1 lone pair) for sp\(^3\) hybridization. In PCl\(_5\), phosphorus is surrounded by 5 electron groups for sp\(^3\)\(^d\) hybridization.

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{P} \\
\text{Cl}
\end{array} \rightarrow \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{P} \\
\text{Cl}
\end{array} \]

c) C changes from sp → sp\(^2\). Two electron groups surround C in C\(_2\)H\(_2\) and 3 electron groups surround C in C\(_2\)H\(_4\).

\[ \begin{array}{c}
\text{H} \\
\text{C} \equiv \text{C} \\
\text{H}
\end{array} \rightarrow \begin{array}{c}
\text{H} \\
\text{C} \equiv \text{C} \\
\text{H}
\end{array} \]

d) Si changes from sp\(^3\) → sp\(^3\)\(^d\). Four electron groups surround Si in SiF\(_4\) and 6 electron groups surround Si in SiF\(_6\)^{2–}.

\[ \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{Si} \\
\text{F}
\end{array} \rightarrow \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{Si} \\
\text{F}
\end{array} \]

e) No change, S in SO\(_2\) is surrounded by three electron groups (one single bond, one double bond and one lone pair) and in SO\(_3\) is surrounded by 3 electron groups (two single bonds and one double bond); both have sp\(^3\) hybridization.

\[ \begin{array}{c}
\text{O} \\
\text{S} \equiv \text{O}
\end{array} \rightarrow \begin{array}{c}
\text{O} \\
\text{S} \equiv \text{O}
\end{array} \]
11.45 a) Original molecules:

- NO: \((\sigma^2_2s^2)(\sigma^*2s^2)(\sigma^2_2p^2)(\pi^2_2p^2)(\pi^*2p^1)\)
  bond order = 2.5 paramagnetic

- O\(_2\): \((\sigma^2_2s^2)(\sigma^*2s^2)(\sigma^2_2p^2)(\pi^2_2p^2)(\pi^*2p^1)(\pi^2_2p^1)\)
  bond order = 2.0 paramagnetic

- N\(_2\): \((\sigma^2_2s^2)(\sigma^*2s^2)(\pi^2_2p^2)(\pi^2_2p^2)(\sigma^2_2p^1)\)
  bond order = 3.0 diamagnetic

Ions:

- NO\(^+\): \((\sigma^2_2s^2)(\sigma^*2s^2)(\pi^2_2p^2)(\pi^*2p^1)\)
  bond order = 3.0 diamagnetic

- O\(_2^+\): \((\sigma^2_2s^2)(\sigma^*2s^2)(\pi^2_2p^2)(\pi^*2p^1)(\pi^2_2p^1)\)
  bond order = 2.5 paramagnetic

- N\(_2^+\): \((\sigma^2_2s^2)(\pi^2_2p^2)(\pi^2_2p^2)(\sigma^2_2p^1)\)
  bond order = 2.5 paramagnetic

b) Changing: NO\(^+\), N\(_2^+\)

11.46 Count the electron groups, both bonds and lone pairs, about each atom. (Do not forget to count double bonds only once.)

- P (3 single bonds and one double bond) AX\(_4\) \text{tetrahedral} \text{ sp}^3
- N (3 single bonds and one lone pair) AX\(_3E\) \text{trigonal pyramid} \text{ sp}^3
- C\(_1\) and C\(_2\) (4 single bonds) AX\(_4\) \text{tetrahedral} \text{ sp}^3
- C\(_3\) (2 single bonds and one double bond) AX\(_3\) \text{trigonal planar} \text{ sp}^2

11.47 a) The representation with two S=O double bonds:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{S} \\
\text{O} \\
\text{O}
\end{array}
\]

FC\(_S\) = 6 \(– (0 + 1/2(12))\) = 0
FC\(_O\) (single bond) = 6 \(– (6 + 1/2(2))\) = −1

FC\(_O\) (double bond) = 6 \(– (4 + 1/2(4))\) = 0

The representation with four S–O single bonds:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{S} \\
\text{O} \\
\text{O}
\end{array}
\]

FC\(_S\) = 6 \(– (0 + 1/2(8))\) = +2
FC\(_O\) = 6 \(– (6 + 1/2(2))\) = −1

The representation with two S=O double bonds is better since it minimizes formal charges. For sulfur, the formal charge in the single bond representation is +2 while in the double bond representation it decreases to zero. The formal charge for the oxygen atoms double bonded to the sulfur increases from −1 in the representation with four single bonds to 0 in the representation with two double bonds. The oxygens that are single bonded in both cases have the same formal charge in both representations, −1.

b) In both representations the sulfate ion is \text{tetrahedral} because 4 electron groups surround S in both cases. The double bonded representation would show some deviation from the ideal angle of 109.5° due to the double bonds. The single bond hybridization is \text{sp}^3.
c) Since sulfur’s valence $p$-orbitals are used in the sigma bonds, the $\pi$ bonds are formed from the valence $3d$ orbitals in sulfur overlapping with $2p$ orbitals in oxygen.

\[ \begin{array}{c}
\text{3s} & \text{3p} & \text{3d} \\
\uparrow & \uparrow & \uparrow \\
\end{array} \]

\[ \begin{array}{c}
\text{sp}^3 & \text{3d} \\
\uparrow & \uparrow & \uparrow & \uparrow \\
\end{array} \]

\[ \begin{array}{c}
\text{sulfur} & \text{oxygen} \\
\text{4d}_{yz} & \text{2p}_y \\
\end{array} \]

\[ \begin{array}{c}
\text{used for } \sigma \text{ bonds} & \text{used for } \pi \text{ bonds} \\
\end{array} \]

d)

\[ \begin{array}{c}
\text{p} \\
\end{array} \]

11.48

a) 1: $sp^3$  2: $sp^2$  3: $sp^3$  4: $sp^3$  5: $sp^2$  6: $sp^2$

b) 28

c) a: $< 109.5^\circ$  b: $120^\circ$  c: $120^\circ$

11.49

Draw the Lewis structures.

\[ \begin{array}{c}
\text{SO}_2 & \text{SO}_3 & \left[ \begin{array}{c}
\text{O} \\
\text{O} \\
\text{S} \\
\end{array} \right]^{2-} \\
\text{sp}^3 & \text{sp}^3 & \text{SO}_3^- \text{ sp}^3 \\
\text{SCl}_4 & \text{SCl}_6 & \text{S}_2\text{Cl}_2 \text{ sp}^3 \\
\text{sp}^3 \text{ d} & \text{sp}^3 \text{ d} & \text{sp}^3 \\
\end{array} \]

11.50

The central C is $sp$ hybridized, and the other two C’s are $sp^2$. 

11-16
11.51 \( O_2 \quad (\sigma_{2s})^2(\pi_{2p})^2(\pi_{2p})^2(\pi^*_{2p})^2 \) bond order = 2.0 paramagnetic

\( O_2^+ \quad (\sigma_{2s})^2(\pi_{2p})^2(\pi_{2p})^2(\pi^*_{2p})^2 \) bond order = 2.5 paramagnetic

\( O_2^+ \quad (\sigma_{2s})^2(\pi_{2p})^2(\pi_{2p})^2(\pi^*_{2p})^2 \) bond order = 1.5 paramagnetic

\( O_2^{2-} \quad (\sigma_{2s})^2(\pi_{2p})^2(\pi_{2p})^2(\pi^*_{2p})^2(\pi^*_{2p})^2 \) bond order = 1.0 diamagnetic

Bond Length: \( O_2^+ < O_2 < O_2^+ < O_2^{2-} \)

11.52 a) All the diagrams are identical: \( (\sigma_{2s})^2(\pi_{2p})^2(\pi_{2p})^2(\pi^*_{2p})^2 \)
b) Nitrogen molecules are not polar, but CN\(^-\) and CO are polar.

11.53 a) Yes, each one is \( sp^2 \) hybridized.
b) Yes, each one is \( sp^3 \) hybridized.
c) C–O bonds: 6 \( \sigma \) bonds, 1 \( \pi \) bond.
d) No, the C=O lone pair electrons are in \( sp^2 \) hybrid orbitals, while the other oxygen lone pairs occupy \( sp^3 \) hybrid orbitals.

11.54 a) B and D show hybrid orbitals that are present in the molecule. B shows \( sp^3 \) hybrid orbitals, used by atoms that have four groups of electrons. In the molecule, the C atom in the CH\(_3\) group, the S atom and the O atom all have four groups of electrons and would have \( sp^3 \) hybrid orbitals. D shows \( sp^2 \) hybrid orbitals, used by atoms that have three groups of electrons. In the molecule, the C bonded to the nitrogen atom, the C atoms involved in the C=C bond, and the nitrogen atom all have three groups of electrons and would have \( sp^2 \) hybrid orbitals.
b) The C atoms in the C≡C bond have only two electron groups and would have \( sp \) hybrid orbitals. These orbitals are not shown in the picture.
c) There are two sets of \( sp \) hybrid orbitals, four sets of \( sp^2 \) hybrid orbitals and three sets of \( sp^3 \) hybrid orbitals in the molecule.

11.55 a) 

b) SiF\(_4\) \( sp^3 \) 
GeF\(_6\) \( sp^3d^2 \) 
CF\(_4\) \( sp^3 \)
c) Carbon has no d-orbitals available to form \( sp^3d^2 \) hybrids.

11.56 The resonance gives the C-N bond some double bond character, which hinders rotation about the C-N bond. The C-N single bond is a \( \sigma \) bond; the resonance interaction exchanges a C-O \( \pi \) bond for a C-N \( \pi \) bond.

11.57 a) N has \( sp^2 \) hybridization, formed from one 2s and two 2p orbitals.
b) The lone pair is in a \( sp^2 \) hybrid orbital.
c) Hybridization of C in CH\(_3\) is \( sp^3 \); C in the ring is \( sp^2 \).
11.58  

a) The 6 carbons in the ring each have three surrounding electron groups (two single bonds and one double bond) with \(sp^2\) hybrid orbitals. The two carbons participating in the C=O bond are also \(sp^2\) hybridized. The single carbon in the –CH\(_3\) group has 4 electron groups (four single bonds) and is \(sp^3\) hybridized. There are only 2 central oxygen atoms, one in a C–O–H configuration and the other in a C–O–C configuration. Both of these atoms have 4 surrounding electron groups (two single bonds and two lone pairs) and are \(sp^3\) hybridized. 

Summary: C in –CH\(_3\): \(sp^3\), all other C atoms (8 total): \(sp^2\), O (2 total): \(sp^3\) 

b) The two C=O bonds are localized; the double bonds on the ring are delocalized as in benzene. 

c) Each carbon with three surrounding groups has \(sp^2\) hybridization and trigonal planar shape; therefore, 8 carbons have this shape. Only 1 carbon in the CH\(_3\) group has four surrounding groups with \(sp^3\) hybridization and tetrahedral shape.

11.59  

a) **Four** different isomeric fatty acids: trans-cis, cis-cis, cis-trans, trans-trans. 

b) With three double bonds, there are \(2^3 = 2^3 = 8\) isomers possible. 

- cis-cis-cis: trans-trans-trans 
- cis-trans-cis: trans-cis-trans 
- cis-cis-trans: trans-cis-cis 
- cis-trans-trans: trans-trans-cis