

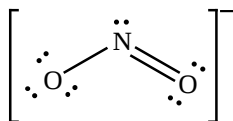
CHAPTER 11 THEORIES OF COVALENT BONDING

END-OF-CHAPTER PROBLEMS

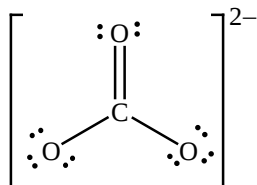
- 11.1 **Plan:** Table 11.1 describes the types of hybrid orbitals that correspond to the various electron-group arrangements. The number of hybrid orbitals formed by a central atom is equal to the number of electron groups arranged around that central atom.
Solution:
a) trigonal planar: three electron groups - three hybrid orbitals: sp^2
b) octahedral: six electron groups - six hybrid orbitals: sp^3d^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^3d
- 11.2 a) sp^2 b) sp^3 c) sp^3d d) sp^3d^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 six hybrid orbitals, whereas carbon has only $2s$ and $2p$ 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 sp^3d^2 since one s , three p , and two d atomic orbitals were mixed.
b) **Four** sp^3 hybrid orbitals form from three p and one s atomic orbitals.
- 11.6 a) **two sp orbitals** b) **five sp^3d 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 sp^2 .
$$\begin{array}{c} \cdot\cdot \\ \cdot\text{N}=\ddot{\text{O}} \\ \cdot \end{array}$$

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 sp^2 .
$$\begin{array}{c} \cdot \\ \cdot\text{O}-\text{N}=\ddot{\text{O}} \\ \cdot \end{array}$$

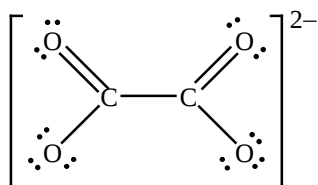
c) The nitrogen has three electron groups (one single bond, one double bond, and one lone pair) so the hybridization is sp^2 .



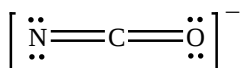
11.8 a) sp^2



b) sp^2



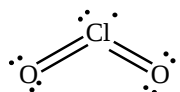
c) sp



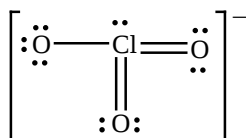
11.9 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central chlorine atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.

Solution:

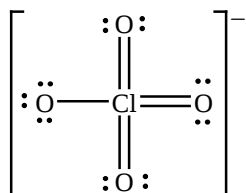
a) The Cl has four electron groups (one lone pair, one lone electron, and two double bonds) and therefore four hybrid orbitals are required; the hybridization is sp^3 . Note that in ClO_2 , the π bond is formed by the overlap of d orbitals from chlorine with p orbitals from oxygen.



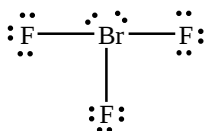
b) The Cl has four electron groups (one lone pair and three bonds) and therefore four hybrid orbitals are required; the hybridization is sp^3 .



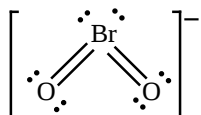
c) The Cl has four electron groups (four bonds) and therefore four hybrid orbitals are required; the hybridization is sp^3 .



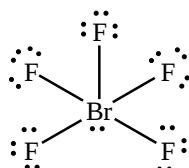
11.10 a) sp^3d



b) sp^3



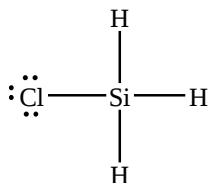
c) sp^3d^2



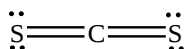
11.11 Plan: Draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Once the type of hybridization is known, the types of atomic orbitals that will mix to form those hybrid orbitals are also known.

Solution:

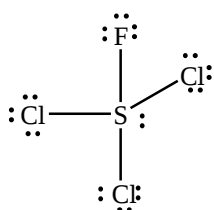
a) Silicon has four electron groups (four bonds) requiring four hybrid orbitals; four sp^3 hybrid orbitals are made from **one s and three p atomic orbitals**.



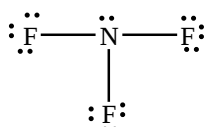
b) Carbon has two electron groups (two double bonds) requiring two hybrid orbitals; two sp hybrid orbitals are made from **one s and one p orbital**.



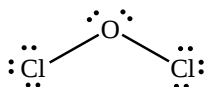
c) Sulfur is surrounded by five electron groups (four bonding pairs and one lone pair), requiring five hybrid orbitals; five sp^3d hybrid orbitals are formed from **one s orbital, three p orbitals, and one d orbital**.



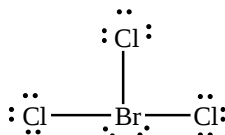
d) Nitrogen is surrounded by four electron groups (three bonding pairs and one lone pair) requiring four hybrid orbitals; four sp^3 hybrid orbitals are formed from **one s orbital and three p orbitals**.



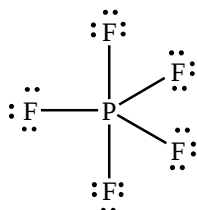
11.12 a) $sp^3 \leftarrow s + 3p$



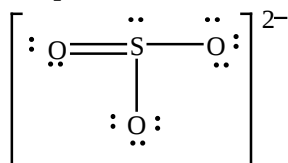
b) $sp^3d \leftarrow s + 3p + d$



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



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

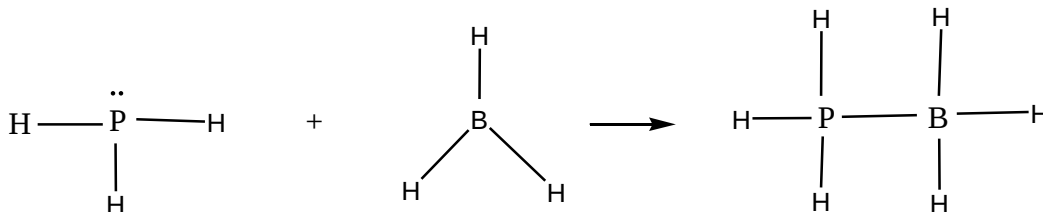


11.13 Plan: To determine hybridization, draw the Lewis structure of the reactants and products and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons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

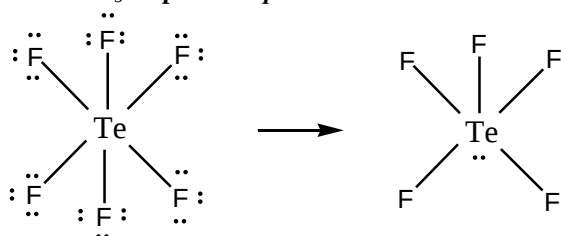
Solution:

a) The P in PH_3 has four electron groups (one lone pair and three bonds) and therefore four hybrid orbitals are required; the hybridization is sp^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 sp^3 . There is no change in hybridization. Illustration **B** best shows the hybridization of P during the reaction as $sp^3 \rightarrow sp^3$.

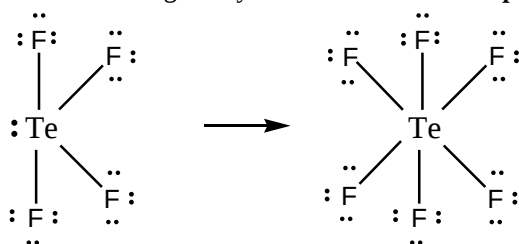
b) The B in BH_3 has three electron groups (three bonds) and therefore three hybrid orbitals are required; the hybridization is sp^2 . The B in the product has four electron groups (four bonds) and four hybrid orbitals are required. The hybridization of B is now sp^3 . The hybridization of B changes from sp^2 to sp^3 ; this is best shown by illustration **A**.



- 11.14 a) The Te in TeF_6 has six electron groups (six bonds) and therefore six hybrid orbitals are required; the hybridization is sp^3d^2 . Te in 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 sp^3d^2 . There is no change in hybridization. Illustration A best shows the hybridization of Te when TeF_6 forms TeF_5^- : $sp^3d^2 \rightarrow sp^3d^2$.



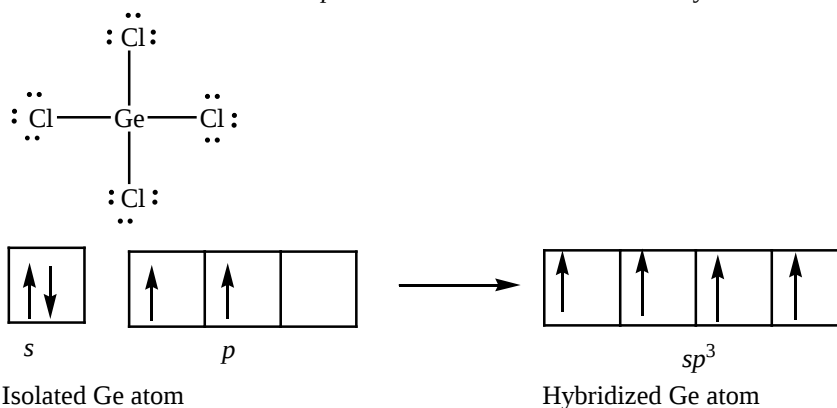
- b) The Te in TeF_4 has five electron groups (four bonds and one unshared pair) and therefore five hybrid orbitals are required; the hybridization is sp^3d . Te in TeF_6 has six electron groups (six bonds) and therefore six hybrid orbitals are required; the hybridization is sp^3d^2 . Illustration C best shows the change in hybridization of Te from sp^3d to sp^3d^2 .



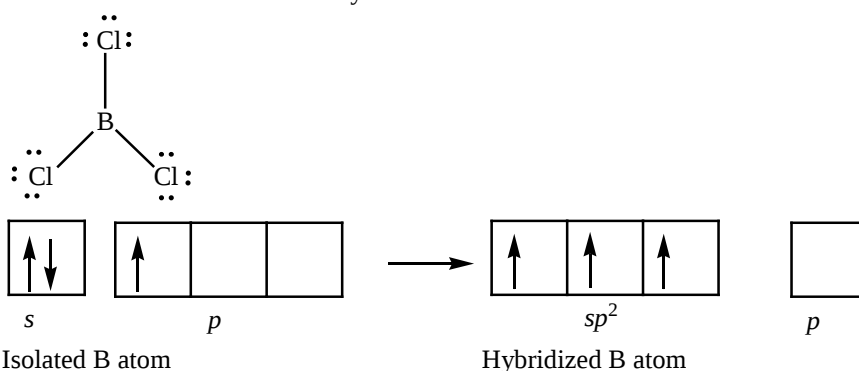
- 11.15 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also 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:

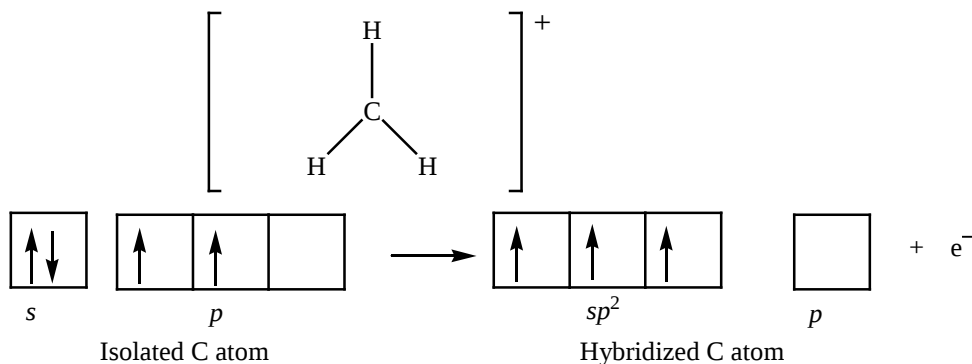
- a) Germanium is the central atom in GeCl_4 . Its electron configuration is $[\text{Ar}]4s^23d^{10}4p^2$. Ge has four electron groups (four bonds), requiring four hybrid orbitals. Hybridization is sp^3 around Ge. One of the 4s electrons is moved to a 4p orbital and the four orbitals are hybridized.



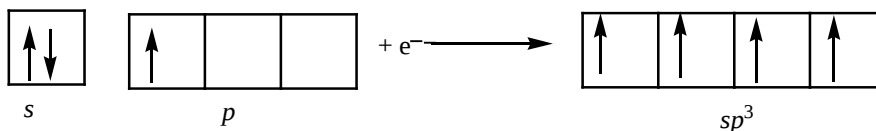
b) Boron is the central atom in BCl_3 . Its electron configuration is $[\text{He}]2s^2 2p^1$. B has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is sp^2 around B. One of the 2s electrons is moved to an empty 2p orbital and the three atomic orbitals are hybridized. One of the 2p atomic orbitals is not involved in the hybridization.



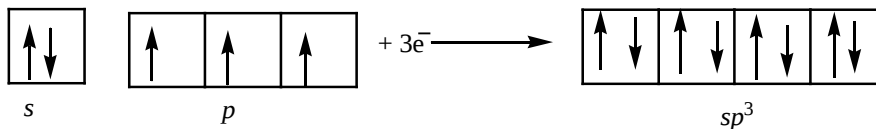
c) Carbon is the central atom in CH_3^+ . Its electron configuration is $[\text{He}]2s^2 2p^2$. C has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is sp^2 around C. One of the 2s electrons is moved to an empty 2p orbital; three orbitals are hybridized and one electron is removed to form the +1 ion.



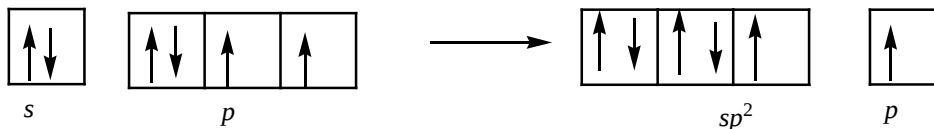
11.16 a)



b)



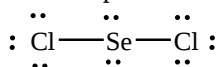
c)



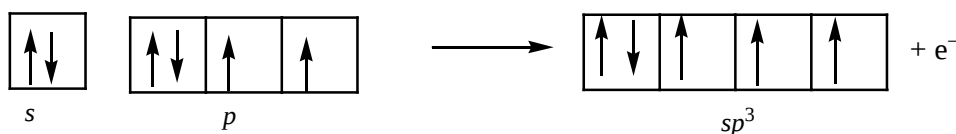
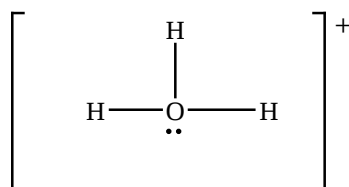
- 11.17 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also 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:

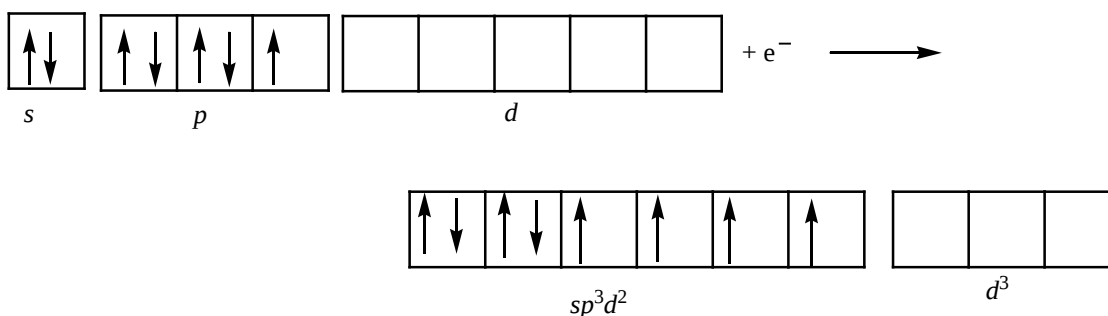
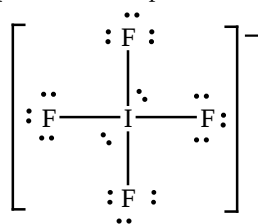
a) In SeCl_2 , Se is the central atom and has four electron groups (two single bonds and two lone pairs), requiring four hybrid orbitals so Se is sp^3 hybridized. The electron configuration of Se is $[\text{Ar}]4s^23d^{10}4p^4$. The 4s and 4p atomic orbitals are hybridized. Two sp^3 hybrid orbitals are filled with lone electron pairs and two sp^3 orbitals bond with the chlorine atoms.



b) In H_3O^+ , 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. The electron configuration of O is $[\text{He}]2s^22p^4$. The 2s and 2p orbitals are hybridized. One sp^3 hybrid orbital is filled with a lone electron pair and three sp^3 orbitals bond with the hydrogen atoms.



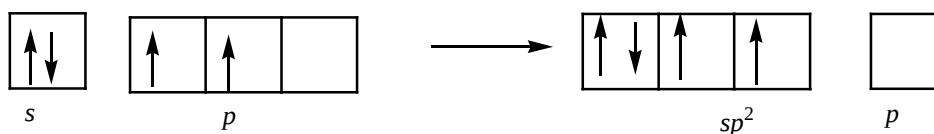
c) I is the central atom in IF_4^- with six electron groups (four single bonds and two lone pairs) surrounding it. Six hybrid orbitals are required and I has sp^3d^2 hybrid orbitals. The sp^3d^2 hybrid orbitals are composed of one s orbital, three p orbitals, and two d orbitals. Two sp^3d^2 orbitals are filled with a lone pair and four sp^3d^2 orbitals bond with the fluorine atoms.



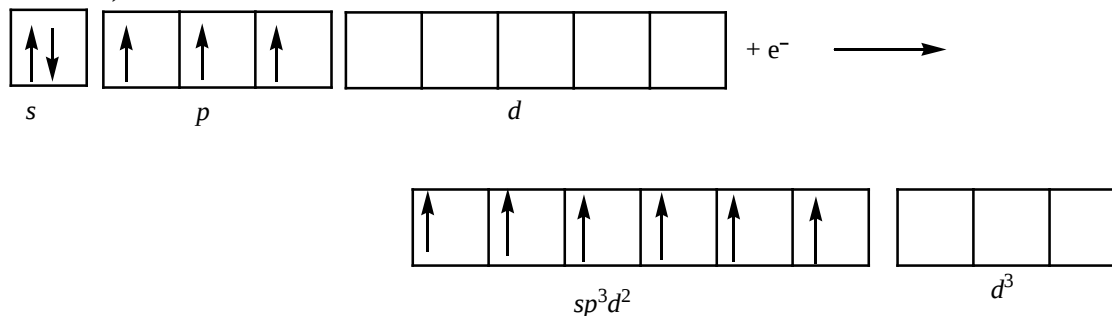
11.18 a)



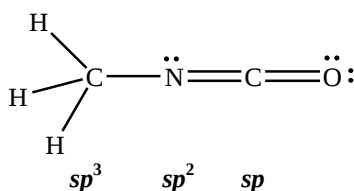
b)



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.

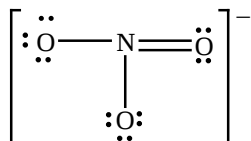
Solution:

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

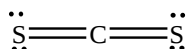
11.21 **Plan:** To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron 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:

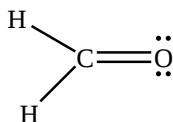
- a) Nitrogen is the central atom in NO_3^- . Nitrogen has three surrounding electron groups (two single bonds and one double bond), so it is sp^2 hybridized. Nitrogen forms **three σ bonds** (one each for the N–O bonds) and **one π bond** (part of the N=O double bond).



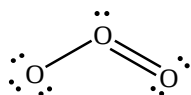
b) Carbon is the central atom in CS_2 . Carbon has two surrounding electron groups (two double bonds), so it is **sp** hybridized. Carbon forms **two σ bonds** (one each for the C–S bonds) and **two π bonds** (part of the two C=S double bonds).



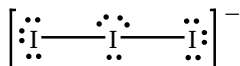
c) Carbon is the central atom in CH_2O . Carbon has three surrounding electron groups (two single bonds and one double bond), so it is **sp^2** hybridized. Carbon forms **three σ bonds** (one each for the two C–H bonds and one C–O bond) and **one π bond** (part of the C=O double bond).



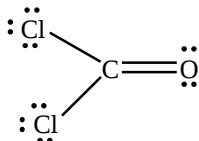
11.22 a) **sp^2 2 σ bonds and 1 π bond**



b) **sp^3d 2 σ bonds**



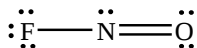
c) **sp^2 3 σ bond and 1 π bond**



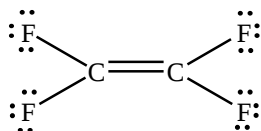
11.23 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central nitrogen atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron 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:

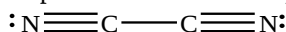
a) In FNO, three electron groups (one lone pair, one single bond, and one double bond) surround the central N atom. Hybridization is **sp^2** around nitrogen. One sigma bond exists between F and N, and one sigma and one pi bond exist between N and O. Nitrogen participates in a total of **2 σ and 1 π bonds**.



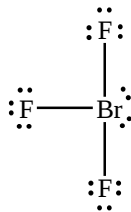
b) In C_2F_4 , each carbon has three electron groups (two single bonds and one double bond) with **sp^2** hybridization. The bonds between C and F are sigma bonds. The C–C bond consists of one sigma and one pi bond. Each carbon participates in a total of **three σ bonds and one π bond**.



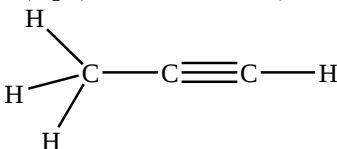
c) In $(\text{CN})_2$, each carbon has two electron groups (one single bond and one triple bond) and is ***sp*** hybridized with a sigma bond between the two carbons and a sigma and two pi bonds comprising each C–N triple bond. Each carbon participates in a total of **two σ and two π bonds**.



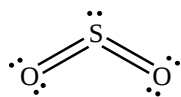
11.24 a) ***sp*³*d* three σ bonds**



b) ***sp*³ (CH_3) *sp* (other two C atoms) six σ and two π bonds**



c) ***sp*² two σ and two π 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_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 π 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 σ -bonding molecular orbital. Each molecular orbital requires two electrons.
- b) **Two** electrons are required to fill a π -antibonding molecular orbital. There are two π -antibonding orbitals, each holding a maximum of two electrons.
- c) **Four** electrons are required to fill the two σ molecular orbitals (two electrons to fill the σ -bonding and two to fill the σ -antibonding) formed from two $1s$ atomic orbitals.

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

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 σ and MOs formed by the side-to-side overlap of p orbitals are called π . A superscript star (*) is used to designate an antibonding MO. To write the electron configuration of 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 π_{2p}^* molecular orbital (two p orbitals overlapping side to side with a node between them); B is the σ_{2p} molecular orbital (two p orbitals overlapping end to end with no node); C is the π_{2p} molecular orbital (two p orbitals overlapping side to side with no node); D is the σ_{2p}^* molecular orbital (two p orbitals overlapping end to end with a node).

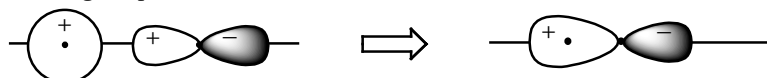
b) F_2^+ has thirteen valence electrons: $[2 \times F(7e^-) - 1 \text{ (from + charge)}]$. The MO electron configuration is $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)^2(\pi_{2p}^*)^1$. The π_{2p}^* molecular orbital, A, σ_{2p} molecular orbital, B, and π_{2p} molecular orbital, C, are all occupied by at least one electron. The σ_{2p}^* molecular orbital is unoccupied.

c) A π_{2p}^* molecular orbital, A, has only one electron.

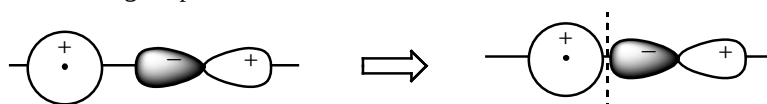
- 11.32 a) A is the π_{2p}^* molecular orbital; B is the σ_{2p} molecular orbital; C is the π_{2p} molecular orbital; D is the σ_{2p}^* molecular orbital; E is the σ_{2s} molecular orbital; F is the σ_{2s}^* molecular orbital.
- b) The σ_{2p}^* molecular orbital, D, is the highest in energy.
- c) The σ_{2s} molecular orbital, E, is the lowest in energy.
- d) $\sigma_{2s} < \sigma_{2s}^* < \pi_{2p} < \sigma_{2p} < \pi_{2p}^* < \sigma_{2p}^*$ ($E < F < C < B < A < D$)

11.33 The horizontal line in all cases represents the bond axis.

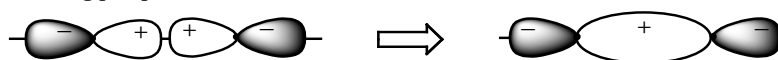
a) Bonding $s + p$



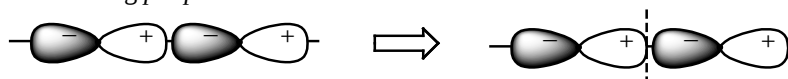
Antibonding $s - p$



b) Bonding $p + p$



Antibonding $p - p$



11.34 a)
 $s + s =$



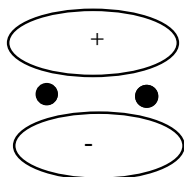
Bonding

$s - s =$



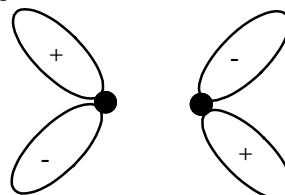
Antibonding

b)
 $p + p =$



Bonding

$p - p =$



Antibonding

- 11.35 Plan: To write the electron configuration of 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 = $\frac{1}{2}[(\text{no. of electrons in bonding MO}) - (\text{no. of electrons in antibonding MO})]$. Recall that a diamagnetic substance has no unpaired electrons.

Solution:

a) Be_2^+ has a total of seven electrons [$2 \times \text{Be}(4e^-) - 1$ (from + charge)]. The molecular orbital configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^1$ and bond order = $\frac{1}{2}(4 - 3) = 1/2$. With a bond order of $1/2$ the Be_2^+ ion will be **stable**.

b) No, the ion has one unpaired electron in the σ_{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 $(\sigma_{2s})^2(\sigma_{2s}^*)^1$.

- 11.36 a) The molecular orbital configuration for O_2^- with a total of seventeen electrons is $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)^2(\pi_{2p}^*)^1$.
 Bond order = $\frac{1}{2}(10 \text{ bonding} - 7 \text{ antibonding } e^-) = 3/2 = 1.5$. **O_2^- is stable.**

b) O_2^- is **paramagnetic** with an unpaired electron in the π_{2p}^* MO.

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

- 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 = $\frac{1}{2}[(\text{no. of electrons in bonding MO}) - (\text{no. of electrons in antibonding MO})]$. Bond energy increases as bond order increases; bond length decreases as bond order increases.

Solution:

C_2^- Total electrons = $6 + 6 + 1 = 13$

MO configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$

Bond order = $1/2(9 - 4) = 2.5$

C_2 Total electrons = $6 + 6 = 12$

MO configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$

Bond order = $1/2(8 - 4) = 2$

C_2^+ Total electrons = $6 + 6 - 1 = 11$

MO configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^3$

Bond order = $1/2(7 - 4) = 1.5$

a) Bond energy increases as bond order increases: $\text{C}_2^+ < \text{C}_2 < \text{C}_2^-$

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: $\text{C}_2^- < \text{C}_2 < \text{C}_2^+$

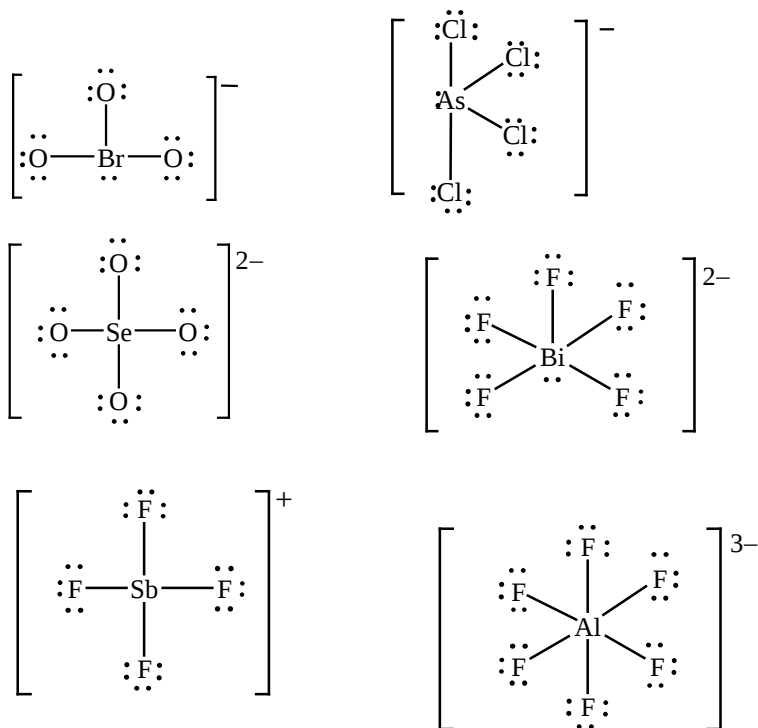
11.38

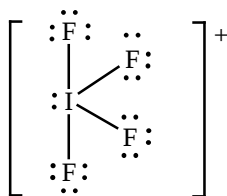
		<u>Bond order</u>
B_2^+ :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^1$	0.5
B_2 :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^1(\pi_{2p})^1$	1.0
B_2^- :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2(\pi_{2p})^1$	1.5
a) $B_2^- > B_2 > B_2^+$		
b) $B_2^+ > B_2 > B_2^-$		

11.39

			<u>Ideal</u>	<u>Deviations</u>
a) BrO_3^-	AX_3E	trigonal pyramidal sp^3 hybrid AO	109.5°	<109.5°
b) $AsCl_4^-$	AX_4E	seesaw sp^3d hybrid AO	120°, 90°	<120°, <90°
c) SeO_4^{2-}	AX_4	tetrahedral sp^3 hybrid AO	109.5°	none
d) BiF_5^{2-}	AX_5E	square pyramidal sp^3d^2 hybrid AO	90°	<90°
e) SbF_4^+	AX_4	tetrahedral sp^3 hybrid AO	109.5°	none
f) AlF_6^{3-}	AX_6	octahedral sp^3d^2 hybrid AO	90°	none
g) IF_4^+	AX_4E	seesaw sp^3d hybrid AO	120°, 90°	<120°, <90°

Lewis structures:





11.40 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.

11.41 Plan: To determine hybridization, count the number of electron groups around each of the C, 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:

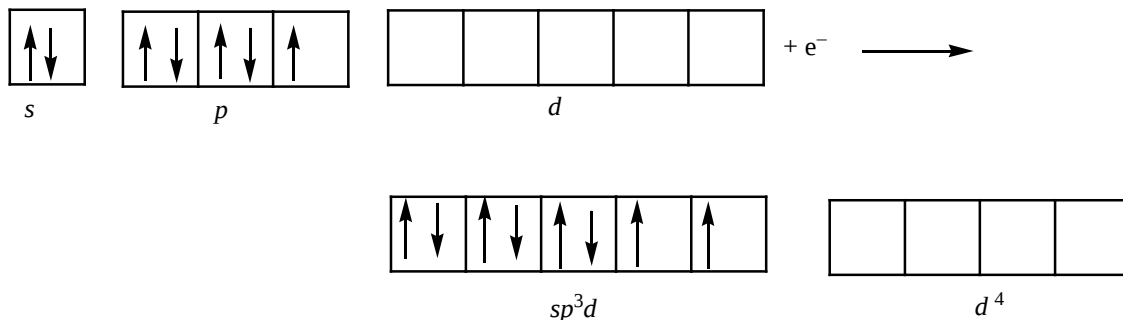
a) Each of the six C atoms in the ring has three electron groups (two single bonds and a double bond) and has **sp^2** hybridization; all of the other C atoms have four electron groups (four single bonds) and have **sp^3** hybridization; all of the O atoms have four electron groups (two single bonds and two lone pairs) and have **sp^3** hybridization; the N atom has four electron groups (three single bonds and a lone pair) and has **sp^3** hybridization.

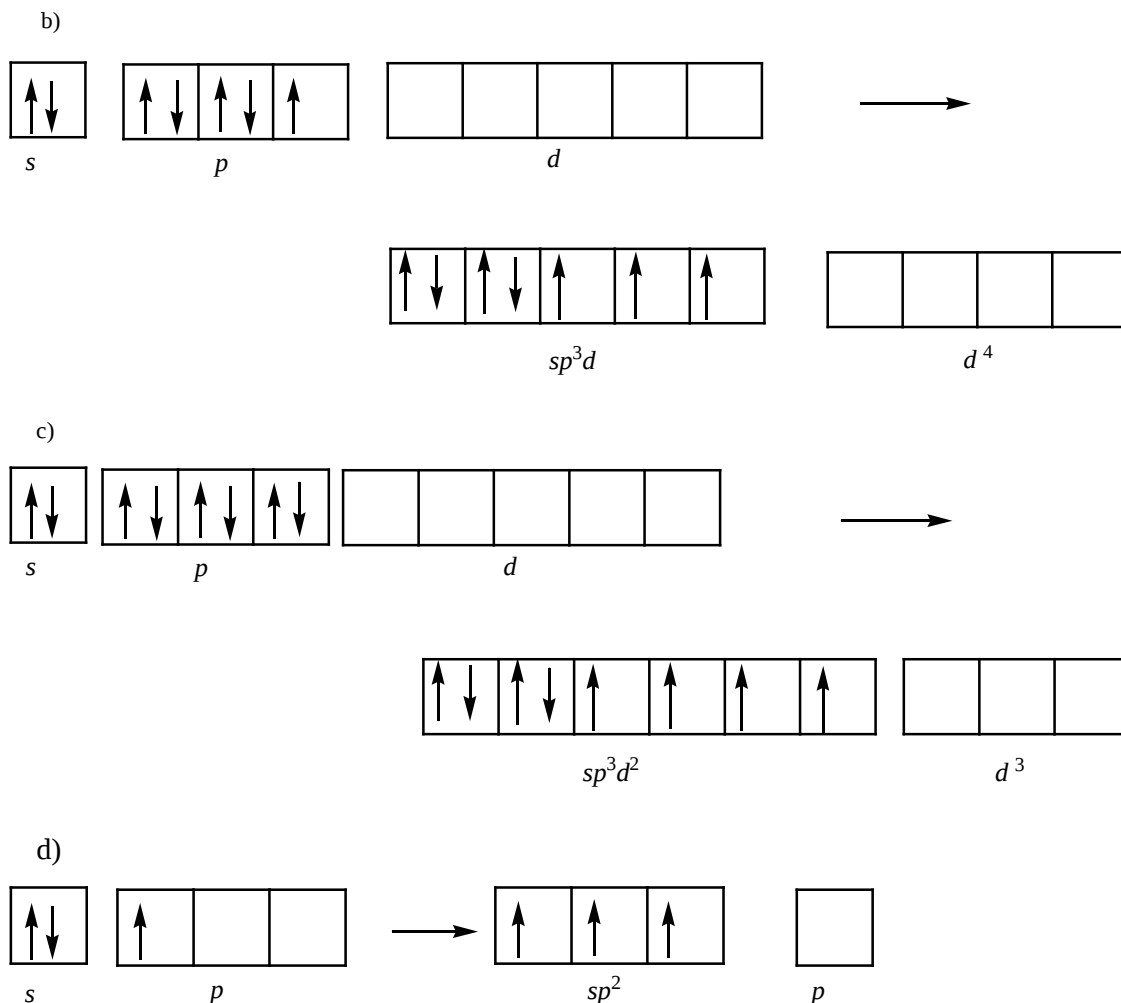
b) Each of the single bonds is a sigma bond; each of the double bonds has one sigma bond for a total of **26 sigma bonds**.

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)



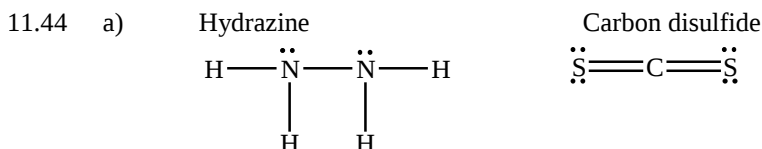


11.43 **Plan:** To determine hybridization, count the number of electron groups around each C and N atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron 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 **17 σ** bonds in isoniazid. Every atom-to-atom connection contains a σ bond.

b) All carbons have three surrounding electron groups (two single and one double bond), so their hybridization is 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 sp^2 . The other two N atoms have four surrounding electron groups (three single bonds and one lone pair) and are sp^3 hybridized.



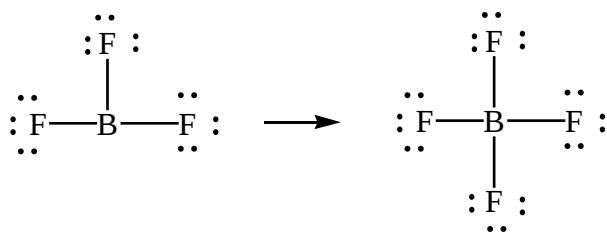
b) The electron-group arrangement around each nitrogen changes from tetrahedral to trigonal planar. The molecular shape changes from trigonal pyramidal to bent and the hybridization changes from sp^3 to sp^2 .

c) The electron-group arrangement and molecular shape around carbon change from linear to trigonal planar. The hybridization changes from sp to sp^2 .

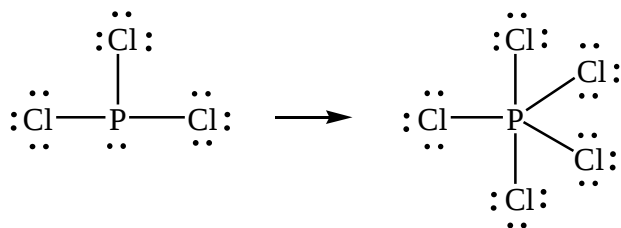
- 11.45 **Plan:** To determine the hybridization in each species, count the number of electron groups around the underlined atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.

Solution:

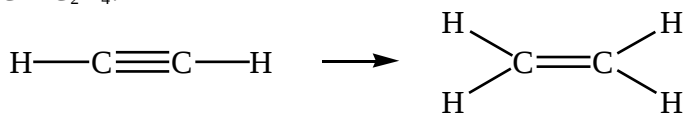
a) B changes from $sp^2 \rightarrow sp^3$. Boron in BF_3 has three electron groups with sp^2 hybridization. In BF_4^- , four electron groups surround B with sp^3 hybridization.



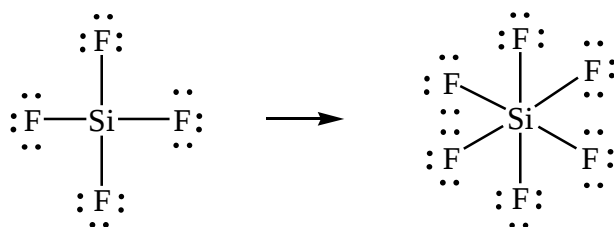
b) P changes from $sp^3 \rightarrow sp^3d$. Phosphorus in PCl_3 is surrounded by four electron groups (three bonds to Cl and one lone pair) for sp^3 hybridization. In PCl_5 , phosphorus is surrounded by five electron groups for sp^3d hybridization.



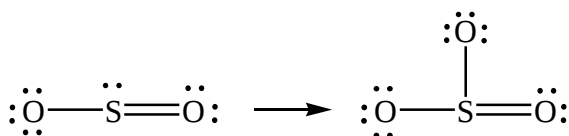
c) C changes from $sp \rightarrow sp^2$. Two electron groups surround C in C_2H_2 and three electron groups surround C in C_2H_4 .



d) Si changes from $sp^3 \rightarrow sp^3d^2$. Four electron groups surround Si in SiF_4 and six electron groups surround Si in SiF_6^{2-} .



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 three electron groups (two single bonds and one double bond); both have sp^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)

AX₄ **tetrahedral**

*sp*³

N (3 single bonds and 1 lone pair)

AX₃E **trigonal pyramidal**

*sp*³

C₁ and C₂ (4 single bonds)

AX₄ **tetrahedral**

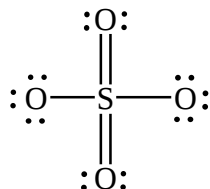
*sp*³

C₃ (2 single bonds and 1 double bond)

AX₃ **trigonal planar**

*sp*²

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

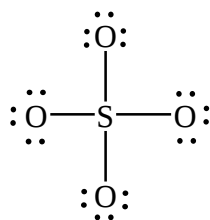


$$FC_S = 6 - [0 + 1/2(12)] = 0$$

$$FC_{O(\text{single bond})} = 6 - [6 + 1/2(2)] = -1$$

$$FC_{O(\text{double bond})} = 6 - [4 + 1/2(4)] = 0$$

The representation with four S-O single bonds:



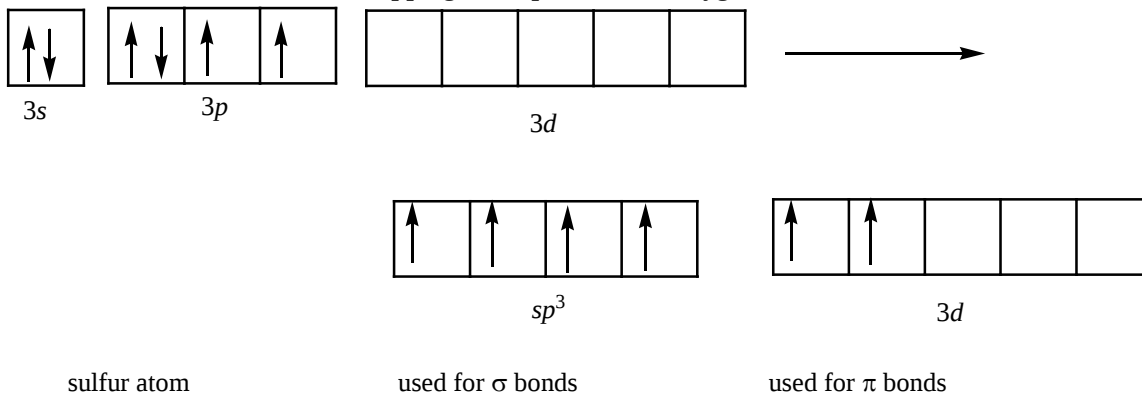
$$FC_S = 6 - [0 + 1/2(8)] = +2$$

$$FC_O = 6 - [6 + 1/2(2)] = -1$$

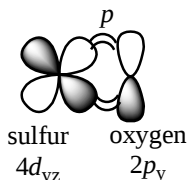
The representation with **two S=O double bonds** is better since it minimizes formal charges. For sulfur, the formal charge in the single bond representation is +2 while in the double bond representation it decreases to zero. The formal charge for the oxygen atoms double bonded to the sulfur increases 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 **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 *sp*³.

c) Since sulfur's valence *p*-orbitals are used in the sigma bonds, the π bonds are formed from the valence **3d orbitals in sulfur overlapping with 2p orbitals in oxygen.**



d)



- 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° b: 120° c: 120°

- 11.49
- | | | |
|------------|---|-------------------------------|
| O_2 | $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)^1(\pi_{2p}^*)^1$
(2 unpaired) | bond order = 2.0 paramagnetic |
| O_2^+ | $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)^1$
(1 unpaired) | bond order = 2.5 paramagnetic |
| O_2^- | $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)^2(\pi_{2p}^*)^1$
(1 unpaired) | bond order = 1.5 paramagnetic |
| O_2^{2-} | $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)^2(\pi_{2p}^*)^2$
(0 unpaired) | bond order = 1.0 diamagnetic |
- Bond length: $O_2^+ < O_2 < O_2^- < O_2^{2-}$

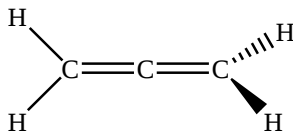
- 11.50 a) **Yes**, each one is sp^2 hybridized.
 b) **Yes**, each one is sp^3 hybridized.
 c) C–O bonds: **6 σ bonds, 1 π bond.**
 d) No, the C=O lone pair electrons are in sp^2 hybrid orbitals, while the other oxygen lone pairs occupy sp^3 hybrid orbitals.

- 11.51 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:

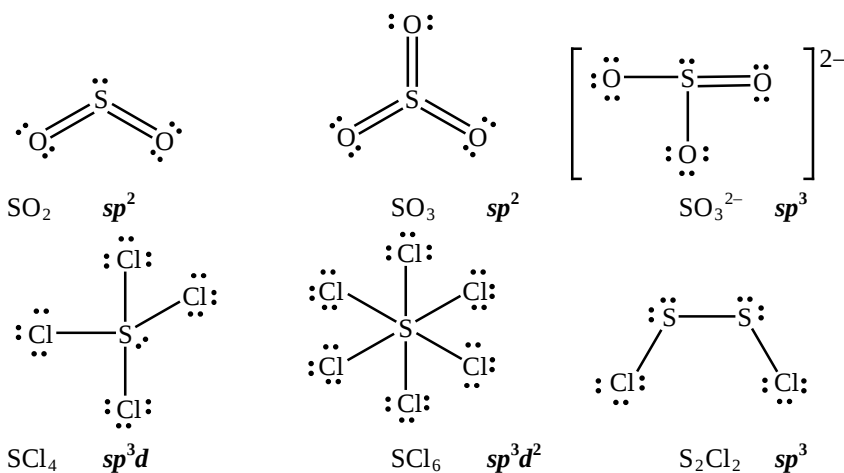
- a) **B and D** show hybrid orbitals that are present in the molecule. B shows sp^3 hybrid orbitals, used by atoms that have four groups of electrons. In the molecule, the C atom in the CH_3 group, the S atom, and the O atom all have four groups of electrons and would have sp^3 hybrid orbitals. D shows 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 $C \equiv C$ 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.

11.52

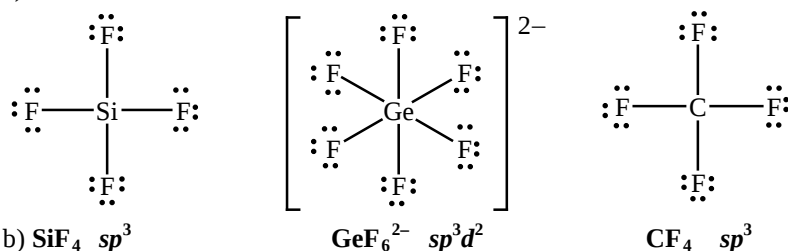


The central C is sp hybridized, and the other two C atoms are sp^2 .

11.53 Draw the Lewis structures.



11.54 a)



c) Carbon has no d -orbitals available to form sp^3d^2 hybrids.

11.55 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 .

11.56 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 sp^2 hybrid orbitals. The two carbons participating in the $\text{C}=\text{O}$ bond are also sp^2 hybridized. The single carbon in the $-\text{CH}_3$ group has four electron groups (four single bonds) and is sp^3 hybridized. The two central oxygen atoms, one in a $\text{C}-\text{O}-\text{H}$ configuration and the other in a $\text{C}-\text{O}-\text{C}$ configuration, each have four surrounding electron groups (two single bonds and two lone pairs) and are sp^3 hybridized. The O atoms in the two $\text{C}=\text{O}$ bonds have three electron groups (one double bond and two lone pairs) and are sp^2 hybridized.

Summary: C in $-\text{CH}_3$: sp^3 , all other C atoms (8 total): sp^2 , O in $\text{C}=\text{O}$ (2 total): sp^2 , O in the $\text{C}-\text{O}$ bonds (2 total): sp^3 .

b) The **two** $\text{C}=\text{O}$ 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, **eight** carbons have this shape. Only **one** carbon in the CH_3 group has four surrounding groups with sp^3 hybridization and tetrahedral shape.

