## CHAPTER 11 THEORIES OF COVALENT BONDING

## END-OF-CHAPTER PROBLEMS

11.1 Plan: Table 11.1 describes the types of hybrid orbitals that correspond to the various electrongroup arrangements. The number of hybrid orbitals formed by a central atom is equal to the number of electron groups arranged around that central atom.
Solution:
a) trigonal planar: three electron groups - three hybrid orbitals: $\boldsymbol{s p}{ }^{2}$
b) octahedral: six electron groups - six hybrid orbitals: $\boldsymbol{s p ^ { 3 }} \boldsymbol{d}^{2}$
c) linear: two electron groups - two hybrid orbitals: $\boldsymbol{s p}$
d) tetrahedral: four electron groups - four hybrid orbitals: $\boldsymbol{s \boldsymbol { p } ^ { 3 }}$
e) trigonal bipyramidal: five electron groups - five hybrid orbitals: $\boldsymbol{s p}^{\mathbf{3}} \boldsymbol{d}$
a) $\boldsymbol{s} \boldsymbol{p}^{2}$
b) $\boldsymbol{s p}{ }^{3}$
c) $\boldsymbol{s} \boldsymbol{p}^{3} \boldsymbol{d}$
d) $\boldsymbol{s} \boldsymbol{p}^{3} \boldsymbol{d}^{2}$
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 $3 d$ orbitals in addition to $3 s$ and $3 p$ orbitals available for bonding in its outer level, to form up to six hybrid orbitals, whereas carbon has only $2 s$ and $2 p$ orbitals available in its outer level to form up to four hybrid orbitals.
11.4 Four. The same number of hybrid orbitals will form as the initial number of atomic orbitals mixed.
11.5 Plan: The number of hybrid orbitals is the same as the number of atomic orbitals before hybridization. The type depends on the orbitals mixed. The name of the type of hybrid orbital comes from the number and type of atomic orbitals mixed. The number of each type of atomic orbital appears as a superscript in the name of the hybrid orbital.
Solution:
a) There are six unhybridized orbitals, and therefore six hybrid orbitals result. The type is $\boldsymbol{s} \boldsymbol{p}^{3} \boldsymbol{d}^{2}$ since one $s$, three $p$, and two $d$ atomic orbitals were mixed.
b) Four $\boldsymbol{s p}^{3}$ hybrid orbitals form from three $p$ and one $s$ atomic orbitals.
a) two $s p$ orbitals
b) five $\boldsymbol{s p}^{\mathbf{3}} \boldsymbol{d}$ orbitals
11.7 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central nitrogen atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.
Solution:
a) The three electron groups (one double bond, one lone pair, and one unpaired electron) around nitrogen require three hybrid orbitals. The hybridization is $\boldsymbol{s \boldsymbol { p } ^ { 2 }}$.

b) The nitrogen has three electron groups (one single bond, one double bond, and one unpaired electron), requiring three hybrid orbitals so the hybridization is $\boldsymbol{s \boldsymbol { p } ^ { 2 }}$.

c) The nitrogen has three electron groups (one single bond, one double bond, and one lone pair) so the hybridization is $\boldsymbol{s} \boldsymbol{p}^{2}$.

11.8
a) $\boldsymbol{s} \boldsymbol{p}^{2}$

b) $s p^{2}$

c) $\boldsymbol{s p}$

11.9 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central chlorine atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.
Solution:
a) The Cl has four electron groups (one lone pair, one lone electron, and two double bonds) and therefore four hybrid orbitals are required; the hybridization is $\boldsymbol{s} \boldsymbol{p}^{3}$. Note that in $\mathrm{ClO}_{2}$, the $\pi$ bond is formed by the overlap of $d$ orbitals from chlorine with $p$ orbitals from oxygen.

b) The Cl has four electron groups (one lone pair and three bonds) and therefore four hybrid orbitals are required; the hybridization is $\boldsymbol{s \boldsymbol { p } ^ { 3 }}$.

c) The Cl has four electron groups (four bonds) and therefore four hybrid orbitals are required; the hybridization is $\boldsymbol{s p}{ }^{3}$.

a) $\boldsymbol{s} \boldsymbol{p}^{3} \boldsymbol{d}$

b) $s p^{3}$

c) $\boldsymbol{s p} \boldsymbol{p}^{3}{ }^{2}$

11.11 Plan: Draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Once the type of hybridization is known, the types of atomic orbitals that will mix to form those hybrid orbitals are also known.
Solution:
a) Silicon has four electron groups (four bonds) requiring four hybrid orbitals; four $s p^{3}$ hybrid orbitals are made from one $\boldsymbol{s}$ and three $\boldsymbol{p}$ atomic orbitals.

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

c) Sulfur is surrounded by five electron groups (four bonding pairs and one lone pair), requiring five hybrid orbitals; five $s p^{3} d$ hybrid orbitals are formed from one $\boldsymbol{s}$ orbital, three $\boldsymbol{p}$ orbitals, and one $d$ orbital.

d) Nitrogen is surrounded by four electron groups (three bonding pairs and one lone pair) requiring four hybrid orbitals; four $s p^{3}$ hybrid orbitals are formed from one $\boldsymbol{s}$ orbital and three $\boldsymbol{p}$ orbitals.

a) $s p^{3} \leftarrow \boldsymbol{s}+\mathbf{3} \boldsymbol{p}$

b) $s p^{3} d \leftarrow \boldsymbol{s}+3 \boldsymbol{p}+\boldsymbol{d}$

c) $s p^{3} d \leftarrow \boldsymbol{s}+3 \boldsymbol{p}+\boldsymbol{d}$

d) $s p^{3} \leftarrow \boldsymbol{s}+3 \boldsymbol{p}$

11.13 Plan: To determine hybridization, draw the Lewis structure of the reactants and products and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Recall that $s p$ hydrid orbitals are oriented in a linear geometry, $s p^{2}$ in a trigonal planar geometry, $s p^{3}$ in a tetrahedral geometry, $s p^{3} d$ in a trigonal bipyramidal geometry, and $s p^{3} d^{2}$ in an octahedral geometry.

## Solution:

a) The P in $\mathrm{PH}_{3}$ has four electron groups (one lone pair and three bonds) and therefore four hybrid orbitals are required; the hybridization is $s p^{3}$. The P in the product also has four electron groups (four bonds) and again four hybrid orbitals are required. The hybridization of P remains $s p^{3}$. There is no change in hybridization. Illustration $\mathbf{B}$ best shows the hybridization of $\mathbf{P}$ during the reaction as $\boldsymbol{s} \boldsymbol{p}^{\mathbf{3}} \rightarrow \boldsymbol{s} \boldsymbol{p}^{\mathbf{3}}$.
b) The B in $\mathrm{BH}_{3}$ has three electron groups (three bonds) and therefore three hybrid orbitals are required; the hybridization is $s p^{2}$. The B in the product has four electron groups (four bonds) and four hybrid orbitals are required. The hybridization of B is now $s p^{3}$. The hybridization of B changes from $\boldsymbol{s p}^{2}$ to $\boldsymbol{s \boldsymbol { p } ^ { 3 }}$; this is best shown by illustration $\mathbf{A}$.

11.14 a) The Te in $\mathrm{TeF}_{6}$ has six electron groups (six bonds) and therefore six hybrid orbitals are required; the hybridization is $s p^{3} d^{2}$. Te in $\mathrm{TeF}_{5}{ }^{-}$also has six electron groups (five bonds and one unshared pair) and again six hybrid orbitals are required. The hybridization of Te remains $s p^{3} d^{2}$. There is no change in hybridization. Illustration $\mathbf{A}$ best shows the hybridization of Te when $\mathrm{TeF}_{6}$ forms $\mathrm{TeF}_{5}{ }^{-}: \boldsymbol{s p}^{3} \boldsymbol{d}^{2} \rightarrow \boldsymbol{s} \boldsymbol{p}^{3} \boldsymbol{d}^{2}$.

b) The Te in $\mathrm{TeF}_{4}$ has five electron groups (four bonds and one unshared pair) and therefore five hybrid orbitals are required; the hybridization is $s p^{3} d$. Te in $\mathrm{TeF}_{6}$ has six electron groups (six bonds) and therefore six hybrid orbitals are required; the hybridization is $s p^{3} d^{2}$. Illustration $\mathbf{C}$ best shows the change in hybridization of Te from $\boldsymbol{s p} \boldsymbol{p}^{\mathbf{d}} \boldsymbol{d}$ to $\boldsymbol{p}^{\mathbf{3}} \boldsymbol{d}^{2}$.


11.15 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Write the electron configuration of the central atom and mix the appropriate atomic orbitals to form the hybrid orbitals.
Solution:
a) Germanium is the central atom in $\mathrm{GeCl}_{4}$. Its electron configuration is $[\mathrm{Ar}] 4 s^{2} 3 d^{10} 4 p^{2}$. Ge has four electron groups (four bonds), requiring four hybrid orbitals. Hybridization is $s p^{3}$ around Ge . One of the $4 s$ electrons is moved to a $4 p$ orbital and the four orbitals are hybridized.


b) Boron is the central atom in $\mathrm{BCl}_{3}$. Its electron configuration is $[\mathrm{He}] 2 s^{2} 2 p^{1}$. B has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is $s p^{2}$ around B . One of the $2 s$ electrons is moved to an empty $2 p$ orbital and the three atomic orbitals are hybridized. One of the $2 p$ atomic orbitals is not involved in the hybridization.



Isolated B atom


Hybridized B atom
c) Carbon is the central atom in $\mathrm{CH}_{3}{ }^{+}$. Its electron configuration is $[\mathrm{He}] 2 s^{2} 2 p^{2}$. C has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is $s p^{2}$ around C. One of the $2 s$ electrons is moved to an empty $2 p$ orbital; three orbitals are hybridized and one electron is removed to form the +1 ion.

11.16 a)

b)

c)

11.17 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Write the electron configuration of the central atom and mix the appropriate atomic orbitals to form the hybrid orbitals.
Solution:
a) In $\mathrm{SeCl}_{2}$, Se is the central atom and has four electron groups (two single bonds and two lone pairs), requiring four hybrid orbitals so Se is $s p^{3}$ hybridized. The electron configuration of Se is [Ar] $4 s^{2} 3 d^{10} 4 p^{4}$. The $4 s$ and $4 p$ atomic orbitals are hybridized. Two $s p^{3}$ hybrid orbitals are filled with lone electron pairs and two $s p^{3}$ orbitals bond with the chlorine atoms.

b) In $\mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{O}$ is the central atom and has four electron groups (three single bonds and one lone pair), requiring four hybrid orbitals. O is $s p^{3}$ hybridized. The electron configuration of O is $[\mathrm{He}] 2 s^{2} 2 p^{4}$. The $2 s$ and $2 p$ orbitals are hybridized. One $s p^{3}$ hybrid orbital is filled with a lone electron pair and three $s p^{3}$ orbitals bond with the hydrogen atoms.

c) I is the central atom in $\mathrm{IF}_{4}{ }^{-}$with six electron groups (four single bonds and two lone pairs) surrounding it. Six hybrid orbitals are required and I has $s p^{3} d^{2}$ hybrid orbitals. The $s p^{3} d^{2}$ hybrid orbitals are composed of one $s$ orbital, three $p$ orbitals, and two $d$ orbitals. Two $s p^{3} d^{2}$ orbitals are filled with a lone pair and four $s p^{3} d^{2}$ orbitals bond with the fluorine atoms.


11.18 a)

b)

c)

11.19

11.20 Plan: A single bond is a sigma bond which is the result of two orbitals overlapping end to end; a double bond consists of one sigma bond and one pi bond; and a triple bond consists of one sigma bond and two pi bonds. A pi bond is the result of orbitals overlapping side to side.
Solution:
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 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a sigma bond which is the result of two orbitals overlapping end to end; a double bond consists of one sigma bond and one pi bond; and a triple bond consists of one sigma bond and two pi bonds.
Solution:
a) Nitrogen is the central atom in $\mathrm{NO}_{3}{ }^{-}$. Nitrogen has three surrounding electron groups (two single bonds and one double bond), so it is $\boldsymbol{s} \boldsymbol{p}^{2}$ hybridized. Nitrogen forms three $\sigma$ bonds (one each for the $\mathrm{N}-\mathrm{O}$ bonds) and one $\pi$ bond (part of the $\mathrm{N}=\mathrm{O}$ double bond).

b) Carbon is the central atom in $\mathrm{CS}_{2}$. Carbon has two surrounding electron groups (two double bonds), so it is $\boldsymbol{s p}$ hybridized. Carbon forms two $\boldsymbol{\sigma}$ bonds (one each for the C-S bonds) and two $\boldsymbol{\pi}$ bonds (part of the two $\mathrm{C}=\mathrm{S}$ double bonds).

c) Carbon is the central atom in $\mathrm{CH}_{2} \mathrm{O}$. Carbon has three surrounding electron groups (two single bonds and one double bond), so it is $\boldsymbol{s} \boldsymbol{p}^{2}$ hybridized. Carbon forms three $\sigma$ bonds (one each for the two $\mathrm{C}-\mathrm{H}$ bonds and one $\mathrm{C}-\mathrm{O}$ bond) and one $\pi$ bond (part of the $\mathrm{C}=\mathrm{O}$ double bond).

11.22
a) $s p^{2} \quad 2 \sigma$ bonds and $1 \pi$ bond

b) $s^{3} d \quad 2 \sigma$ bonds

c) $s p^{2} \quad 3 \sigma$ bond and $1 \pi$ bond

11.23 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central nitrogen atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a sigma bond which is the result of two orbitals overlapping end to end; a double bond consists of one sigma bond and one pi bond; and a triple bond consists of one sigma bond and two pi bonds.

## Solution:

a) In FNO, three electron groups (one lone pair, one single bond, and one double bond) surround the central $N$ atom. Hybridization is $\boldsymbol{s} \boldsymbol{p}^{2}$ 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.

b) In $\mathrm{C}_{2} \mathrm{~F}_{4}$, each carbon has three electron groups (two single bonds and one double bond) with $\boldsymbol{s} \boldsymbol{p}^{2}$ hybridization. The bonds between C and F are sigma bonds. The $\mathrm{C}-\mathrm{C}$ bond consists of one sigma and one pi bond. Each carbon participates in a total of three $\boldsymbol{\sigma}$ bonds and one $\boldsymbol{\pi}$ bond.

c) In $(\mathrm{CN})_{2}$, each carbon has two electron groups (one single bond and one triple bond) and is $\boldsymbol{s} \boldsymbol{p}$ hybridized with a sigma bond between the two carbons and a sigma and two pi bonds comprising each $\mathrm{C}-\mathrm{N}$ triple bond. Each carbon participates in a total of two $\sigma$ and two $\pi$ bonds.
$: \mathrm{N} \equiv \mathrm{C}-\mathrm{C} \equiv \mathrm{N}$ :
11.24 a) $\boldsymbol{s} \boldsymbol{p}^{3} \boldsymbol{d} \quad$ three $\boldsymbol{\sigma}$ bonds

b) $\boldsymbol{s} \boldsymbol{p}^{3}\left(\mathrm{CH}_{3}\right) \boldsymbol{s} \boldsymbol{p}$ (other two C atoms) $\boldsymbol{s i x} \boldsymbol{\sigma}$ and two $\pi$ bonds

c) $\boldsymbol{s p}^{2} \quad$ two $\sigma$ and two $\pi$ bonds

11.25 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.
11.26 Two $p_{\mathrm{x}}$ 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.
11.27 a) Bonding MOs have lower energy than antibonding MOs. 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 MOs must equal the sum of energy of the AOs.
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.
c) The bonding MO has higher electron density between nuclei than the antibonding MO.
11.28 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.
11.29 Plan: Like atomic orbitals, any one MO holds a maximum of two electrons. Two atomic orbitals combine to form two molecular orbitals, a bonding and an antibonding MO.

## Solution:

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 $1 s$ atomic orbitals.
11.30 a) twelve $\begin{array}{lll}\text { b) two } & \text { c) four }\end{array}$
11.31 Plan: Recall that a bonding MO has a region of high electron density between the nuclei while an antibonding MO has a node, or region of zero electron density between the nuclei. MOs formed from $s$ orbitals, or from $p$ orbitals overlapping end to end, are called $\sigma$ and MOs formed by the side-to-side overlap of $p$ orbitals are called $\pi$. A superscript star $\left(^{*}\right)$ is used to designate an antibonding MO. To write the electron configuration of $\mathrm{F}_{2}{ }^{+}$, determine the number of valence electrons and write the sequence of MO energy levels, following the sequence order given in the text.
Solution:
a) A is the $\pi^{*}{ }_{2 p}$ molecular orbital (two $p$ orbitals overlapping side to side with a node between them); B is the $\sigma_{2 p}$ molecular orbital (two $p$ orbitals overlapping end to end with no node); C is the $\pi_{2 p}$ molecular orbital (two $p$ orbitals overlapping side to side with no node); D is the $\boldsymbol{\sigma}^{*}{ }_{2 p}$ molecular orbital (two $p$ orbitals overlapping end to end with a node).
b) $\mathrm{F}_{2}^{+}$has thirteen valence electrons: [2 $\times \mathrm{F}\left(7 \mathrm{e}^{-}\right)-1$ (from + charge)]. The MO electron configuration is $\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\sigma_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{1}$. The $\pi^{*}{ }_{2 p}$ molecular orbital, A, $\sigma_{2 p}$ molecular orbital, B, and $\pi_{2 p}$ molecular orbital, C , are all occupied by at least one electron. The $\sigma^{*}{ }_{2 p}$ molecular orbital is unoccupied.
c) A $\pi^{*}{ }_{2 p}$ molecular orbital, A, has only one electron.
11.32 a) A is the $\pi^{*}{ }_{2 p}$ molecular orbital; B is the $\sigma_{2 p}$ molecular orbital; C is the $\pi_{2 p}$ molecular orbital; D is the $\sigma^{*}{ }_{2 p}$ molecular orbital; E is the $\sigma_{2 s}$ molecular orbital; F is the $\sigma^{*}{ }_{2 s}$ molecular orbital.
b) The $\sigma^{*}{ }_{2 p}$ molecular orbital, D , is the highest in energy.
c) The $\sigma_{2 s}$ molecular orbital, E, is the lowest in energy.
d) $\sigma_{2 s}<\sigma^{*}{ }_{2 s}<\pi_{2 p}<\sigma_{2 p}<\pi^{*}{ }_{2 p}<\sigma^{*}{ }_{2 p}(\mathrm{E}<\mathrm{F}<\mathrm{C}<\mathrm{B}<\mathrm{A}<\mathrm{D})$
11.33 The horizontal line in all cases represents the bond axis.
a) Bonding $s+p$


Antibonding $s-p$

b) Bonding $p+p$


Antibonding $p-p$

11.34 a)
$s+s=$


Bonding
$s-s=$


Antibonding
$p-p=$


Antibonding
11.35 Plan: To write the electron configuration of $\mathrm{Be}_{2}{ }^{+}$, determine the number of electrons and write the sequence of MO energy levels, following the sequence order given in the text.
Bond order $=1 / 2[($ no. of electrons in bonding MO) - (no. of electrons in antibonding MO)]. Recall that a diamagnetic substance has no unpaired electrons.
Solution:
a) $\mathrm{Be}_{2}{ }^{+}$has a total of seven electrons [2 $\mathrm{x} \mathrm{Be}\left(4 \mathrm{e}^{-}\right)-1$ (from + charge)]. The molecular orbital configuration is $\left(\sigma_{1 s}\right)^{2}\left(\sigma_{1 s}^{*}\right)^{2}\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{1}$ and bond order $=1 / 2(4-3)=1 / 2$. With a bond order of $1 / 2$ the $\mathrm{Be}_{2}{ }^{+}$ion will be stable.
b) No, the ion has one unpaired electron in the $\sigma^{*}{ }_{2 s} \mathrm{MO}$, 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 $\left(\sigma_{2 s}\right)^{\mathbf{2}}\left(\sigma^{*}{ }_{2 s}\right)^{\mathbf{1}}$.
11.36 a) The molecular orbital configuration for $\mathrm{O}_{2}^{-}$with a total of seventeen electrons
is $\left(\sigma_{1 s}\right)^{2}\left(\sigma^{*}{ }_{1 s}\right)^{2}\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\sigma_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{1}$.
Bond order $=1 / 2\left(10\right.$ bonding -7 antibonding $\left.\mathrm{e}^{-}\right)=3 / 2=1.5 . \mathbf{O}_{2}^{-}$is stable.
b) $\mathrm{O}_{2}{ }^{-}$is paramagnetic with an unpaired electron in the $\pi^{*}{ }_{2 p} \mathrm{MO}$.
c) $\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\sigma_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{1}$
11.37 Plan: Write the electron configuration of each species by determining the number of electrons and writing the sequence of MO energy levels, following the sequence order given in the text.
Calculate the bond order: bond order $=1 / 2[($ no. of electrons in bonding MO) $-($ no. of electrons in antibonding MO)]. Bond energy increases as bond order increases; bond length decreases as bond order increases.
Solution:
$\mathrm{C}_{2}{ }^{-} \quad$ Total electrons $=6+6+1=13$
MO configuration: $\left(\sigma_{1 s}\right)^{2}\left(\sigma^{*}{ }_{1 s}\right)^{2}\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\pi_{2 p}\right)^{4}\left(\sigma_{2 p}\right)^{1}$
Bond order $=1 / 2(9-4)=2.5$
$\mathrm{C}_{2}$ Total electrons $=6+6=12$
MO configuration: $\left(\sigma_{1 s}\right)^{2}\left(\sigma^{*}{ }_{1 s}\right)^{2}\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\pi_{2 p}\right)^{4}$
Bond order $=1 / 2(8-4)=2$
$\mathrm{C}_{2}{ }^{+} \quad$ Total electrons $=6+6-1=11$
MO configuration: $\left(\sigma_{1 s}\right)^{2}\left(\sigma_{1 s}^{*}\right)^{2}\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\pi_{2 p}\right)^{3}$
Bond order $=1 / 2(7-4)=1.5$
a) Bond energy increases as bond order increases: $\mathbf{C}_{2}{ }^{+}<\mathbf{C}_{2}<\mathbf{C}_{2}{ }^{-}$
b) Bond length decreases as bond energy increases, so the order of increasing bond length will be opposite that of increasing bond energy. Increasing bond length: $\mathbf{C}_{2}{ }^{-}<\mathbf{C}_{2}<\mathbf{C}_{2}{ }^{+}$
$\mathrm{B}_{2}{ }^{+}: \quad\left(\sigma_{2 \mathrm{~s}}\right)^{2}\left(\sigma^{*}{ }_{2 \mathrm{~s}}\right)^{2}\left(\pi_{2 p}\right)^{1} \quad 0.5$
$\mathrm{B}_{2}: \quad\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\pi_{2 p}\right)^{1}\left(\pi_{2 p}\right)^{1} \quad 1.0$
$\mathrm{B}_{2}{ }^{-}: \quad\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{1}$
a) $\mathbf{B}_{2}{ }^{-}>\mathbf{B}_{2}>\mathbf{B}_{2}{ }^{+}$
b) $\mathbf{B}_{2}{ }^{+}>\mathbf{B}_{2}>\mathbf{B}_{2}{ }^{-}$
11.39

| a) $\mathrm{BrO}_{3}{ }^{-}$ | $\mathrm{AX}_{3} \mathrm{E}$ |  | Ideal | eviations |
| :---: | :---: | :---: | :---: | :---: |
|  |  | trigonal pyramidal |  |  |
|  |  | $s p^{3}$ hybrid AO | $109.5^{\circ}$ | $<109.5^{\circ}$ |
| b) $\mathrm{AsCl}_{4}^{-}$ | $\mathrm{AX}_{4} \mathrm{E}$ | seesaw |  |  |
|  |  | $s p^{3} d$ hybrid AO | $120^{\circ}, 90^{\circ}$ | $<120^{\circ},<90^{\circ}$ |
| c) $\mathrm{SeO}_{4}{ }^{2-}$ | $\mathrm{AX}_{4}$ | tetrahedral |  |  |
|  |  | $s p^{3}$ hybrid AO | $109.5^{\circ}$ | none |
| d) $\mathrm{BiF}_{5}{ }^{2-}$ |  | $\mathrm{AX}_{5} \mathrm{E}$ square pyramidal |  |  |
|  |  | $s p^{3} d^{2}$ hybrid AO | $90^{\circ}$ | $<90^{\circ}$ |
| e) $\mathrm{SbF}_{4}{ }^{+}$ | $\mathrm{AX}_{4}$ | tetrahedral |  |  |
|  |  | $s p^{3}$ hybrid AO | $109.5^{\circ}$ | none |
| f) $\mathrm{AlF}_{6}{ }^{3-}$ | $\mathrm{AX}_{6}$ | octahedral |  |  |
|  |  | $s p^{3} d^{2}$ hybrid AO | $90^{\circ}$ | none |
| g) $\mathrm{IF}_{4}{ }^{+}$ | $\mathrm{AX}_{4} \mathrm{E}$ | seesaw |  |  |
|  |  | $s p^{3} d$ hybrid AO | $120^{\circ}, 9{ }^{\circ}$ | $<120^{\circ},<90^{\circ}$ |

Lewis structures:






11.40 a) There are $9 \boldsymbol{\sigma}$ and $2 \pi$ bonds. Each of the six $\mathrm{C}-\mathrm{H}$ bonds are sigma bonds. The $\mathrm{C}-\mathrm{C}$ bond contains a sigma bond. The double bonds between the carbons consist of a pi bond in addition to the sigma bond.
11.41 Plan: To determine hybridization, count the number of electron groups around each of the $\mathrm{C}, \mathrm{O}$, and N atoms. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a sigma bond which is the result of two orbitals overlapping end to end; a double bond consists of one sigma bond and one pi bond; and a triple bond consists of one sigma bond and two pi bonds.
Solution:
a) Each of the six C atoms in the ring has three electron groups (two single bonds and a double bond) and has $\boldsymbol{s} \boldsymbol{p}^{2}$ hybridization; all of the other C atoms have four electron groups (four single bonds) and have $\boldsymbol{s p}^{3}$ hybridization; all of the O atoms have four electron groups (two single bonds and two lone pairs) and have $\boldsymbol{s} \boldsymbol{p}^{3}$ hybridization; the N atom has four electron groups (three single bonds and a lone pair) and has $\boldsymbol{s p}^{3}$ hybridization.
b) Each of the single bonds is a sigma bond; each of the double bonds has one sigma bond for a total of 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 two electrons for a total of six pi electrons.
11.42
a)

s

b)


S

p

$s p^{3} d$

$d^{4}$
c)

$S$

$s p^{3} d^{2}$

$d^{3}$
d)

s

p

$p$
11.43 Plan: To determine hybridization, count the number of electron groups around each C and N atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a sigma bond which is the result of two orbitals overlapping end to end; a double bond consists of one sigma bond and one pi bond; and a triple bond consists of one sigma bond and two pi bonds.
Solution:
a) Every single bond is a sigma bond. There is one sigma bond in each double bond as well. There are $\mathbf{1 7} \boldsymbol{\sigma}$ 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 $\boldsymbol{s} \boldsymbol{p}^{2}$. The ring N also has three surrounding electron groups (one single bond, one double bond, and one lone pair), so its hybridization is also $\boldsymbol{s p ^ { 2 }}$. The other two N atoms have four surrounding electron groups (three single bonds and one lone pair) and are $\boldsymbol{s p}^{3}$ hybridized.
11.44 a)


Carbon disulfide
$\ddot{S}=C=\ddot{S}$
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 $s p^{3}$ to $s p^{2}$.
c) The electron-group arrangement and molecular shape around carbon change from linear to trigonal planar. The hybridization changes from $s p$ to $s p^{2}$.
11.45 Plan: To determine the hybridization in each species, count the number of electron groups around the underlined atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.
Solution:
a) B changes from $\boldsymbol{s} \boldsymbol{p}^{2} \rightarrow \boldsymbol{s} \boldsymbol{p}^{3}$. Boron in $\mathrm{BF}_{3}$ has three electron groups with $s p^{2}$ hybridization. In $\mathrm{BF}_{4}^{-}$, four electron groups surround B with $s p^{3}$ hybridization.

b) P changes from $\boldsymbol{s} \boldsymbol{p}^{\mathbf{3}} \boldsymbol{\rightarrow} \boldsymbol{s p}^{\mathbf{3}} \boldsymbol{d}$. Phosphorus in $\mathrm{PCl}_{3}$ is surrounded by four electron groups (three bonds to Cl and one lone pair) for $s p^{3}$ hybridization. In $\mathrm{PCl}_{5}$, phosphorus is surrounded by five electron groups for $s p^{3} d$ hybridization.

c) C changes from $\boldsymbol{s p} \boldsymbol{\boldsymbol { s }} \boldsymbol{p}^{2}$. Two electron groups surround C in $\mathrm{C}_{2} \mathrm{H}_{2}$ and three electron groups surround C in $\mathrm{C}_{2} \mathrm{H}_{4}$.

 surround Si in $\mathrm{SiF}_{6}{ }^{2-}$.

e) No change, S in $\mathrm{SO}_{2}$ is surrounded by three electron groups (one single bond, one double bond, and one lone pair) and in $\mathrm{SO}_{3}$ is surrounded by three electron groups (two single bonds and one double bond); both have $s p^{2}$ hybridization.

11.46 Plan: To determine the molecular shape and hybridization, count the number of electron groups around the P, N, and C atoms. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.
Solution:

| P (3 single bonds and 1 double bond) | $\mathrm{AX}_{4}$ | tetrahedral <br> N (3 single bonds and 1 lone pair) | $\mathrm{AX}_{3} \mathrm{E}$ |
| :--- | :--- | :--- | :--- | | $\boldsymbol{s} \boldsymbol{p}^{\mathbf{3}}$ |
| :--- |
| $\mathrm{C}_{1}$ and $\mathrm{C}_{2}$ (4 single bonds) pyramidal |
| $\boldsymbol{s p}^{\mathbf{3}}$ |

11.47 a) The representation with two $\mathrm{S}=\mathrm{O}$ double bonds:

$\mathrm{FC}_{\mathrm{S}}=6-[0+1 / 2(12)]=0 \quad \mathrm{FC}_{\mathrm{O}(\text { single bond) }}=6-[6+1 / 2(2)]=-1$
$\mathrm{FC}_{\mathrm{O} \text { (double bond) }}=6-[4+1 / 2(4)]=0$
The representation with four S-O single bonds:

$\mathrm{FC}_{\mathrm{S}}=6-[0+1 / 2(8)]=+2 \quad \mathrm{FC}_{\mathrm{O}}=6-[6+1 / 2(2)]=-1$
The representation with two $\mathbf{S}=\mathbf{O}$ 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 tetrahedral because 4 electron groups surround $S$ in both cases. The double bonded representation would show some deviation from the ideal angle of $109.5^{\circ}$ due to the double bonds. The single bond hybridization is $\boldsymbol{s p}{ }^{3}$.
c) Since sulfur's valence $p$-orbitals are used in the sigma bonds, the $\pi$ bonds are formed from the valence $3 d$ orbitals in sulfur overlapping with $2 p$ orbitals in oxygen.

d)

11.48
a) $1: s p^{3}$
2: $\boldsymbol{s p}^{2}$
3: $s p^{3}$
4: $s p^{3} \quad$ 5: $s p^{2}$
6: $s p^{2}$
b) 28
c) a: $<\mathbf{1 0 9 . 5}^{\circ}$ b: $\mathbf{1 2 0}^{\circ}$ c: $\mathbf{1 2 0}^{\circ}$
$11.49 \mathrm{O}_{2} \quad\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\sigma_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{1}\left(\pi^{*}{ }_{2 p}\right)^{1} \quad$ bond order $=2.0$ paramagnetic
$\mathrm{O}_{2}{ }^{+} \quad\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\sigma_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{1} \quad$ bond order $=2.5$ paramagnetic
(1 unpaired)
$\mathrm{O}_{2}{ }^{-} \quad\left(\sigma_{2 s}\right)^{2}\left(\sigma_{2 s}^{*}\right)^{2}\left(\sigma_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{1} \quad$ bond order $=1.5$ paramagnetic
(1 unpaired)
$\mathrm{O}_{2}{ }^{2-} \quad\left(\sigma_{2 s}\right)^{2}\left(\sigma^{*}{ }_{2 s}\right)^{2}\left(\sigma_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{2}\left(\pi^{*}{ }_{2 p}\right)^{2} \quad$ bond order $=1.0$ diamagnetic
(0 unpaired)
Bond length: $\quad \mathrm{O}_{2}^{+}<\mathrm{O}_{2}<\mathrm{O}_{2}^{-}<\mathrm{O}_{2}{ }^{2-}$
11.50 a) Yes, each one is $s p^{2}$ hybridized.
b) Yes, each one is $s p^{3}$ hybridized.
c) C-O bonds: $\mathbf{6} \sigma$ bonds, $\mathbf{1} \pi$ bond.
d) No, the $\mathrm{C}=\mathrm{O}$ lone pair electrons are in $s p^{2}$ hybrid orbitals, while the other oxygen lone pairs occupy $s p^{3}$ hybrid orbitals.
11.51 Plan: To determine the hybridization, count the number of electron groups around the atoms. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.
Solution:
a) $\mathbf{B}$ and $\mathbf{D}$ show hybrid orbitals that are present in the molecule. B shows $s p^{3}$ hybrid orbitals, used by atoms that have four groups of electrons. In the molecule, the C atom in the $\mathrm{CH}_{3}$ group, the S atom, and the O atom all have four groups of electrons and would have $s p^{3}$ hybrid orbitals. D shows $s p^{2}$ 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 $\mathrm{C}=\mathrm{C}$ bond, and the nitrogen atom all have three groups of electrons and would have $s p^{2}$ hybrid orbitals.
b) The C atoms in the $\mathrm{C} \equiv \mathrm{C}$ bond have only two electron groups and would have $\boldsymbol{s p}$ hybrid orbitals. These orbitals are not shown in the picture.
c) There are two sets of $\boldsymbol{s} \boldsymbol{p}$ hybrid orbitals, four sets of $\boldsymbol{s} \boldsymbol{p}^{2}$ hybrid orbitals, and three sets of $\boldsymbol{s} \boldsymbol{p}^{3}$ hybrid orbitals in the molecule.
11.52


The central C is $\boldsymbol{s} \boldsymbol{p}$ hybridized, and the other two C atoms are $\boldsymbol{s} \boldsymbol{p}^{2}$.
(
11.54 a)



b) $\mathrm{SiF}_{4} \boldsymbol{s p}^{3}$
$\mathrm{GeF}_{6}{ }^{2-}{ }^{-} p^{3} d^{2}$
$\mathrm{CF}_{4} \quad \boldsymbol{s p}^{3}$
c) Carbon has no $d$-orbitals available to form $s p^{3} d^{2}$ hybrids.
11.55 a) N has $s p^{2}$ hybridization, formed from one $2 s$ and two $2 p$ orbitals.
b) The lone pair is in a $\boldsymbol{s} \boldsymbol{p}^{2}$ hybrid orbital.
c) Hybridization of C in $\mathrm{CH}_{3}$ is $\boldsymbol{s} \boldsymbol{p}^{3}$; C in the ring is $\boldsymbol{s} \boldsymbol{p}^{2}$.
11.56 Plan: To determine hybridization, count the number of electron groups around each C and O atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a sigma bond which is the result of two orbitals overlapping end to end; a double bond consists of one sigma bond and one pi bond; and a triple bond consists of one sigma bond and two pi bonds.

## Solution:

a) The six carbons in the ring each have three surrounding electron groups (two single bonds and one double bond) with $s p^{2}$ hybrid orbitals. The two carbons participating in the $\mathrm{C}=\mathrm{O}$ bond are also $s p^{2}$ hybridized. The single carbon in the $-\mathrm{CH}_{3}$ group has four electron groups (four single bonds) and is $s p^{3}$ hybridized. The two central oxygen atoms, one in a $\mathrm{C}-\mathrm{O}-\mathrm{H}$ configuration and the other in a $\mathrm{C}-\mathrm{O}-\mathrm{C}$ configuration, each have four surrounding electron groups (two single bonds and two lone pairs) and are $s p^{3}$ hybridized. The O atoms in the two $\mathrm{C}=\mathrm{O}$ bonds have three electron groups (one double bond and two lone pairs) and are $s p^{2}$ hybridized.
Summary: C in $-\mathrm{CH}_{3}$ : $\boldsymbol{s} \boldsymbol{p}^{\mathbf{3}}$, all other C atoms (8 total): $\boldsymbol{s} \boldsymbol{p}^{2}$, O in $\mathrm{C}=\mathrm{O}$ (2 total): $\boldsymbol{s} \boldsymbol{p}^{2}$, O in the $\mathrm{C}-\mathrm{O}$ bonds (2 total): $\boldsymbol{s} \boldsymbol{p}^{\mathbf{3}}$.
b) The two $\mathrm{C}=\mathrm{O}$ bonds are localized; the double bonds on the ring are delocalized as in benzene.
c) Each carbon with three surrounding groups has $s p^{2}$ hybridization and trigonal planar shape; therefore, eight carbons have this shape. Only one carbon in the $\mathrm{CH}_{3}$ group has four surrounding groups with $s p^{3}$ hybridization and tetrahedral shape.
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