CHAPTER 11

CHEMICAL BONDING II: ADDITIONAL ASPECTS

PRACTICE EXAMPLES

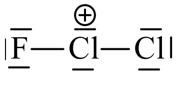
1A The valence-shell orbital diagrams of N and I are as follows:

$\text{N [He]}_{2s}\boxed{\uparrow\downarrow}\ {}_{2p}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\quad$ $\text{I [Kr] } 4d^{10}{}_{5s}\boxed{\uparrow\downarrow}\ {}_{5p}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

There are three half-filled $2p$ orbitals on N, and one half-filled $5p$ orbital on I. Each half-filled $2p$ orbital from N will overlap with one half-filled $5p$ orbital of an I. Thus, there will be three N—I bonds. The I atoms will be oriented in the same direction as the three $2p$ orbitals of N: toward the $x-, y-$, and z-directions of a Cartesian coordinate system. Thus, the I—N—I angles will be approximately 90° (probably larger because the I atoms will repel each other). The three I atoms will lie in the same plane at the points of a triangle, with the N atom centered above them. The molecule is trigonal pyramidal. (The same molecular shape is predicted if N is assumed to be sp^3 hybridized, but with 109.5° rather than 90° bond angles.)

1B The valence-shell orbital diagrams of N and H are as follows. N: [He] $_{2s}\boxed{\uparrow\downarrow}\ {}_{2p}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ H: $_{1s}\boxed{\uparrow}$ There are three half-filled orbitals on N and one half-filled orbital on each H. There will be three N—H bonds, with bond angles of approximately 90°. The molecule is trigonal pyramid. (We obtain the same molecular shape if N is assumed to be sp^3 hybridized, but bond angles are closer to 109.5°, the tetrahedral bond angle.) VSEPR theory begins with the Lewis structure and notes that there are three bond pairs and one lone pair attached to N. This produces a tetrahedral electron pair geometry and a trigonal pyramidal molecular shape with bond angles a bit less than the tetrahedral angle of 109.5° because of the lone pair. Since VSEPR theory makes a prediction closer to the experimental bond angle of 107°, it seems more appropriate in this case.

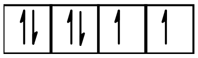
2A Following the strategy outlined in the textbook, we begin by drawing a plausible Lewis structure for the cation in question. In this case, the Lewis structure must contain 20 valence electrons. The skeletal structure for the cation has a chlorine atom, the least electronegative element present, in the central position. Next we join the terminal chlorine and fluorine atoms to the central chlorine atom via single covalent bonds and then complete the octets for all three atoms by placing three lone pairs around the terminal atoms and two lone pairs around the central atom.



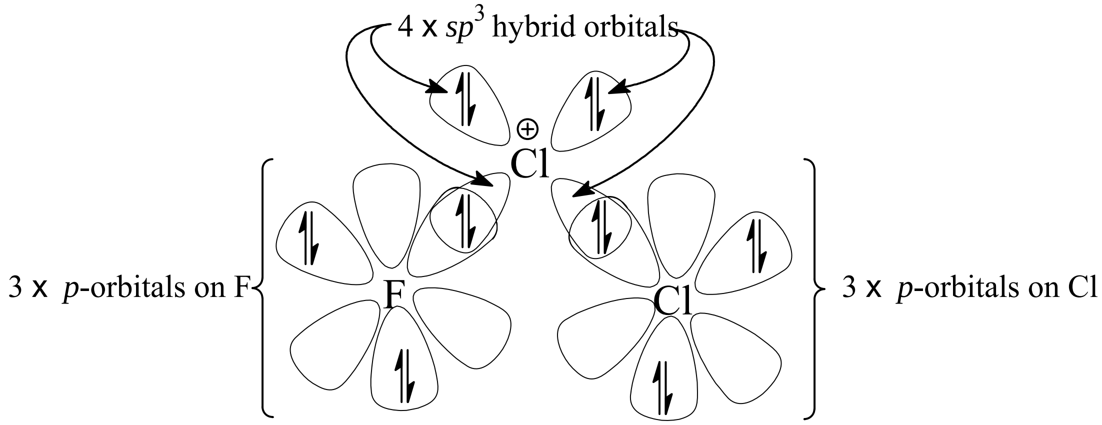
$$|\overline{\underline{F}}-\overset{\oplus}{\overline{\underline{Cl}}}-\overline{\underline{Cl}}|$$

With this bonding arrangement, the central chlorine atom ends up with a 1+ formal charge.

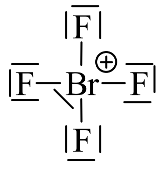
Once the Lewis diagram is complete, we can then use the VSEPR method to establish the geometry for the electron pairs on the central atom. The Lewis structure has two bonding electron pairs and two lone pairs of electrons around the central chlorine atom. These four pairs of electrons assume a tetrahedral geometry to minimize electron-electron repulsions. The VSEPR notation for the Cl_2F^+ ion is AX_2E_3. According to Table 11.1, molecules of this type exhibit an <u>angular</u> molecular geometry. Our next task is to select a hybridization scheme that is consistent with the predicted shape. It turns out that the only way we can end up with a tetrahedral array of electron groups is if the central chlorine atom is sp^3 hybridized. In this scheme, two of the sp^3 hybrid orbitals are filled, while the remaining two are half occupied.


sp^3 hybridized central chlorine atom (Cl^+)

The Cl—F and Cl—Cl bonds in the cation are then formed by the overlap of the half-filled sp^3 hybrid orbitals of the central chlorine atom with the half-filled *p*-orbitals of the terminal Cl and F atoms. Thus, by using sp^3 hybridization, we end up with the same <u>bent</u> molecular geometry for the ion as that predicted by VSEPR theory (when the lone pairs on the central atom are ignored)



2B As was the case in 2A, we begin by drawing a plausible Lewis structure for the cation in question. This time, the Lewis structure must contain 34 valence electrons. The skeletal structure has bromine, the least electronegative element present, as the central atom. Next, we join the four terminal fluorine atoms to the central bromine atom via single covalent bonds and complete the octets for all of the fluorine atoms by assigning three lone pairs to each fluorine atom. Placing the last two electrons on the central bromine atom completes the diagram.

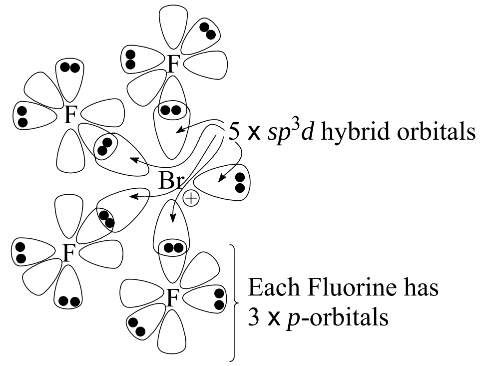


In order to accommodate ten electrons, the bromine atom is forced to expand its valence shell. Notice that the Br ends up with a 1+ formal charge in this structure. With the completed Lewis structure in hand, we can then use VSEPR theory to establish the geometry for the electron pairs around the central atom. The Lewis structure has four bonding pairs and one lone pair of electrons around the central bromine atom. These five pairs of electrons assume a trigonal bipyramidal geometry to minimize electron-electron repulsions. The VSEPR notation for the BrF_4^+ cation is AX_4E. According to Table 11.1, molecules of this type exhibit a see-saw molecular geometry.

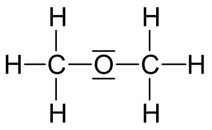
Next we must select a hybridization scheme for the Br atom that is compatible with the predicted shape. It turns out that only sp^3d hybridization will provide the necessary trigonal bipyramidal distribution of electron pairs around the bromine atom. In this scheme, one of the sp^3d hybrid orbitals is filled, while the remaining four are half-occupied.

$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ sp^3d hybridized central bromine atom (Br^+)

The four Br—F bonds in the cation are then formed by the overlap of the four half-filled sp^3d hybrid orbitals of the bromine atom with the half-filled *p*-orbitals of the four separate terminal fluorine atoms. Thus, by using sp^3d hybridization, we end up with the same see-saw molecular geometry for the cation as that predicted by VSEPR theory (when the lone pair on Br is ignored).

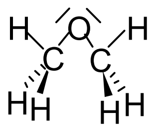


3A We begin by writing the Lewis structure. The H atoms are terminal atoms. There are three central atoms and $(3\times1)+4+6+4+(3\times1)=20$ valence electrons, or 10 pairs. A plausible Lewis structure is drawn at right. Each central atom is surrounded by four electron pairs, requiring sp^3 hybridization. The valence-shell orbital diagrams for the atoms follow.



H $_{1s}\boxed{\uparrow}$ C [He]$_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$ O [He]$_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

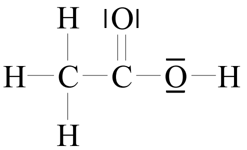
The valence-shell orbital diagrams for the hybridized central atoms then are:



C$_{sp^3}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ O$_{sp^3}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

All bonds in the molecule are σ bonds. The H—C—H bond angles are 109.5°, as are the H—C—O bond angles. The C—O—C bond angle is possibly a bit smaller than 109.5° because of the repulsion of the two lone pairs of electrons on O. A wedge-and-dash sketch of the molecule is at right.

3B The H atoms and one O are terminal atoms in the Lewis structure, which has $3\times1+4+4+2\times6+1=24$ valence electrons, or 12 pairs. The left-most C and the right-most O are surrounded by four electron pairs, and thus require sp^3 hybridization. The central carbon is surrounded by three electron groups and is sp^2 hybridized. The orbital diagrams for the un-hybridized atoms are:

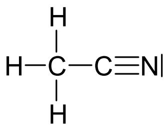


H:$_{1s}\boxed{\uparrow}$ C: [He]$_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$ O: [He]$_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

Hybridized orbital diagrams:

C: [He]$_{sp^3}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ C: [He]$_{sp^2}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $_{2p}\boxed{\uparrow}$ O:[He]$_{sp^3}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$ terminal O: [He]$_{sp^2}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$ $_{2p}\boxed{\uparrow}$

There is one π bond in the molecule: between the 2*p* on the central C and the 2*p* on the terminal O. The remaining bonds are σ bonds. The H—C—H and H—C—C bond angles are109.5°. The H—O—C angle is somewhat less, perhaps 105° because of lone pair repulsion. The C—C—O bond angles and O—C—O bond angles are all 120°.



4A There are four bond pairs around the left-hand C, requiring sp^3 hybridization. Three of the bonds that form are C—H sigma bonds resulting from the overlap of a half-filled sp^3 hybrid orbital on C with a half-filled $1s$ orbital on H. The other C has two attached electron groups, utilizing *sp* hybridization.
C: [He]$_{sp}\boxed{\uparrow}\boxed{\uparrow}$ $_{2p}\boxed{\uparrow}\boxed{\uparrow}$ The N atom is *sp* hybridized. N: [He] $_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$
The two C atoms join with a sigma bond: overlap of sp^2 on the left-hand C with *sp* on the right-hand C. The three bonds between C and N consist of a sigma bond (*sp* on C with *sp* on N), and two pi bonds (2*p* on C with 2*p* on N).

4B The bond lengths that are given indicate that N is the central atom. The molecule has $(2 \times 5) + 6 = 16$ valence electrons, or 8 pairs. Average bond lengths are: N—N = 145 pm, $\mathrm{N{=}N} = 123\text{ pm}$, $\mathrm{N \equiv N} = 110\text{ pm}$, N—O = 136 pm, $\mathrm{N{=}O} = 120\text{ pm}$. Plausible resonance structures are (with subscripts for identification):

$$\text{structure(1)} \quad |\mathrm{N_a} \equiv \mathrm{N_b^{\oplus}} - \overline{\underline{\mathrm{O}}}^{\ominus}| \leftrightarrow |\underline{\mathrm{N}}_{\mathrm{a}}^{\ominus} = \mathrm{N_b^{\oplus}} = \overline{\underline{\mathrm{O}}} \quad \text{structure(2)}$$

In both structures, the central N is attached to two other atoms, and possesses no lone pairs. The geometry of the molecule thus is linear and the hybridization on this central N is *sp*. $\mathrm{N_b}$ [He]$_{sp}\boxed{\uparrow\downarrow}\boxed{\uparrow}$ $_{2p}\boxed{\uparrow}\boxed{\uparrow}$ We will assume that the terminal atoms are not hybridized in either structure. Their valence-shell orbital diagrams are:
terminal N: $\mathrm{N_a}$ [He] $_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ O [He] $_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

In structure (1) the $\mathrm{N \equiv N}$ bond results from the overlap of three pairs of half-filled orbitals: (1) sp_x on $\mathrm{N_b}$ with $2p_x$ on $\mathrm{N_a}$ forming a σ bond, (2) $2p_y$ on $\mathrm{N_b}$ with $2p_y$ on $\mathrm{N_a}$ forming a π bond, and (3) $2p_z$ on $\mathrm{N_b}$ with $2p_z$ on $\mathrm{N_a}$ also forming a π bond. The N—O bond is a coordinate covalent bond, and requires that the electron configuration of O be written as O [He]$_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{}$ The N—O bond then forms by the overlap of the full sp_x orbital on $\mathrm{N_b}$ with the empty $2p$ orbital on O.

In structure (2) the $\mathrm{N{=}O}$ bond results from the overlap of two pairs of half-filled orbitals: (1) sp_y on $\mathrm{N_b}$ with $2p_y$ on O forming a σ bond and (2) $2p_z$ on $\mathrm{N_b}$ with $2p_z$ on O forming a π bond. The $\mathrm{N{=}N}$ σ bond is a coordinate covalent bond, and requires that the configuration of $\mathrm{N_a}$ be written $\mathrm{N_a}$ [He]$_{2s}\boxed{\uparrow\downarrow}$ $_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{}$. The $\mathrm{N{=}N}$ bond is formed by two overlaps: (1) the overlap of the full sp_y orbital on $\mathrm{N_b}$ with the empty $2p_y$ orbital on $\mathrm{N_a}$ to form a σ bond, and (2) the overlap of the half-filled $2p_x$ orbital on $\mathrm{N_b}$ with the half-filled $2p_x$ orbital on $\mathrm{N_a}$ to form a π bond. Based on formal charge arguments, structure (1) is preferred, because the negative formal charge is on the more electronegative atom, O.

5A An electron from $\mathrm{Li_2}$ removes a bonding electron because the valence molecular orbital diagram for $\mathrm{Li_2}$ is the same as that for $\mathrm{H_2}$, only it is just moved up a principal quantum level: $\sigma_{1s}{}^{b}\boxed{\uparrow\downarrow}$ $\sigma_{1s}{}^{*}\boxed{\uparrow\downarrow}$ $\sigma_{2s}{}^{b}\boxed{\uparrow\downarrow}$ $\sigma_{2s}{}^{*}\boxed{}$.

The molecular orbital diagram for $\mathrm{Li_2^+}$ is: $\sigma_{1s}{}^{b}\boxed{\uparrow\downarrow}$ $\sigma_{1s}{}^{*}\boxed{\uparrow\downarrow}$ $\sigma_{2s}{}^{b}\boxed{\uparrow}$ $\sigma_{2s}{}^{*}\boxed{}$

The bond order in Li_2^+ is: 1/2, while that in Li_2 is one. Thus, the Li-Li bond in Li_2^+ should be one half as strong as the Li-Li bond in Li_2: $106\ \text{kJ/mol} \div 2 = 53\ \text{kJ/mol}\ Li_2^+$

5B The H_2^- ion contains 1 electron from each H plus 1 electron for the negative charge for a total of three electrons. Its molecular orbital diagram is $\sigma_{1s}\boxed{\uparrow\downarrow}\ \sigma_{1s}^*\boxed{\uparrow}$. There are two bonding and one antibonding electrons. The bond order in H_2^- is obtained as follows:

$$\text{bond order} = \frac{(2\text{ bonding e}^- - 1\text{ antibonding e}^-)}{2} = \frac{1}{2}$$

Thus, we would expect the ion H_2^- to be stable, with a bond strength about half that of a hydrogen molecule.

6A For each case, the empty molecular-orbital diagram has the following appearance. (KK indicates that the molecular orbitals formed from 1*s* atomic orbitals are full: KK = $\sigma_{1s}\boxed{\uparrow\downarrow}\ \sigma_{1s}^*\boxed{\uparrow\downarrow}$

KK = $\sigma_{2s}\square\ \sigma_{2s}^*\square\ \ \sigma_{2p}\square\ \ \pi_{2p}\square\square\ \ \pi_{2p}^*\square\square\ \sigma_{2p}^*\square$. We need to simply count up the total number of electrons in each species, and place them in the valence-shell molecular-orbital diagram.

(a) N_2^+ has $(2\times5)-1=9$ valence electrons. Its molecular orbital diagram is

N_2^+ KK $\sigma_{2s}\boxed{\uparrow\downarrow}\ \sigma_{2s}^*\boxed{\uparrow\downarrow}\ \ \pi_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\ \sigma_{2p}\boxed{\uparrow}\ \ \pi_{2p}^*\square\square\ \sigma_{2p}^*\square$

bond order = (7 bonding electrons −2 antibonding electrons) ÷2 = 2.5

(b) Ne_2^+ has $(2\times8)-1=15$ valence electrons. Its molecular orbital diagram is

Ne_2^+ KK $\sigma_{2s}\boxed{\uparrow\downarrow}\ \sigma_{2s}^*\boxed{\uparrow\downarrow}\ \ \sigma_{2p}\boxed{\uparrow\downarrow}\ \ \pi_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\ \ \pi_{2p}^*\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\ \sigma_{2p}^*\boxed{\uparrow}$

bond order = (8 bonding electrons −7 antibonding electrons) ÷2 = 0.5

(c) C_2^{2-} has $(2\times4)+2=10$ valence electrons. Its molecular orbital diagram is

C_2^{2-} KK $\sigma_{2s}\boxed{\uparrow\downarrow}\ \sigma_{2s}^*\boxed{\uparrow\downarrow}\ \ \pi_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\ \sigma_{2p}\boxed{\uparrow\downarrow}\ \ \pi_{2p}^*\square\square\ \sigma_{2p}^*\square$

bond order = (8 bonding electrons −2 antibonding electrons) ÷2 = 3.0

6B For each case, the empty molecular-orbital diagram has the following appearance. (KK indicates that the molecular orbitals formed from 1*s* atomic orbitals are full:

KK = $\sigma_{1s}\boxed{\uparrow\downarrow}\ \sigma_{1s}^*\boxed{\uparrow\downarrow}$

KK $\sigma_{2s}\square\ \sigma_{2s}^*\square\ \ \sigma_{2p}\square\ \pi_{2p}\square\square\ \ \pi_{2p}^*\square\square\sigma_{2p}^*\square$. All of these species are based on O_2, which has 2×6 = 12 valence electrons. We simply put the appropriate number of valence electrons in each diagram and determine the bond order.

O_2^+ 11 v.e. KK $\sigma_{2s}\boxed{\uparrow\downarrow}\ \sigma_{2s}^*\boxed{\uparrow\downarrow}\ \sigma_{2p}\boxed{\uparrow\downarrow}\ \ \pi_{2p}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\ \ \pi_{2p}^*\boxed{\uparrow}\square\ \ \sigma_{2p}^*\square$

bond order = (8 bonding e^- –5 antibonding e^-) ÷2 = 2.5; bond length =112 pm

O_2 12 v.e. KK

bond order = (8 bonding e^- – 4 antibonding e^-) ÷ 2 = 2.0 ; bond length = 121 pm

O_2^- 13 v.e. KK

bond order = (8 bonding e^- –5 antibonding e^-) ÷ 2 = 1.5 ;bond length = 128 pm

O_2^{2-} 14 v.e. KK σ_{2s}⇅ σ_{2s}^*⇅ σ_{2p}⇅ π_{2p}⇅⇅ π_{2p}^*⇅⇅ σ_{2p}^*☐

bond order = (8 bonding electrons –6 antibonding electrons) ÷2 = 1.0 ;
bond length = 149 pm. We see that the bond length does indeed increase as the bond order decreases. Longer bonds are weaker bonds.

7A There are 8 valence electrons that must be placed into the molecular orbital diagram for CN^+ (5 electrons from nitrogen, four electrons from carbon and one electron is removed to produce the positive charge). Since both C and N precede oxygen and they are not far apart in atomic number, we must use the modified molecular-orbital energy-level diagram to get the correct configuration. By following the Aufbau orbital filling method, one obtains the ground state diagram asked for in the question.

	σ_{2s}	σ^*_{2s}	π_{2p}	σ_{2p}	π^*_{2p}	σ^*_{2p}
CN^+	⇅	⇅	⇅ ⇅	☐	☐☐	☐

The bond order for the C—N bond in CN^+ is $\frac{6 \text{ bonding } e^- - 2 \text{ antibonding } e^-}{2} = 2.0$

Thus the C and N atoms in CN^+ are joined by a double bond.

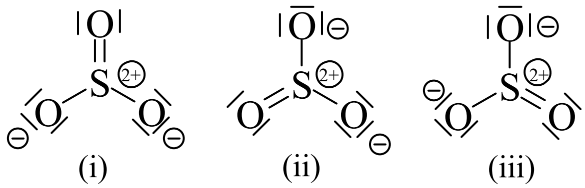
7B There are 8 valence electrons that must be placed in the molecular orbital diagram for BN (3 electrons from boron and five electrons from nitrogen). Since both B and N precede oxygen and they are not far apart in atomic numbers, we must use the modified molecular-orbital energy-level diagram to get the correct configuration. By following the Aufbau orbital filling method, one obtains the ground-state diagram asked for in the question.

	σ_{2s}	σ^*_{2s}	π_{2p}	σ_{2p}	π^*_{2p}	σ^*_{2p}
BN	⇅	⇅	⇅ ⇅	☐	☐☐	☐

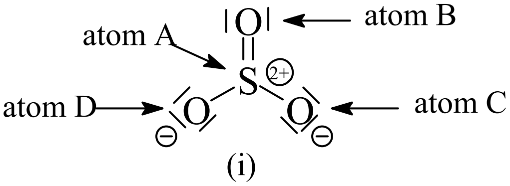
The bond order for the B—N bond in BN is $\frac{6 \text{ bonding } e^- - 2 \text{ antibonding } e^-}{2} = 2$

Thus, the B and N atoms in BN are joined by a double bond.

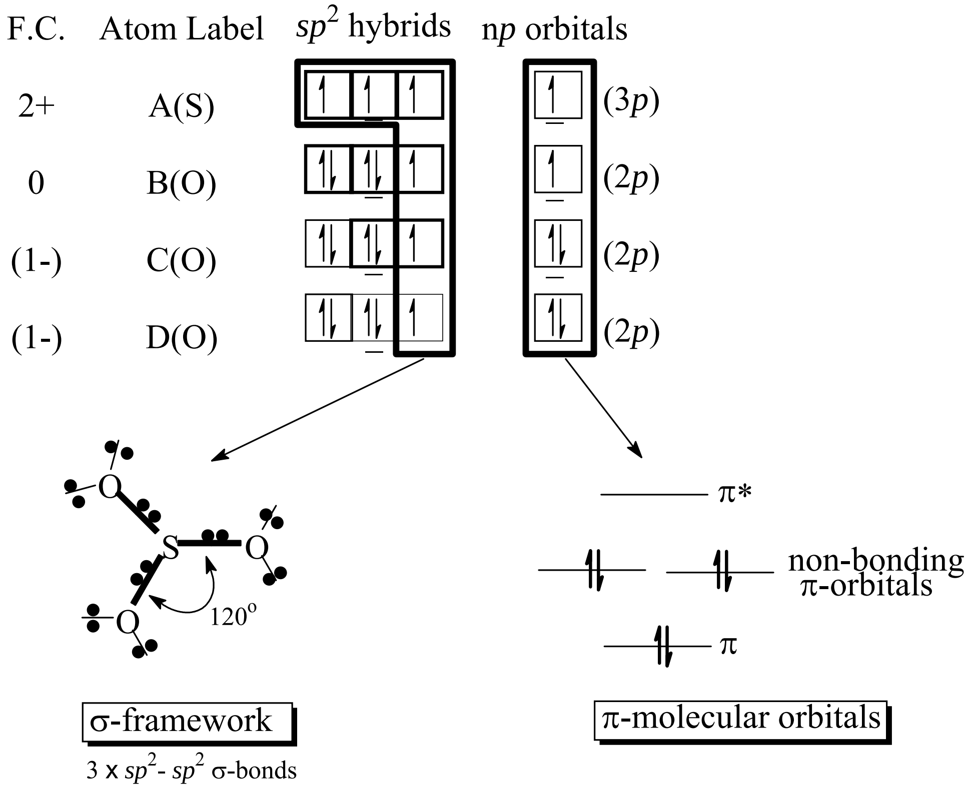
8A In this exercise we will combine valence-bond and molecular orbital methods to describe the bonding in the SO_3 molecule. By invoking a π-bonding scheme, we can replace the three resonance structures for SO_3 (shown below) with just one structure that exhibits both σ-bonding and delocalized π-bonding.



We will use structure (i) to develop a combined localized/delocalized bonding description for the molecule. (Note: Any one of the three resonance contributors can be used as the starting structure.) We begin by assuming that every atom in the molecule is *sp*^{2} hybridized to produce the σ-framework for the molecule. The half-filled *sp*^{2} hybrid orbitals of the oxygen atoms will each be overlapped with a half-filled *sp*^{2} hybrid orbital on sulfur. By contrast, to generate a set of π molecular orbitals, we will combine one unhybridized 2*p* orbital from each of three oxygen atoms with an unhybridized 3*p* orbital on the sulfur atom. This will generate four π molecular orbitals: a bonding molecular orbital, two nonbonding molecular orbitals, and an antibonding orbital. Remember that the number of valence electrons assigned to each atom must reflect the formal charge for that atom. Accordingly, sulfur, with a 2+ formal charge, can have only four valence electrons, the two oxygens with a 1- formal charge must each end up with 7 electrons and the oxygen with a zero formal charge must have its customary six electrons

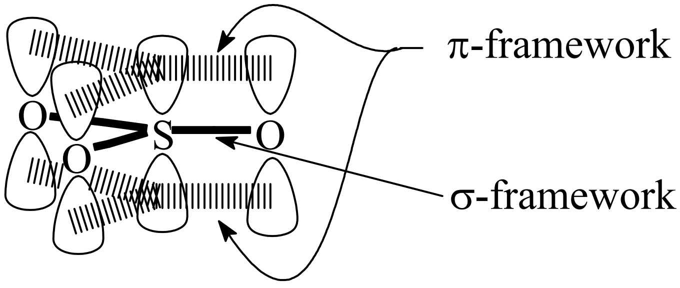


Let's begin assigning valence electrons by half-filling three *sp*^{2} hybrid orbitals on the sulfur atom (atom A) and one *sp*^{2} hybrid orbital on each of the oxygen atoms (atoms B, C and D) Next, we half-fill the lone unhybridized 3*p* orbital on sulfur and the lone 2*p* orbital on the oxygen atom with a formal charge of zero (atom B). Following this, the 2*p* orbital of the other two oxygen atoms (atoms C and D), are filled and then lone pairs are placed in the *sp*^{2} hybrid orbitals that are still empty. At this stage, then, all 24 valence electrons have been put into atomic and hybrid orbitals on the four atoms. Now we overlap the six half-filled *sp*^{2} hybrid orbitals to generate the σ-bond framework and combine the three 2*p* orbitals (2 filled, one half-filled) and the 3*p* orbital (half-filled) to form the four π-molecular orbitals, as shown below:



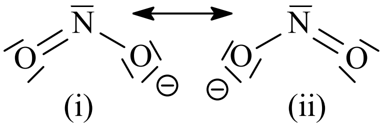
Overall bond order for this set of π-molecular orbitals $\frac{2 \text{ bonding e}^- - 0 \text{ antibonding e}^-}{2} = 1$

The π-bond is spread out evenly over the three S—O linkages. This leads to an average bond order of 1.33 for the three S—O bonds in SO_3. By following this "combined approach", we end up with a structure that has the σ-bond framework sandwiched within the delocalized π-molecular orbital framework:

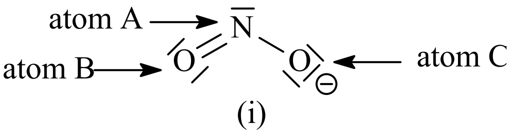


This is a much more accurate description of the bonding in SO_3 than that provided by any one of the three Lewis diagrams shown above.

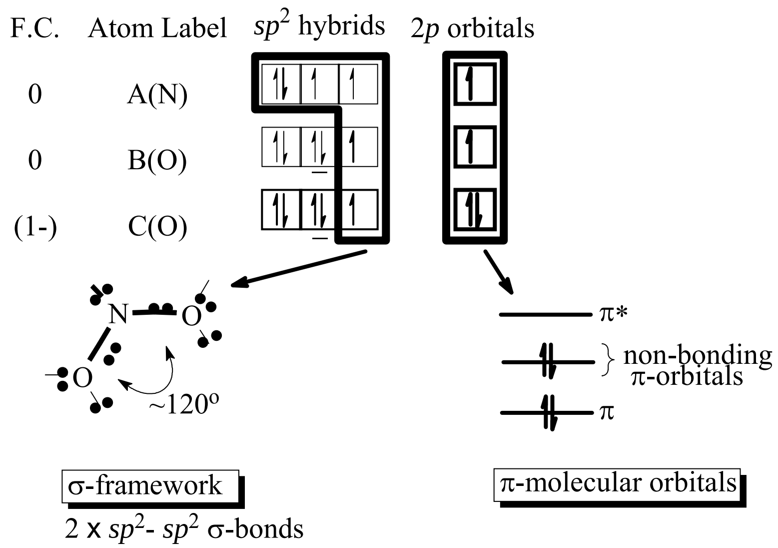
8B We will use the same basic approach to answer this question as was used to solve Practice Example 11-8A. This time, the bonding in NO_2^- will be described by combining valence-bond and molecular orbital theory. With this approach we will be able to generate a structure that more accurately describes the bonding in NO_2^- than either of the two equivalent Lewis diagrams that can be drawn for the nitrate ion (below).



Structure (i) will be used to develop the combined localized/delocalized bonding description for the anion (either structure could have been used as the starting structure). We begin by assuming that every atom in the molecule is sp^2 hybridized. To produce the σ-framework for the molecule, the half-filled sp^2 orbitals of the oxygen atoms will be overlapped with a half-filled sp^2 orbital of nitrogen. By contrast, to generate a set of π-molecular orbitals, we will combine one unhybridized 2*p* orbital from each of the two oxygen atoms with an unhybridized 2*p* orbital on nitrogen. This will generate three π molecular orbitals: a bonding molecular orbital, a non-bonding molecular orbital and an antibonding molecular orbital.

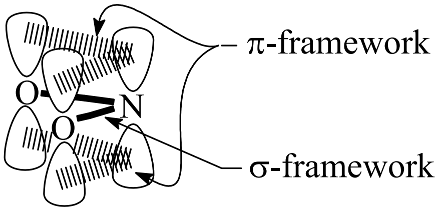


Remember that the number of valence electrons assigned to each atom must reflect the formal charge for that atom. Accordingly, the oxygen with a 1- formal charge (atom C) must end up with 7 electrons, whereas the nitrogen atom (atom A) and the other oxygen atom (atom B) must have their customary 5 and 6 valence electrons, respectively, because they both have a formal charge of zero. Let's begin assigning valence electrons by half-filling two sp^2 hybrid orbitals on the nitrogen atom (atom A) and one sp^2 hybrid orbital on each oxygen atom (atoms B and C). Next, we half-fill the lone 2*p* orbital on nitrogen (atom A) and the lone 2*p* orbital on the oxygen atom with a formal charge of zero (atom B). Following this, the 2*p* orbital for the remaining oxygen (atom C) is filled and then lone pairs are placed in the sp^2 hybrid orbitals that are still empty. At this stage, then, all 18 valence electrons have been put into atomic and hybrid orbitals on the three atoms. Now, we overlap the four half-filled sp^2 hybrid orbitals to generate the σ-bond framework and combine the three 2*p* orbitals (two half-filled, one filled) to form three π-molecular orbitals as shown below



Overall bond order for this set of π-molecular orbitals

$\frac{2\text{ bonding e}^- - 0\text{ antibonding e}^-}{2} = 1$ The π bond is spread out evenly over the two N—O linkages. This leads to an average bond order of 1.5 for each of the two N—O bonds in NO_2^-. By following this combined approach, we end up with a structure that has the σ-bond framework sandwiched within the delocalized π-molecular orbitals:

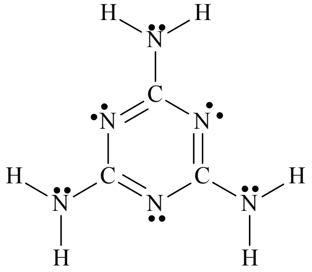


This is a much more accurate depiction of the bonding in NO_2^- than that provided by one of the two Lewis diagrams given above.

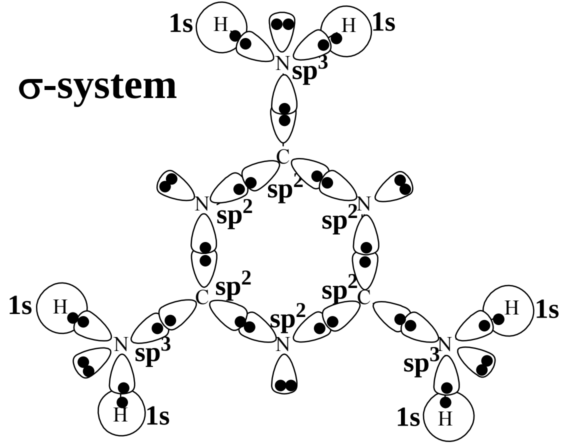
INTEGRATIVE EXAMPLE

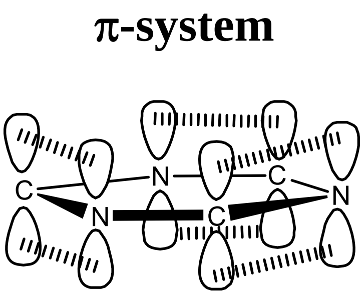
A. We will assume 100 g of the compound and find the empirical formula in the usual way.
moles of carbon = 28.57 g(1 mole/12.011g) = 2.379 mol
moles of hydrogen = 4.80 g(1 mole/1.008g) = 4.76 mol
moles of nitrogen = 66.64 g(mole/14.01g) = 4.76 mol
Dividing by 2.38 we get: C(2.379/2.379) H(4.76/2.379) N(4.758/2.379)
This yields an empirical formula of: CH_2N_2 From the description given in the question, the molecular formula is $C_3N_6H_6$

(a) Lewis structure for $C_3N_6H_6$ (based on info provided)

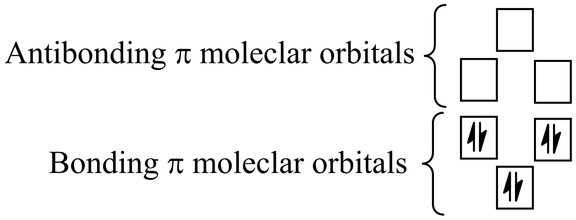


(b) Valence-bond description σ and π-bonding systems





(c) The bonds in the ring system are similar to those seen in benzene (C_6H_6) and pyridine (C_5H_5N), namely



One 2p electron
from each of the
atoms is placed
in the ring

<u>**B.**</u> We have 2.464 g of dimethylglyoxime (DMG)

moles C : 3.735(1 mol C/44.01g CO_2) = 0.08487 mol C
moles H : 1.530(2 mol H/18.01g H_2O) = 0.1698 mol C

First we find the excess H_2SO_4 left over from the nitrogen determination:

$$18.6\text{ml}\times\frac{1\text{L}}{1000\text{ ml}}\times\frac{0.2050\text{ mol NaOH}}{1\text{L}}\times\frac{1\text{ mol H}_2\text{SO}_4}{2\text{ mol NaOH}}=1.910\times10^{-3}\text{mol H}_2\text{SO}_4\text{ in excess}$$

Next we find the moles of H_2SO_4 initially added:

$$50.00\text{ mL}\times\frac{1\text{L}}{1000\text{ml}}\times\frac{0.3600\text{ mol H}_2\text{SO}_4}{1\text{L}}=1.800\times10^{-2}\text{mol H}_2\text{SO}_4\text{ used}$$

Now we find the moles of H_2SO_4 that reacted:

$$\text{mole } H_2SO_4 \text{that reacted } = 1.800\times10^{-2}\text{mol } H_2SO_4 \text{ initially used} - 1.910\times10^{-3}\text{mol } H_2SO_4 \text{ in excess}$$

mole H_2SO_4 that reacted = 1.609×10^{-2} mol H_2SO_4
Therefore, the moles of nitrogen in 1.868 g DMG sample is:

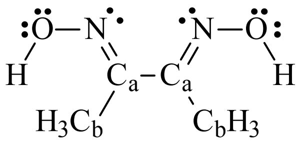
$$0.01609 \text{ mol } H_2SO_4 \times \frac{2 \text{ mol } NH_3}{1 \text{ mol } H_2SO_4} \times \frac{1 \text{ mol N}}{1 \text{ mol } NH_3} = 3.218\times10^{-2}\text{mol nitrogen (0.4507 g nitrogen)}$$

For a 1.868 g sample, moles of C and H present are fond as follows:
C: (1.868/2.464)(0.08487) = 0.06434 mol C (0.7728 g C)
H: (1.868/2.464)(0.1698) = 0.1287 mol H (0.1297 g H)

Mass of oxygen in 1.868 g DMG sample is 1.868 - 0.4507- 0.7728 -0.1298 = 0.515 g oxygen (0.0322 mol O)

Empirical formula: C(0.0643/0.0322) H(0.1287/0.0322) N(0.03218/0.0322) O(0.0322/0.0322) or C_2H_4NO The empirical molecular mass is 58 u and the true molecular mass is 116.12 u so we multiply the empirical formula by two to get the molecular formula of $C_4H_8N_2O_2$. The structure is $H_3C\text{-}C(=NOH)\text{-}C(=NOH)\text{-}CH_3$

Hybrid orbitals used:
C_b-H : σ H(1s) – $C_b(sp^3)$
C_a=N: σ $C_a(sp^2)$ –$N(sp^2)$, π: C_a(2p) – N(2p)
N-O: σ $N(sp^2)$ –$O(sp^3)$
C_a-C_a: σ $C_a(sp^2)$ –$C_a(sp^2)$
C_a-C_b: σ $C_b(sp^3)$ –$C_a(sp^2)$
O-H : σ H(1s) – $O(sp^3)$



EXERCISES

Valence-Bond Method

Note: In VSEPR theory, the term “bond pair” is used for a single bond, a double bond, or a triple bond, even though a single bond consists of one pair of electrons, a double bond two pairs of electrons, and a triple bond three pairs of electrons. To avoid any confusion between the number of electron pairs actually involved in the bonding to a central atom, and the number of atoms bonded to that central atom, we shall occasionally use the term “ligand” to indicate an atom or a group of atoms attached to the central atom.

1. There are several ways in which valence-bond theory is superior to Lewis structures in describing covalent bonds. *First*, valence-bond theory clearly distinguishes between sigma and pi bonds. In Lewis theory, a double bond appears to be just two bonds and it is not clear why a double bond is not simply twice as strong as a single bond. In valence-bond theory, it is clear that a sigma bond must be stronger than a pi bond, for the orbitals overlap more effectively in a sigma bond (end-to-end) than they do in a pi bond (side-to-side). *Second*, molecular geometries are more directly obtained in valence-bond theory than in Lewis theory. Although valence-bond theory requires the introduction of hybridization to explain these geometries, Lewis theory does not predict geometries at all; it simply provides the basis from which VSEPR theory predicts geometries. *Third*, Lewis theory does not explain hindered rotation about double bonds. With valence-bond theory, any rotation about a double bond involves cleavage of the π-bond, which would require the input of considerable energy.

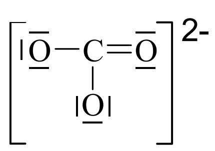
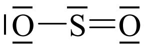
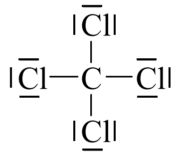
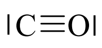
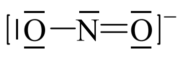
3. **(a)** Lewis theory does not describe the shape of the water molecule. It does indicate that there is a single bond between each H atom and the O atom, and that there are two lone pairs attached to the O atom, but it says nothing about molecular shape.

(b) In valence-bond theory using simple atomic orbitals, each H—O bond results from the overlap of a 1*s* orbital on H with a 2*p* orbital on O. The angle between 2*p* orbitals is 90° so this method initially predicts a 90° bond angle. The observed 104° bond angle is explained as arising from repulsion between the two slightly positively charged H atoms.

(c) In VSEPR theory the H_2O molecule is categorized as being of the AX_2E_2 type, with two atoms and two lone pairs attached to the central oxygen atom. The lone pairs repel each other more than do the bond pairs, explaining the smaller than 109.5° tetrahedral bond angle.

(d) In valence-bond theory using hybrid orbitals, each H—O bond results from the overlap of a 1*s* orbital on H with an sp^3 orbital on O. The angle between sp^3 orbitals is 109.5°. The observed bond angle of 104° is rationalized based on the greater repulsion of lone pair electrons when compared to bonding pair electrons.

5. Determining hybridization is made easier if we begin with Lewis structures. Only one resonance form is drawn for CO_3^{2-}, SO_2, and NO_2^-.

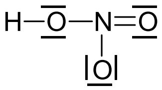






The C atom is attached to three ligands and no lone pairs and thus is sp^2 hybridized in CO_3^{2-}. The S atom is attached to two ligands and one lone pair and thus is sp^2 hybridized in SO_2. The C atom is attached to four ligands and no lone pairs and thus is sp^3 hybridized in CCl_4. Both the oxygen and the carbon in Co are *sp* hybridized. The N atom is attached to two ligands and one lone pair in NO_2^- and thus is sp^2 hybridized. Thus, the central atom is sp^2 hybridized in SO_2, CO_3^{2-}, and NO_2^-.

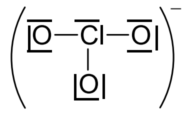
7. For each species, we first draw the Lewis structure, to help explain the bonding.

(a) In CO_2, there are a total of $4+(2\times 6)=16$ valence electrons, or 8 pairs. C is the central atom. The Lewis structure is $\underline{\overline{O}}=C=\underline{\overline{O}}$ The molecule is linear and C is *sp* hybridized.

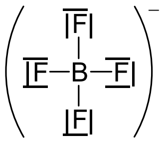
(b) In $HONO_2$, there are a total of $1+5+(3\times 6)=24$ valence electrons, or 12 pairs. N is the central atom, and a plausible Lewis structure is shown on the right The molecule is trigonal planar around N which is sp^2 hybridized. The O in the H—O—N portion of the molecule is sp^3 hybridized.



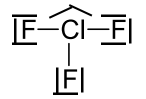
(c) In ClO_3^-, there are a total of $7+(3\times 6)+1=26$ valence electrons, or 13 pairs. Cl is the central atom, and a plausible Lewis structure is shown on the right. The electron-group geometry around Cl is tetrahedral, indicating that Cl is sp^3 hybridized.



(d) In BF_4^-, there are a total of $3+(4\times 7)+1=32$ valence electrons, or 16 pairs. B is the central atom, and a plausible Lewis structure is shown on the right. The electron-group geometry is tetrahedral, indicating that B is sp^3 hybridized.



9. The Lewis structure of ClF_3 is shown on the right. There are three atoms and two lone pairs attached to the central atom, its hybridization is sp^3d, which is achieved as follows. $\mathrm{Cl_{unhyb}}[\mathrm{Ne}]\ {}_{3s}\boxed{\uparrow\downarrow}\ {}_{3p}\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow}\ {}_{3d}\boxed{||||} \longrightarrow \mathrm{Cl_{hyb}}\ [\mathrm{Ne}]\ {}_{dsp^3}\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow|\uparrow|\uparrow}\ {}_{3d}\boxed{|||}$ The orbital diagram of F is $[\mathrm{He}]_{2s}\boxed{\uparrow\downarrow}\ {}_{2p}\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow}$ Each of the three sigma bonds are formed by the overlap of a $2p$ orbital on F with one of the half-filled dsp^3 orbitals on Cl. Since the dsp^3 hybridization has a trigonal bipyramidal shape, and the two lone pairs occupy the equatorial positions in the molecule, ClF_3 is T-shaped.



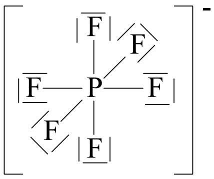
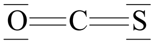
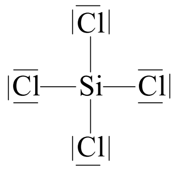
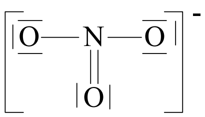
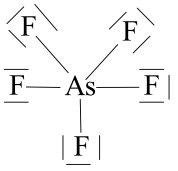
11. **(a)** In PF_6^- there are a total of $5+(6\times 7)+1=48$ valence electrons, or 24 pairs. A plausible Lewis structure is shown below. In order to form the six P—F bonds, the hybridization on P must be sp^3d^2.

(b) In COS there are a total of $4+6+6=16$ valence electrons, or 8 pairs. A plausible Lewis structure is shown below. In order to bond two atoms to the central C, the hybridization on that C atom must be *sp*.

(c) In $SiCl_4$, there are a total of $4+(4\times 7)=32$ valence electrons, or 16 pairs. A plausible Lewis structure is given below. In order to form four Si—Cl bonds, the hybridization on Si must be sp^3.

(d) In NO_3^-, there are a total of $5+(3\times 6)+1=24$ valence electrons, or 12 pairs. A plausible Lewis structure is given below. In order to bond three O atoms to the central N atom, with no lone pairs on that N atom, its hybridization must be sp^2.

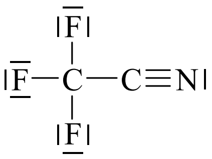
(e) In AsF_5, there are a total of $5+(5\times 7)=40$ valence electrons, or 20 pairs. A plausible Lewis structure is shown below. This is a molecule of the type AX_5. To form five As—F bonds, the hybridization on As must be sp^3d.

13. **(a)** This is a planar molecule. The hybridization on C is sp^2 (one bond to each of the three attached atoms).

(b) $|N\equiv C—C\equiv N|$ is a linear molecule. The hybridization for each C is *sp* (one bond to each of the two ligands).

(c) Trifluoroacetonitrile is neither linear nor planar. The shape around the left-hand C is tetrahedral and that C has sp^3 hybridization. The shape around the right-hand carbon is linear and that C has *sp* hybridization.(N atom is *sp* hybridized).

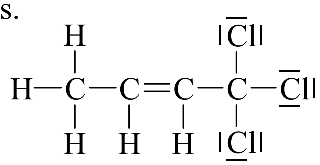


(d) $[|\underline{\overline{S}}-C\equiv N|]^-$ is a linear molecule. The hybridization for C is *sp*.

15. **(a)** In HCN, there are a total of $1+4+5=10$ valence electrons, or 5 electron pairs. A plausible Lewis structure follows. $H—C\equiv N|$. The H—C bond is a σ bond, and the $C\equiv N$ bond is composed of 1 σ and 2 π bonds.

(b) In C_2N_2, there are a total of $(2\times 4)+(2\times 5)=18$ valence electrons, or 9 electron pairs. A plausible Lewis structure follows: $|N\equiv C—C\equiv N|$ The C—C bond is a σ bond, and each $C\equiv N$ bond is composed of 1 σ and 2 π bonds.

(c) In $CH_3CHCHCCl_3$, there are a total of 42 valence electrons, or 21 electron pairs. A plausible Lewis structure is shown to the right. All bonds are σ bonds except one of the bonds that comprise the $C=C$ bond. The $C=C$ bond is composed of one σ and one π bond.

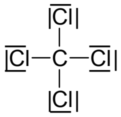


(d) In HONO, there is a total of $1+5+(2\times 6)=18$ valence electrons, or 9 electron pairs. A plausible Lewis structure is shown below:

$H-\underline{\overline{O}}-\overline{N}=\underline{\overline{O}}$

All single bonds in this structure are σ bonds. The double bond is composed of one σ and one π bond.

17. **(a)** In CCl_4, there are a total of $4+(4\times 7)=32$ valence electrons, or 8 electron pairs. C is the central atom. A plausible Lewis structure is shown to the right. The geometry at C is tetrahedral; C is sp^3 hybridized. Cl—C—Cl bond angles are 109.5°. Each C—Cl bond is represented by σ: $C(sp^3)^1$ — $Cl(3p)^1$



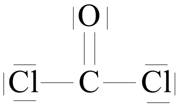
(b) In ONCl, there are a total of $6+5+7=18$ valence electrons, or 9 electron pairs. N is the central atom. A plausible Lewis structure is $\underline{\overline{O}}=\overline{N}-\underline{\overline{C}}l|$ The e$^-$ group geometry around N is triangular planar, and N is sp^2 hybridized. The O—N—C bond angle is about 120°. The bonds are: σ: $O(2p_y)^1$—$N(sp^2)^1$ σ: $N(sp^2)^1$—$Cl(3p_z)^1$

$\pi: O(2p_z)^1$—$N(2p_z)^1$

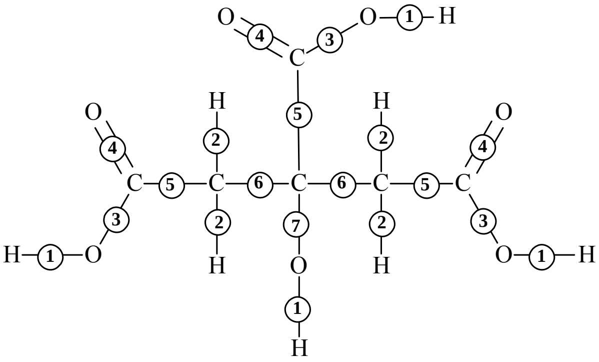
(c) In HONO, there are a total of $1+(2\times 6)+5=18$ valence electrons, or 9 electron pairs. A plausible Lewis structure is $H-\underline{\overline{O}}_a-\overline{N}=\underline{\overline{O}}_b$. The geometry of O_a is tetrahedral, O_a is sp^3 hybridized and the $H—O_a—N$ bond angle is (at least close to) 109.5°. The e$^-$ group geometry at N is trigonal, N is sp^2 hybridized, and the $O_a—N—O_b$ bond angle is 120°. The four bonds are represented as follows. σ: $H(1s)^1—O_a(sp^3)^1$

σ: $O_a(sp^3)^1—N(sp^2)^1$ σ: $N(sp^2)^1—O_b(2p_y)^1$ π: $N(2p_z)^1—O_b(2p_z)^1$.

(d) In $COCl_2$, there are a total of $4+6+(2\times 7)=24$ valence electrons, or 12 electron pairs. A plausible Lewis structure is shown to the right. The e$^-$ group geometry around C is trigonal planar; all bond angles around C are 120°, and the hybridization of C is sp^2. The four bonds in the molecules are: $2\times\sigma: Cl(3p_x)^1—C(sp^2)^1$ σ: $O(2p_y)^1—C(sp^2)^1$ π: $O(2p_z)^1—C(2p_z)^1$.



19. Citric acid has the molecular structure shown below. Using Figure 11-17 as a guide, the flowing hybridization and bonding scheme is obtained for citric acid:

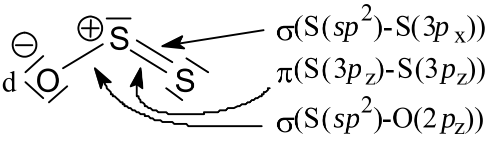


① σ(O(*sp*^{3}) - H(1*s*))
② σ(C(*sp*^{3}) - H(1*s*))
③ σ(C(*sp*^{2}) - O(*sp*^{3}))
④ σ(C(*sp*^{2}) - O(2*p*))
+
π(C(2*p*) - O(2*p*))
⑤ σ(C(*sp*^{3}) - C(*sp*^{2}))
⑥ σ(C(*sp*^{3}) - C(*sp*^{3}))
⑦ σ(C(*sp*^{3}) - O(*sp*^{3}))

21.

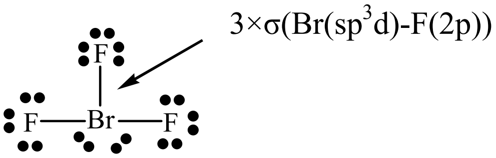
(a)

Central S is sp^2 hybridized and the terrminal O and S atoms are unhybridized

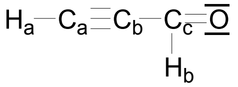


(b)

Br atom is sp^3 hybridized. F atoms are unhybridized.



23. The bond lengths are consistent with the left-hand C—C bond being a triple bond (120 pm), the other C—C bond being a single bond (154 pm) rather than a double bond (134 pm), and the C—O bond being a double bond (123 pm). Of course, the two C—H bonds are single bonds (110 pm). All of this is depicted in the Lewis structure on the right. The overlap that produces each bond follows:

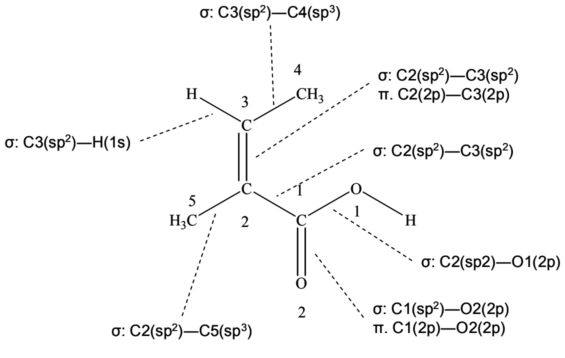


$$\sigma:\ \mathrm{C_a}\left(sp\right)^1\text{—}\mathrm{H_a}\left(1s\right)^1 \qquad \sigma:\ \mathrm{C_a}\left(sp\right)^1\text{—}\mathrm{C_b}\left(sp\right)^1 \qquad \sigma:\ \mathrm{C_b}\left(sp\right)^1\text{—}\mathrm{C_c}\left(sp^2\right)^1$$

$$\sigma:\ \mathrm{C_c}\left(sp^2\right)^1\text{—}\mathrm{H_b}\left(1s\right)^1 \qquad \sigma:\ \mathrm{C_c}\left(sp^2\right)^1\text{—}\mathrm{O}\left(2p_y\right)^1 \qquad \pi:\ \mathrm{C_a}\left(2p_y\right)^1\text{—}\mathrm{C_b}\left(2p_y\right)^1$$

$$\pi:\ \mathrm{C_a}\left(2p_z\right)^1\text{—}\mathrm{C_b}\left(2p_z\right)^1 \qquad \pi:\ \mathrm{C_c}\left(2p_z\right)^1\text{—}\mathrm{O}\left(2p_z\right)^1$$

25. The structure is shown below:



There are 8 atoms that are on the same plane (O1, O2, C1-5, H att. To C3). Furthermore, depending on the angle of rotation of the $–CH_3$ groups (C4 and C5), two H atoms can also be added to this total.

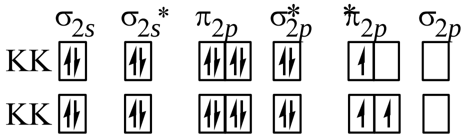
Molecular–Orbital Theory

27. The valence-bond method describes a covalent bond as the result of the overlap of atomic orbitals. The more complete the overlap, the stronger the bond. Molecular orbital theory describes a bond as a region of space in a molecule where there is a good chance of finding the bonding electrons. The molecular orbital bond does not have to be created from atomic orbitals (although it often is) and the orientations of atomic orbitals do not have to be manipulated to obtain the correct geometric shape. There is little concept of the relative energies of bonding in valence-bond theory. In molecular orbital theory, bonds are ordered energetically. These energy orderings, in fact, provide a means of checking the predictions of the theory through the spectroscopic analysis of the molecules.

29. The two molecular orbital diagrams follow:

N_2^- no. valence $e^- = (2\times5)+1=11$

N_2^{2-} no. valence $e^- = (2\times5)+2=12$



N_2^- bond order $= (8-3)\div2 = 2.5$ (stable)　N_2^{2-} bond order $= (8-4)\div2 = 2$ (stable)

31. In order to have a bond order higher than three, there would have to be a region in a molecular orbital diagram where four bonding orbitals occur together in order of increasing energy, with no intervening antibonding orbitals. No such region exists in any of the molecular orbital diagrams in Figure 11-25. Alternatively, three bonding orbitals would have to occur together energetically, following an electron configuration which, when full, results in a bond order greater than zero. This arrangement does not occur in any of the molecular orbital diagrams in Figure 11-25.

33. **(a)** A σ_{1s} orbital must be lower in energy than a σ_{1s}^* orbital. The bonding orbital always is lower than the antibonding orbital if they are derived from the same atomic orbitals.

(b) The σ_{2s} orbital is derived from the 2*s* atomic orbitals while the σ_{2p} molecular orbitals are constructed from 2*p* atomic orbitals. Since the 2s orbitals are lower in energy than the 2*p* orbitals, we would expect that the σ_{2p} molecular orbital would be higher in energy than the σ_{2s} molecular orbital.

(c) A σ_{1s}^* orbital should be lower than a σ_{2s} orbital, since the $1s$ atomic orbital is considerably lower in energy than is the $2s$ orbital.

(d) A σ_{2p} orbital should be lower in energy than a σ_{2p}^* orbital. Both orbitals are from atomic orbitals in the same subshell but we expect a bonding orbital to be more stable than an antibonding orbital.

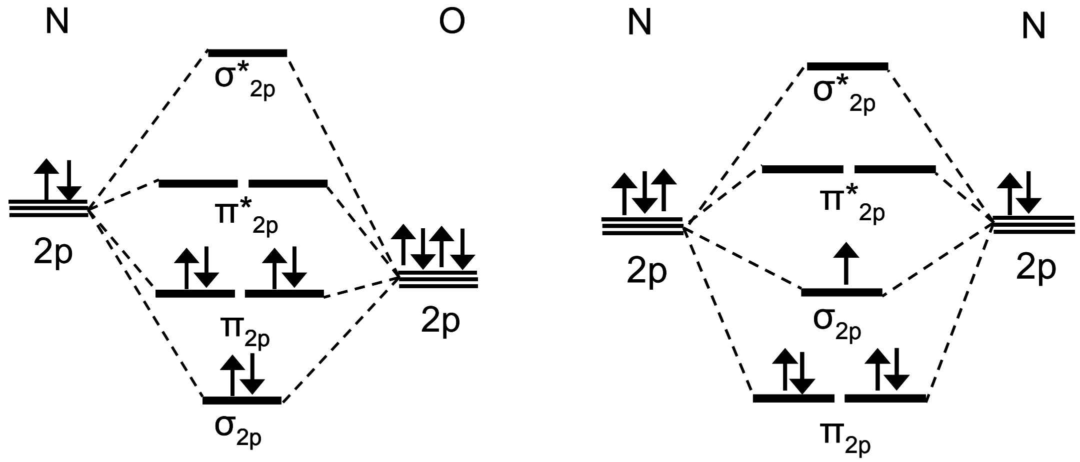
<u>35</u>. (^{b}indicates a bonding orbital)

				$\sigma_{2s}{}^b$	$\sigma_{2s}{}^*$	$\sigma_{2p}{}^b$	$\pi_{2p}{}^b$	$\pi_{2p}{}^*$	$\sigma_{2p}{}^*$
(a)	NO	$5+6=11$	valence electrons KK	↑↓	↑↓	↑↓	↑↓ ↑↓	↑ ☐	☐
(b)	NO^+	$5+6-1=10$	valence electrons KK	↑↓	↑↓	↑↓	↑↓ ↑↓	☐ ☐	☐
(c)	CO	$4+6=10$	valence electrons KK	↑↓	↑↓	↑↓	↑↓ ↑↓	☐ ☐	☐

				$\sigma_{2s}{}^b$	$\sigma_{2s}{}^*$	$\pi_{2p}{}^b$	$\sigma_{2p}{}^b$	$\pi_{2p}{}^*$	$\sigma_{2p}{}^*$
(d)	CN	$4+5=9$	valence electrons KK	↑↓	↑↓	↑↓ ↑↓	↑	☐ ☐	☐
(e)	CN^-	$4+5+1=10$	valence electrons KK	↑↓	↑↓	↑↓ ↑↓	↑↓	☐ ☐	☐
(f)	CN^+	$4+5-1=8$	valence electrons KK	↑↓	↑↓	↑↓ ↑↓	☐	☐ ☐	☐
(g)	BN	$3+5=8$	valence electrons KK	↑↓	↑↓	↑↓ ↑↓	☐	☐ ☐	☐

<u>37</u>. We first produce the molecular orbital diagram for each species. See page 471 in text.

(a)

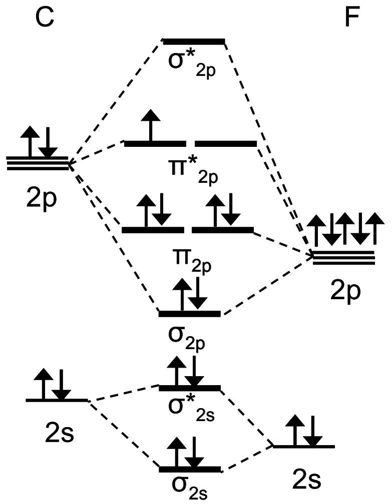


(b) Bond order is 3 for NO^+, 2.5 for $N_2{}^+$

(c) NO^+ is diamagnetic (all paired electrons), $N_2{}^+$ is paramagnetic

(d) $N_2{}^+$ has the greater bond length, because there is less electron density between the two nuclei.

39.



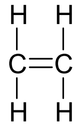
The bond length in CF^+ would be shorter, which means greater electron overlap and bonding between the two atoms. This is because the lone electron in the π* orbital is removed.

Delocalized Molecular Orbitals

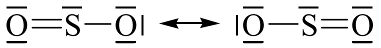
41. With either Lewis structures or the valence-bond method, two structures must be drawn (and "averaged") to explain the π bonding in C_6H_6. The σ bonding is well explained by assuming sp^2 hybridization on each C atom. But the π bonding requires that all six C—C π bonds must be equivalent. This can be achieved by creating six π molecular orbitals—three bonding and three antibonding—into which the 6 π electrons are placed. This creates a single delocalized structure for the C_6H_6 molecule.

43. We expect to find delocalized orbitals in those species for which bonding cannot be represented thoroughly by one Lewis structure, that is, for compounds that require several resonance forms.

(a) In C_2H_4, there are a total of $(2\times 4)+(4\times 1)=12$ valence electrons, or 6 pairs. C atoms are the central atoms. Thus, the bonding description of C_2H_4 does not involve the use of delocalized orbitals.

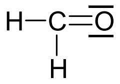


(b) In SO_2, there are a total of $6+(2\times 6)=18$ valence electrons, or 9 pairs. N is the central atom. A plausible Lewis structure has two resonance forms. The bonding description of SO_2 will require the use of delocalized molecular orbitals.



$$\overline{\underline{O}}=\overline{S}-\overline{\underline{O}}| \longleftrightarrow |\overline{\underline{O}}-\overline{S}=\overline{\underline{O}}$$

(c) In H_2CO, there are a total of $(2 \times 1) + 4 + 6 = 12$ valence electrons, or 6 pairs. C is the central atom. A plausible Lewis structure is shown on the right. Because one Lewis structure adequately represents the bonding in the molecule, the bonding description of H_2CO does not involve the use of delocalized molecular orbitals.



Metallic Bonding

45. **(a)** Atomic number, by itself, is not particularly important in determining whether a substance has metallic properties. However, atomic number determines where an element appears in the periodic table, and to the left and toward the bottom of the periodic table is where one finds atoms of high metallic character. Therefore atomic number, which provides the location of the element in the periodic table, has some minimal predictive value in determining metallic character.

(b) The answer for this part is much the same as the answer to part (a), since atomic mass generally parallels atomic number for the elements.

(c) The number of valence electrons has no bearing on the metallic character of an element. Consider, for instance, the sixth row of the periodic table. The number of valence shell electrons ranges from one to eleven across the period, yet all of the elements in this row are metallic. Alternatively, if we look at the group 14 elements, they range from non-metallic carbon to metallic lead, in spite of the fact that they share the same general valence shell configuration, that is, ns^2np^2.

(d) Because metals occur in every period of the periodic table, there is no particular relationship between the number of electron shells and the metallic behavior of an element. (Remember that one shell begins to be occupied at the start of each period.)

47. We first determine the number of Na atoms in the sample.

$$\text{no. Na atoms} = 26.8 \text{ mg Na} \times \frac{1 \text{ g Na}}{1000 \text{ mg Na}} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{6.022 \times 10^{23} \text{ Na atoms}}{1 \text{ mol Na}}$$

$$= 7.02 \times 10^{20} \text{ Na atoms}$$

Because there is one $3s$ orbital per Na atom, and since the number of energy levels (molecular orbitals) created is equal to the number of atomic orbitals initially present, there are 7.02×10^{20} energy levels present in the conduction band of this sample. Also, there is one $3s$ electron contributed by each Na atom, for a total of 7.02×10^{20} electrons. Because each energy level can hold two electrons, the conduction band is half full.

Semiconductors

49. **(a)** stainless steel - electrical conductor
(b) solid NaCl - insulator
(c) sulfur – insulator
(d) germanium - semiconductor
(e) seawater - electrical conductor
(f) solid iodine - insulator

51. A semiconducting element is one that displays poor conductivity when pure, but attains much higher levels of conductivity when doped with small quantities of selected elements or when heated. The best semiconducting materials are made from the Group 14 elements Si and Ge. *P*-type semiconductors result when Group 14 elements are doped with small quantities of an element that has fewer than four valence electrons. For instance, when Si is doped with B, each boron atom ends us forming one silicon bond that has just one electron in it. The transfer of valence electrons from adjacent atoms into these electron-deficient bonds creates a domino effect that results in the movement of an electron-deficient hole through the semiconductor in a direction opposite to the movement of the electrons. Thus, in order to produce a *p*-type semiconductor, the added dopant atom must have at least one less valence electron than the individual atoms that make up the bulk of the material.

(a) Sulfur has six valence electrons, which is three too many, so doping Si with sulfur will not produce a *p*-type semiconductor.

(b) Arsenic has five valence electrons, which is two electrons too many, so doping Si with arsenic will not produce a *p*-type semiconductor.

(c) Lead has four valence electrons, which is one too many, so doping with lead will not produce a *p*-type semiconductor.

(d) Boron, with one less valence electron than silicon, has the requisite number of electrons needed to form a *p*-type semiconductor.

(e) Gallium arsenide is an *n*-type semiconductor with an excess of electrons, so doping Si with GaAs will not produce a *p*-type semiconductor.

(f) Like boron, gallium has three valence electrons. Thus, doping Si with gallium will produce a *p*-type semiconductor.

53. In ultra pure crystalline silicon, there are no extra electrons in the lattice that can conduct an electric current. If, however, the silicon becomes contaminated with arsenic atoms, then there will be one additional electron added to the silicon crystal lattice for each arsenic atom that is introduced. Upon heating, some of those "extra" electrons will be promoted into the conduction band of the solid. The electrons that end up in the conduction band are able to move freely through the structure. In other words, the arsenic atoms increase the conductivity of the solid by providing additional electrons that can carry a current after they are promoted into the conduction band by thermal excitation. Thus, by virtue of having extra electrons in the lattice, silicon contaminated with arsenic will exhibit greater electrical conductance than pure silicon at elevated temperatures.

55. $\Delta E_{\text{Si}} = 110.\ \text{kJ mol}^{-1}$. $\Delta E_{\text{Si atom}} = \dfrac{110.\ \text{kJ mol}^{-1}}{6.022 \times 10^{23}} = 1.83 \times 10^{-19}\ \text{J}$

$$E = h\nu = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E}$$

$$\lambda = \frac{(6.626\times10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \frac{\text{m}}{\text{s}})}{1.83\times10^{-19}\ \text{J}} = 1.09 \times 10^{-6}\ \text{m or 1090 nm. This is IR-radiation.}$$

INTEGRATIVE AND ADVANCED EXERCISES

58. We begin with the orbital diagram for Na to describe the valence-bond picture for Na_2. [Ne] $_{3s}$[↑] The half-filled 3*s* orbital on each Na overlaps with another to form a σ covalent bond. There are 22 electrons in Na_2. These electrons are distributed in the molecular orbitals as follows.

σ_{1s}	σ_{1s}^*	σ_{2s}	σ_{2s}^*	σ_{2p}	π_{2p}	π_{2p}^*	σ_{2p}^*	σ_{3s}
[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓][↑↓]	[↑↓][↑↓]	[↑↓]	[↑↓]

Again, we predict a single bond for Na_2.

A Lewis-theory picture of the bonding would have the two Lewis symbols for two Na atoms uniting to form a bond: $\text{Na}\cdot\ \cdot\text{Na} \longrightarrow \text{Na}—\text{Na}$ Thus, the bonding in Na_2 is very much like that in H_2.

60. The superoxide ion, O_2^-, has 17 electrons, while the peroxide ion, O_2^{2-}, has a total of 18 electrons,

(a) The molecular orbital diagrams for these two ions are given below.

	σ_{1s}	σ_{1s}^*	σ_{2s}	σ_{2s}^*	σ_{2p}	π_{2p}	π_{2p}^*	σ_{2p}^*
O_2^-	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓][↑↓]	[↑↓][↑]	[ ]

bond order = (no. bonding electrons – no. antibonding electrons) ÷2 = (10 – 7) ÷2 = 1.5

	σ_{1s}	σ_{1s}^*	σ_{2s}	σ_{2s}^*	σ_{2p}	π_{2p}	π_{2p}^*	σ_{2p}^*
O_2^{2-}	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓][↑↓]	[↑][↑↓]	[ ]

bond order = (no. bonding electrons – no. antibonding electrons) ÷2 = (10 – 8) ÷2 = 1.0

(b) O_2^- has (2 × 6) + 1 = 13 electrons, 6 electron pairs plus one electron. O_2^{2-} has (2 × 6) + 2 = 14 electrons, 7 electron pairs. Plausible Lewis structures are

O_2^- $[|\overline{\underline{O}}-\overline{\underline{O}}\cdot]^-$ O_2^{2-} $[|\overline{\underline{O}}-\overline{\underline{O}}|]^{2-}$

64. The O—N—O bond angle of 125° indicates the N atom is sp^2 hybridized, while the F—O_a—N bond angle of 105° indicates the O_a atom is sp^3 hybridized. The orbital diagrams of the atoms follow.

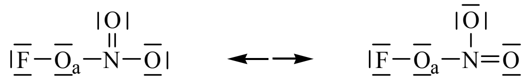
O [He] $_{2s}$[↑↓] $_{2p}$[↑↓][↑][↑] O_a [He] $_{2s}$[↑↓] $_{2p}$[↑↓][↑][↑] $\longrightarrow$ O [He] $_{sp^3}$[↑↓][↑↓][↑][↑]
F [He] $_{2s}$[↑↓] $_{2p}$[↑↓][↑↓][↑]   N [He] $_{2s}$[↑↓] $_{2p}$[↑][↑][↑] $\longrightarrow$ N [He] $_{sp^2}$[↑][↑][↑] $_{2p}$[↑]

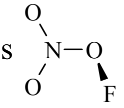
Electron transfer from N to the terminal oxygen atom results in a +1 formal charge for nitrogen, a -1 formal charge for O and a single bond being developed between these two atoms.

O [He] $_{2s}$[↑↓] $_{2p}$[↑↓][↑][↑] $\xrightarrow{+\text{ e-}}$ O^- [He] $_{2s}$[↑↓] $_{2p}$[↑↓][↑↓][↑]

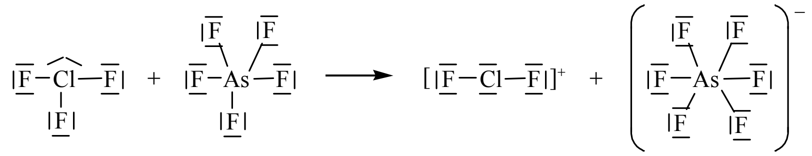
Bonds are formed by the following overlaps.

$$\sigma:\ \text{F}(2p)—\text{O}_\text{a}(sp^3)\quad \sigma:\ \text{O}_\text{a}(sp^3)—\text{N}(sp^2)\quad \sigma:\ \text{N}(sp^2)—\text{O}(2p_y)\quad \pi:\ \text{N}(2p_z)—\text{O}(2p_z)$$

Two resonance structures are required 

With the wedge-and-dash representation, a sketch of the molecule is 

66. **(M)** Let us begin by drawing Lewis structures for the species concerned.



(a) For ClF_3 there are three atoms and two lone pairs attached to the central atom. The electron group geometry is trigonal bipyramidal and the molecule is T-shaped. For AsF_5 there are five atoms attached to the central atom; its electron group geometry and molecular shape are trigonal bipyramidal. For ClF_2^+ there are two lone pairs and two atoms attached to the central atom. Its electron group geometry is tetrahedral and the ion is bent in shape. For AsF_6^- there are six atoms and no lone pairs attached to the central atom. Thus, the electron group geometry and the shape of this ion are octahedral.

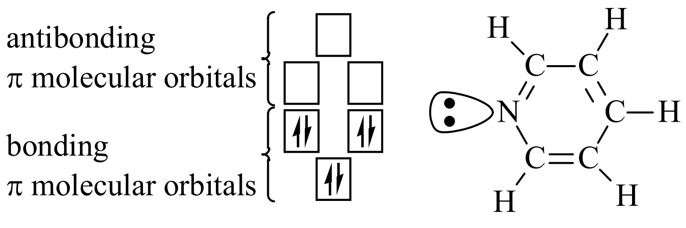
(b) Trigonal bipyramidal electron group geometry is associated with sp^3d hybridization. The Cl in ClF_3 and As in AsF_5 both have sp^3d hybridization. Tetrahedral electron group geometry is associated with sp^3 hybridization. Thus Cl in ClF_2^+ has sp^3 hybridization. Octahedral electron group geometry is associated with sp^3d^2 hybridization, which is the hybridization adopted by As in AsF_6^-.

68. Suppose two He atoms in the excited state $1s^1\ 2s^1$ unite to form an He_2 molecule. One possible configuration is $\sigma_{1s}^2\sigma_{1s}^{*0}\sigma_{2s}^2\sigma_{2s}^{0*}$. The bond order would be (4-0)/2 = 2.

70. The orbital diagrams for C and N are as follows. C [He] sp_2 [↑][↑][↑] 2p [↑]

N [He] sp_2 [↑↓][↑][↑] 2p [↑]

The sp^2 electrons are involved in σ bonding. For N, the lone pair is in one sp^2 orbital; the remaining two half-filled sp^2 orbitals bond to adjacent C atoms. For C, one sp^2 orbital forms a σ bond by overlap with a half-filled 1*s* H atom. The remaining two half-filled sp^2 orbitals bond to either adjacent C or N atoms. The 2*p* electrons are involved in π bonding. The six 2*p* orbitals form six delocalized π molecular orbitals, three bonding and three antibonding. These six π orbitals are filled as shown in the π molecular orbital diagram sketched below.



Number of π-bonds = $\frac{6-0}{2} = 3$
This π-bonding scheme produces three π-bonds, which is identical to the number predicted by Lewis theory.

73. We will assume 100 g of the compound and find the empirical formula in the usual way.

$$\text{moles of carbon} = 53.09\text{ g C} \times \frac{1\text{ mole C}}{12.011\text{g C}} = 4.424\text{ mol}$$

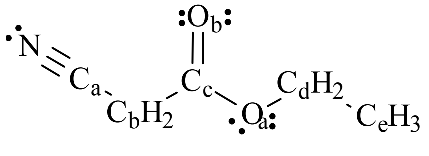
$$\text{moles of hydrogen} = 6.24\text{ g} \times \frac{1\text{ mole H}}{1.008\text{ g H}} = 6.19\text{ mol}$$

$$\text{moles of nitrogen} = 12.39\text{ g} \times \frac{1\text{ mole N}}{14.0067\text{ g N}} = 0.885\text{ mol}$$

$$\text{moles of oxygen} = 28.29\text{ g} \times \frac{1\text{ mole O}}{15.999\text{ g O}} = 1.768\text{ mol}$$

Dividing all result by 0.885 we get: 5.00 moles C, $6.99\underline{5}$ moles H, 1.00 mole N and 2.00 moles O. This yields an empirical formula of $C_5H_7NO_2$.
Structure: $N{\equiv}C\text{-}CH_2(C{=}O)OC_2H_5$

Hybrid orbitals used:
C_b-H , C_d-H , C_e-H : σ H(1s) – C(sp^3) (all tetrahedral carbon uses sp^3 hybrid orbitals)
$C_c{=}O_b$: σ C_c (sp^2) –O_b (2p or sp^2) , π: C_c (2p) – O_b (2p)
C_c-O_a: σ C_c (sp^2) –O_a (2p or sp^3)
C_d-O_a: σ C_d (sp^3) –O_a (2p or sp^3)
$C_a{\equiv}N$: σ C_a (sp) –N(sp)
Two mutually perpendicular π-bonds: C(2p) – N(2p)
C_a-C_b: σ C_b(sp^3) –C_a(sp)
C_d-C_e: σ C_d(sp^3) –C_e(sp^3)
C_c-C_b: σ C_b(sp^3) –C_c(sp^2)



75. **(a)** power output = (1.00 kW/m^2)×(1000 W/kW) × (40.0 cm^2) × (1m^2 /10^4 cm^2) = 4.00 watts
amps = i = w/v

(b) $i = 4.00\text{ watts} = 4.00\ \frac{\text{J}}{\text{s}} \times \frac{1\text{ C}}{0.45\text{ J}} = 8.9\frac{\text{C}}{\text{s}} = 8.9\text{ amps}$

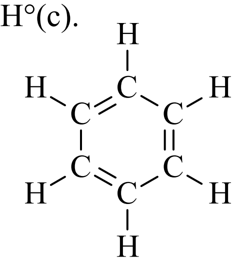
79. The wavelength for both will be the same, because they both have a conjugated π system.

FEATURE PROBLEMS

80. **(a)** $C_6H_6(l) + 3\ H_2(g) \rightarrow C_6H_{12}(l)$ $\Delta H° = \Sigma\Delta H°_{f\text{, products}} - \Sigma\Delta H°_{f\text{, reactants}}$
$\Delta H° = -156.4\text{ kJ} - [3\text{ mol} \times 0\text{ kJ mol}^{-1} + 49.0\text{ kJ}] = -205.4\text{ kJ} = \Delta H°(a)$

(b) $C_6H_{10}(l) + H_2(g) \rightarrow C_6H_{12}(l)$ $\Delta H° = \Sigma\Delta H°_{f\text{ products}} - \Sigma\Delta H°_{f\text{ reactants}}$
$\Delta H° = -156.4\text{ kJ} - [1\text{ mol} \times 0\text{ kJ mol}^{-1} + (-38.5\text{ kJ})] = -117.9\text{ kJ} = \Delta H°(b)$

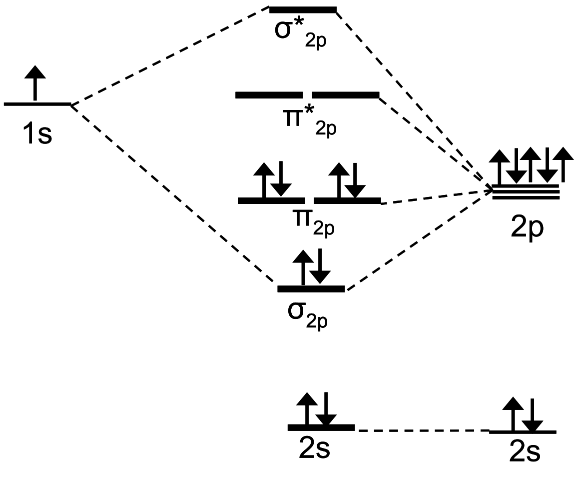
(c) Enthalpy of hydrogenation for 1,3,5-cyclohexatriene = 3 × ΔH°(b)
Enthalpy of hydrogenation = 3 (–117.9 kJ) = –353.7 kJ = ΔH°(c)
$\Delta H°_{f\text{, cyclohexene}} = -38.5$ kJ/mole (given in part b of this question).
Resonance energy is the difference between ΔH°(a) and ΔH°(c).
Resonance energy = –353.7 kJ – (–205.4 kJ) = –148.3 kJ



(d) Using bond energies:
$\Delta H°_{\text{atomization}} = 6(\text{C—H}) + 3(\text{C—C}) + 3(\text{C=C})$
$\Delta H°_{\text{atomization}} = 6(414\text{ kJ}) + 3(347\text{ kJ}) + 3(611\text{ kJ})$
$\Delta H°_{\text{atomization}} = 5358$ kJ (per mole of C_6H_6)

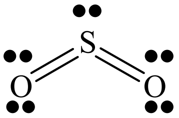
$C_6H_6(g) \rightarrow 6\ C(g) + 6\ H(g)$
$\Delta H° = [6(716.7\text{ kJ}) + 6(218\text{ kJ})] - 82.6\text{ kJ} = 5525.6\text{ kJ}$
Resonance energy = 5358 kJ – 5525.6 kJ = –168 kJ

87.



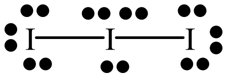
SELF-ASSESSMENT EXERCISES

91. The answer is (c). It is the only option that has three species attached to the central atom (2 oxygen atoms, one electron pair):



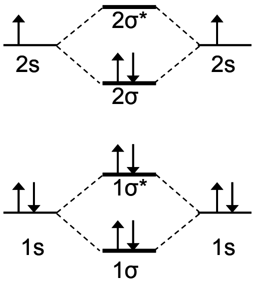
92. The answer is (c). H_2Se has the same geometry as H_2S and H_2O. It is sp^3 hybridized, and the bond angle is less than H_2S, but it has to be more than 90°.

93. The answer is (a). The Lewis structure of I_3^- is shown below:

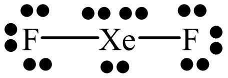


There are 1 s and 3 p orbitals for the central atom. However, there are 5 groups around it, which means that the *d* orbital needs to be used.

94. The answer is (b). Each Li has the electron configuration $1s^22s^1$. The valence electrons occupy the 2σ orbitals completely, and not the 2σ*, so the bond order is (4-2)/2 = 1

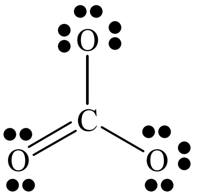


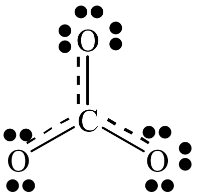
95. The answer is (c). The Lewis structure of XeF_2 is shown below:



Since there are 5 groups around Xe, the hybridization is *sp³d*.

96. The answer is (d). The Lewis structure of CO_3^{2-} and the result of its resonance structures is shown below:



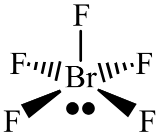


97. The answer is (a), because Li is the only substance that is a metal, and metals are the best electrical conductors.

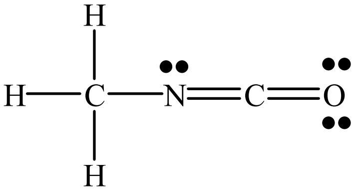
98. The answer is (c). When the valence and conduction bands overlap, the valence electrons can "flow" and move. Only metals have that capability.

99. From VSEPR theory we conclude that BF_3 is a trigonal planar molecule (as seen in Table 11.1). The valence-bond method using pure *s* and *p* orbitals incorrectly predicts a trigonal pyramidal shape with 90° F—B—F bond angles.

100. BrF_5 has six constituents around it; five are fluorine atoms, and the sixth is a lone pair. Therefore, the hybridization is sp^3d^2, but the geometry is square pyramidal. The structure is shown below:

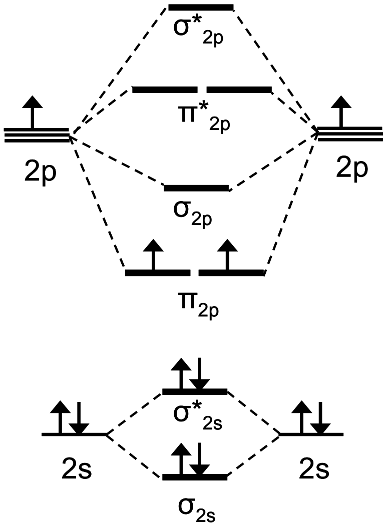


101. The structure of CH_3NCO is shown below:

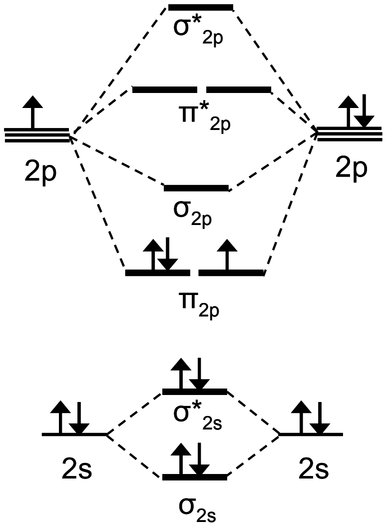


There are two double bonds, which means that there are **(a)** 6 σ and **(b)** 2 π bonds.

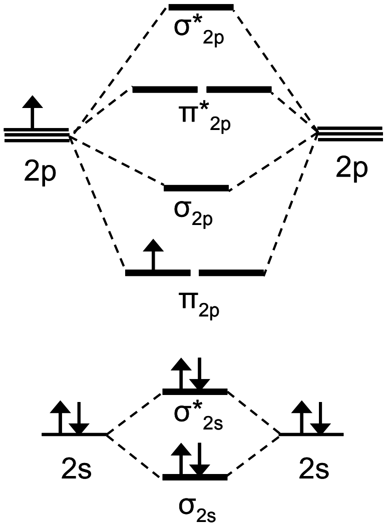
102. All three are paramagnetic, because all three have unpaired electrons. The one with the strongest bond is **(b)**. The molecular orbital diagrams for all three are shown below. B_2^- has 3 bonding electrons, so the B–B bond is the strongest.



B_2

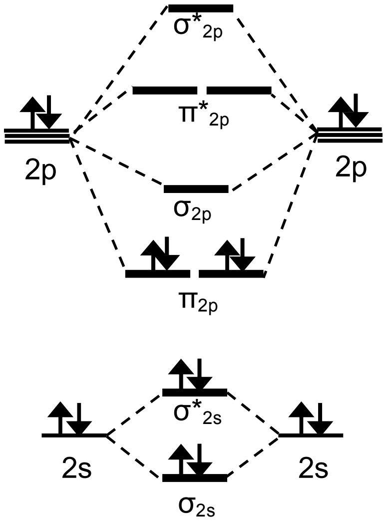


B_2^-

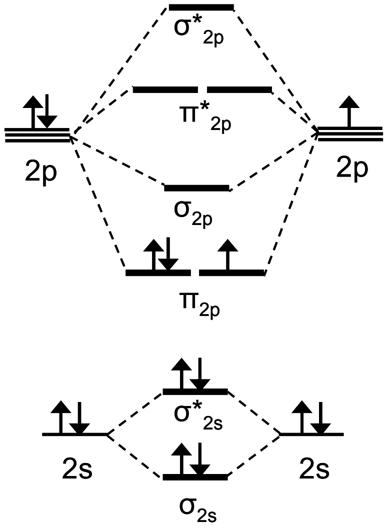


B_2^+

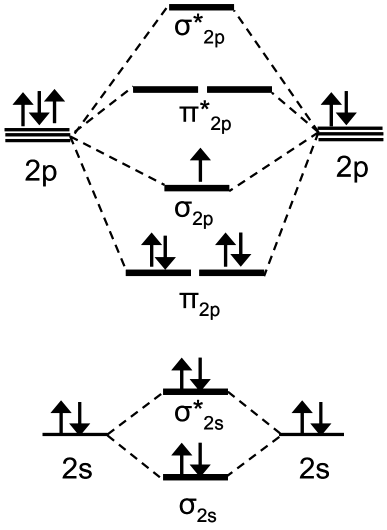
103. The answer is (c), because C_2^- has an unpaired electron in the σ(*2s*) bonding orbital, which is easier to remove than one already paired up because there is no pairing energy to overcome. The other two have electrons in the bonding orbitals, which require more energy to remove.



C_2

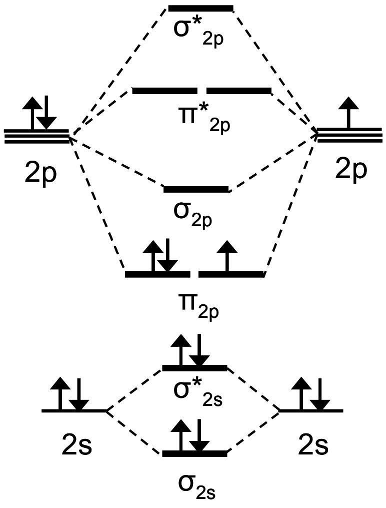


C_2^+

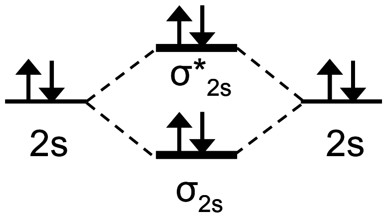


C_2^-

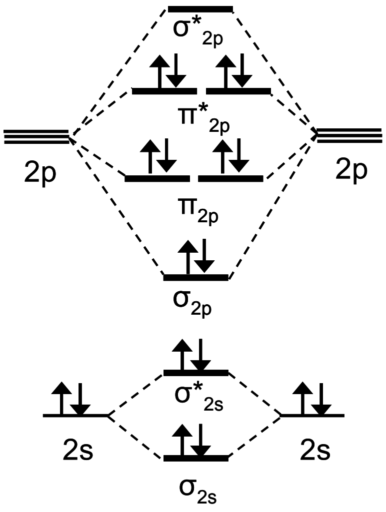
104.



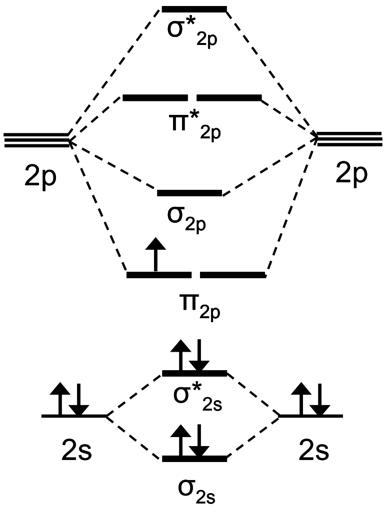
C_2^+



Be_2



F_2



B_2^+

105. The bond order in C_2 is two, whereas in Li_2 is one. Therefore, C_2 has the greater bond energy.