CHAPTER 9

COVALENT BONDING: ORBITALS

Questions

- 9. In hybrid orbital theory, some or all of the valence atomic orbitals of the central atom in a molecule are mixed together to form hybrid orbitals; these hybrid orbitals point to where the bonded atoms and lone pairs are oriented. The sigma bonds are formed from the hybrid orbitals overlapping head to head with an appropriate orbital from the bonded atom. The π bonds, in hybrid orbital theory, are formed from unhybridized p atomic orbitals. The p orbitals overlap side to side to form the π bond, where the π electrons occupy the space above and below a line joining the atoms (the internuclear axis). Assuming the z-axis is the internuclear axis, then the p_z atomic orbital will always be hybridized whether the hybridization is sp, sp², sp³, dsp³ or d²sp³. For sp hybridization, the p_x and p_y atomic orbitals are unhybridized; they are used to form two π bonds to the bonded atom(s). For sp² hybridization, either the p_x or the p_y atomic orbital is hybridized (along with the s and p_z orbitals); the other p orbital is used to form a π bond to a bonded atom. For sp³ hybridization, the s and all the p orbitals are hybridized; no unhybridized p atomic orbitals are present, so no π bonds form with sp³ hybridization. For dsp³ and d²sp³ hybridization, we just mix in one or two d orbitals into the hybridization process. Which specific d orbitals are used is not important to our discussion.
- 10. The MO theory is a mathematical model. The allowed electron energy levels (molecular orbitals) in a molecule are solutions to the mathematical problem. The square of the solutions gives the shapes of the molecular orbitals. A sigma bond is an allowed energy level where the greatest electron probability is between the nuclei forming the bond. Valence s orbitals form sigma bonds, and if the z-axis is the internuclear axis, then valence p_z orbitals also form sigma bonds. For a molecule like HF, a sigma-bonding MO results from the combination of the H 1s orbital and the F $2p_z$ atomic orbital.

For π bonds, the electron density lies above and below the internuclear axis. The π bonds are formed when p_x orbitals are combined (side-to-side overlap) and when p_y orbitals are combined.

11. We use d orbitals when we have to; i.e., we use d orbitals when the central atom on a molecule has more than eight electrons around it. The d orbitals are necessary to accommodate the electrons over eight. Row 2 elements never have more than eight electrons around them, so they never hybridize d orbitals. We rationalize this by saying there are no d orbitals close in energy to the valence 2s and 2p orbitals (2d orbitals are forbidden energy levels). However, for row 3 and heavier elements, there are 3d, 4d, 5d, etc. orbitals that will be close in energy to the valence s and p orbitals. It is row 3 and heavier nonmetals that hybridize d orbitals when they have to.

For phosphorus, the valence electrons are in 3s and 3p orbitals. Therefore, 3d orbitals are closest in energy and are available for hybridization. Arsenic would hybridize 4d orbitals to go with the valence 4s and 4p orbitals, whereas iodine would hybridize 5d orbitals since the valence electrons are in n = 5.

- 12. Rotation occurs in a bond as long as the orbitals that go to form that bond still overlap when the atoms are rotating. Sigma bonds, with the head-to-head overlap, remain unaffected by rotating the atoms in the bonds. Atoms that are bonded together by only a sigma bond (single bond) exhibit this rotation phenomenon. The π bonds, however, cannot be rotated. The p orbitals must be parallel to each other to form the π bond. If we try to rotate the atoms in a π bond, the p orbitals would no longer have the correct alignment necessary to overlap. Because π bonds are present in double and triple bonds (a double bond is composed of 1 σ and 1 π bond, and a triple bond is always 1 σ and 2 π bonds), the atoms in a double or triple bond cannot rotate (unless the bond is broken).
- 13. Bonding and antibonding molecular orbitals are both solutions to the quantum mechanical treatment of the molecule. Bonding orbitals form when in-phase orbitals combine to give constructive interference. This results in enhanced electron probability located between the two nuclei. The end result is that a bonding MO is lower in energy than the atomic orbitals from which it is composed. Antibonding orbitals form when out-of-phase orbitals combine. The mismatched phases produce destructive interference leading to a node of electron probability between the two nuclei. With electron distribution pushed to the outside, the energy of an antibonding orbital is higher than the energy of the atomic orbitals from which it is composed.
- 14. From experiment, B_2 is paramagnetic. If the σ_{2p} MO is lower in energy than the two degenerate π_{2p} MOs, the electron configuration for B_2 would have all electrons paired. Experiment tells us we must have unpaired electrons. Therefore, the MO diagram is modified to have the π_{2p} orbitals lower in energy than the σ_{2p} orbitals. This gives two unpaired electrons in the electron configuration for B_2 , which explains the paramagnetic properties of B_2 . The model allowed for s and p orbitals to mix, which shifted the energy of the σ_{2p} orbital to above that of the π_{2p} orbitals.
- 15. The localized electron model does not deal effectively with molecules containing unpaired electrons. We can draw all of the possible structures for NO with its odd number of valence electrons but still not have a good feel for whether the bond in NO is weaker or stronger than the bond in NO⁻. MO theory can handle odd electron species without any modifications. From the MO electron configurations, the bond order is 2.5 for NO and 2 for NO⁻. Therefore, NO should have the stronger bond (and it does). In addition, hybrid orbital theory does not predict that NO⁻ is paramagnetic. The MO theory correctly makes this prediction.

16.
$$NO_3^-, 5 + 3(6) + 1 = 24 e^-$$

When resonance structures can be drawn, it is usually due to a multiple bond that can be in different positions. This is the case for NO₃⁻. Experiment tells us that the three N–O bonds are equivalent in length and strength. To explain this, we say the π electrons are delocalized in the molecule. For NO₃⁻, the π bonding system is composed of an unhybridized p atomic orbital from all the atoms in NO₃⁻. These p orbitals are oriented perpendicular to the plane of the atoms in NO₃⁻. The π bonding system consists of all of the perpendicular p orbitals overlapping forming a diffuse electron cloud above and below the entire surface of the NO₃⁻ ion. Instead of having the π electrons situated above and below two specific nuclei, we think of the π electrons in NO₃⁻ as extending over the entire surface of the molecule (hence the term delocalized). See Figure 9.48 for an illustration of the π bonding system in NO₃⁻.

Exercises

The Localized Electron Model and Hybrid Orbitals

17. H_2O has 2(1) + 6 = 8 valence electrons.



 H_2O has a tetrahedral arrangement of the electron pairs about the O atom that requires sp³ hybridization. Two of the four sp³ hybrid orbitals are used to form bonds to the two hydrogen atoms, and the other two sp³ hybrid orbitals hold the two lone pairs on oxygen. The two O–H bonds are formed from overlap of the sp³ hybrid orbitals from oxygen with the 1s atomic orbitals from the hydrogen atoms. Each O–H covalent bond is called a sigma (σ) bond since the shared electron pair in each bond is centered in an area on a line running between the two atoms.

18. CCl_4 has 4 + 4(7) = 32 valence electrons.



 CCl_4 has a tetrahedral arrangement of the electron pairs about the carbon atom that requires sp³ hybridization. The four sp³ hybrid orbitals from carbon are used to form the four bonds to chlorine. The chlorine atoms also have a tetrahedral arrangement of electron pairs, and we will assume that they are also sp³ hybridized. The C–Cl sigma bonds are all formed from overlap of sp³ hybrid orbitals from carbon with sp³ hybrid orbitals from each chlorine atom.

19. H_2CO has 2(1) + 4 + 6 = 12 valence electrons.



The central carbon atom has a trigonal planar arrangement of the electron pairs that requires sp^2 hybridization. The two C–H sigma bonds are formed from overlap of the sp^2 hybrid orbitals from carbon with the hydrogen 1s atomic orbitals. The double bond between carbon and oxygen consists of one σ and one π bond. The oxygen atom, like the carbon atom, also has a trigonal planar arrangement of the electrons that requires sp^2 hybridization. The σ bond in the double bond is formed from overlap of a carbon sp^2 hybrid orbital with an oxygen sp^2 hybrid orbital. The π bond in the double bond is formed from overlap of a carbon sp² hybrid orbital with an oxygen sp^2 hybrid orbital. The π bond in the double bond is formed from overlap of a carbon sp² hybridized p atomic orbitals. Carbon and oxygen each has one unhybridized p atomic orbital that is parallel with the other. When two parallel p atomic orbitals overlap, a π bond results where the shared electron pair occupies the space above and below a line joining the atoms in the bond.

20. C_2H_2 has 2(4) + 2(1) = 10 valence electrons.

Each carbon atom in C_2H_2 is sp hybridized since each carbon atom is surrounded by two effective pairs of electrons; i.e., each carbon atom has a linear arrangement of the electrons. Since each carbon atom is sp hybridized, then each carbon atom has two unhybridized p atomic orbitals. The two C–H sigma bonds are formed from overlap of carbon sp hybrid orbitals with hydrogen 1s atomic orbitals. The triple bond is composed of one σ bond and two π bonds. The sigma bond between to the carbon atoms is formed from overlap of sp hybrid orbitals from each carbon atom. The two π bonds of the triple bond are formed from parallel overlap of the two unhybridized p atomic orbitals from each carbon.

21. Ethane, C_2H_6 , has 2(4) + 6(1) = 14 valence electrons.



The carbon atoms are sp^3 hybridized. The six C–H sigma bonds are formed from overlap of the sp^3 hybrid orbitals from C with the 1s atomic orbitals from the hydrogen atoms. The carbon-carbon sigma bond is formed from overlap of an sp^3 hybrid orbital from each C atom.

Ethanol, C_2H_6O has $2(4) + 6(1) + 6 = 20 e^-$



The two C atoms and the O atom are sp³ hybridized. All bonds are formed from overlap with these sp³ hybrid orbitals. The C–H and O–H sigma bonds are formed from overlap of sp³ hybrid orbitals with hydrogen 1s atomic orbitals. The C–C and C–O sigma bonds are formed from overlap of the sp³ hybrid orbitals from each atom.

22. HCN, 1 + 4 + 5 = 10 valence electrons

H—−C<u></u>N:

Assuming N is hybridized, both C and N atoms are sp hybridized. The C–H σ bond is formed from overlap of a carbon sp³ hybrid orbital with a hydrogen 1s atomic orbital. The triple bond is composed of one σ bond and two π bonds. The sigma bond is formed from head-to-head overlap of the sp hybrid orbitals from the C and N atoms. The two π bonds in the triple bond are formed from overlap of the two unhybridized p atomic orbitals from each C and N atom.

 $COCl_2$, 4 + 6 + 2(7) = 24 valence electrons



Assuming all atoms are hybridized, the carbon and oxygen atoms are sp² hybridized, and the two chlorine atoms are sp³ hybridized. The two C–Cl σ bonds are formed from overlap of sp² hybrids from C with sp³ hybrid orbitals from Cl. The double bond between the carbon and oxygen atoms consists of one σ and one π bond. The σ bond in the double bond is formed from head-to-head overlap of an sp² orbital from carbon with an sp² hybrid orbital from oxygen. The π bond is formed from parallel overlap of the unhybridized p atomic orbitals from each atom of C and O.

- 23. See Exercises 8.81 and 8.87 for the Lewis structures. To predict the hybridization, first determine the arrangement of electron pairs about each central atom using the VSEPR model; then use the information in Figure 9.24 of the text to deduce the hybridization required for that arrangement of electron pairs.
 - 8.81 a. CCl_4 : C is sp³ hybridized. b. NCl_3 : N is sp³ hybridized.
 - c. SeCl₂: Se is sp³ hybridized. d. ICl: Both I and Cl are sp³ hybridized.
 - 8.87 a. The central N atom is sp² hybridized in NO_2^- and NO_3^- . In N_2O_4 , both central N atoms are sp² hybridized.
 - b. In OCN⁻ and SCN⁻, the central carbon atoms in each ion are sp hybridized, and in N_3^- , the central N atom is also sp hybridized.
- 24. See Exercises 8.82 and 8.88 for the Lewis structures.
 - 8.82 a. All the central atoms are sp^3 hybridized.

- b. All the central atoms are sp³ hybridized.
- c. All the central atoms are sp³ hybridized.
- 8.88 In O_3 and in SO_2 , the central atoms are sp^2 hybridized, and in SO_3 , the central sulfur atom is also sp^2 hybridized.
- 25. All exhibit dsp³ hybridization. All of these molecules/ions have a trigonal bipyramid arrangement of electron pairs about the central atom; all have central atoms with dsp³ hybridization. See Exercise 8.85 for the Lewis structures.
- 26. All these molecules have an octahedral arrangement of electron pairs about the central atom; all have central atoms with d^2sp^3 hybridization. See Exercise 8.86 for the Lewis structures.
- 27. The molecules in Exercise 8.107 all have a trigonal planar arrangement of electron pairs about the central atom, so all have central atoms with sp² hybridization. The molecules in Exercise 8.108 all have a tetrahedral arrangement of electron pairs about the central atom, so all have central atoms with sp³ hybridization. See Exercises 8.107 and 8.108 for the Lewis structures.
- 28. The molecules in Exercise 8.109 all have central atoms with dsp³ hybridization because all are based on the trigonal bipyramid arrangement of electron pairs. The molecules in Exercise 8.110 all have central atoms with d²sp³ hybridization because all are based on the octahedral arrangement of electron pairs. See Exercises 8.109 and 8.110 for the Lewis structures.



The angles in NF_3 should be slightly less than 109.5° because the lone pair requires more space than the bonding pairs.





Only one resonance form is shown. Resonance does not change the position of the atoms. We can predict the geometry and hybridization from any one of the resonance structures.

c.

e.

g.

i.



trigonal planar, 120°, sp² (plus two other resonance structures)



tetrahedral geometry about each S, 109.5°, sp³ hybrids; V-shaped arrangement about peroxide O's, $\approx 109.5^{\circ}$, sp³



tetrahedral, 109.5°, sp³



trigonal pyramid, <109.5°, sp³



V-shaped, $<109.5^{\circ}$, sp³



octahedral, 90°, d²sp³



tetrahedral, 109.5°, sp³

h.

f.



see-saw, $\approx 90^{\circ}$ and $\approx 120^{\circ}$, dsp³



b.

d.



a) $\approx 109.5^{\circ}$ b) $\approx 90^{\circ}$ c) $\approx 120^{\circ}$ see-saw about S atom with one lone pair (dsp³); bent about S atom with two lone pairs (sp³)



k.

trigonal bipyramid, 90° and 120° , dsp^{3}

31.

j.



For the p orbitals to properly line up to form the π bond, all six atoms are forced into the same plane. If the atoms are not in the same plane, then the π bond could not form since the p orbitals would no longer be parallel to each other.

32. No, the CH₂ planes are mutually perpendicular to each other. The center C atom is sp hybridized and is involved in two π bonds. The p orbitals used to form each π bond must be perpendicular to each other. This forces the two CH₂ planes to be perpendicular.



- 33. a. There are 33 σ and 9 π bonds.
 - b. All carbon atoms are sp² hybridized because all have a trigonal planar arrangement of electron pairs.
- 34. The two nitrogen atoms in urea both have a tetrahedral arrangement of electron pairs, so both of these atoms are sp³ hybridized. The carbon atom has a trigonal planar arrangement of electron pairs, so C is sp² hybridized. O is also sp² hybridized because it also has a trigonal planar arrangement of electron pairs.

Each of the four N–H sigma bonds are formed from overlap of an sp³ hybrid orbital from nitrogen with a 1s orbital from hydrogen. Each of the two N–C sigma bonds are formed from an sp³ hybrid orbital from N with an sp² hybrid orbital from carbon. The double bond

between carbon and oxygen consists of one σ and one π bond. The σ bond in the double bond is formed from overlap of a carbon sp² hybrid orbital with an oxygen sp² hybrid orbital. The π bond in the double bond is formed from overlap of the unhybridized p atomic orbitals. Carbon and oxygen each have one unhybridized p atomic orbital, and they are assumed to be parallel to each other. When two parallel p atomic orbitals overlap side to side, a π bond results.

35. To complete the Lewis structures, just add lone pairs of electrons to satisfy the octet rule for the atoms with fewer than eight electrons.

Biacetyl ($C_4H_6O_2$) has 4(4) + 6(1) + 2(6) = 34 valence electrons.



All CCO angles are 120°. The six atoms are not forced to lie in the same plane because of free rotation about the carboncarbon single (sigma) bonds. There are 11 σ and 2 π bonds in biacetyl.

Acetoin $(C_4H_8O_2)$ has 4(4) + 8(1) + 2(6) = 36 valence electrons.



The carbon with the doubly bonded O is sp² hybridized. The other three C atoms are sp³ hybridized. Angle $a = 120^{\circ}$ and angle $b = 109.5^{\circ}$. There are 13 σ and 1 π bonds in acetoin.

Note: All single bonds are σ bonds, all double bonds are one σ and one π bond, and all triple bonds are one σ and two π bonds.

36. Acrylonitrile: C_3H_3N has 3(4) + 3(1) + 5 = 20 valence electrons.



All atoms of acrylonitrile must lie in the same plane. The π bond in the double bond dictates that the C and H atoms are all in the same plane, and the triple bond dictates that N is in the same plane with the other atoms.

Methyl methacrylate ($C_5H_8O_2$) has 5(4) + 8(1) + 2(6) = 40 valence electrons.



37. a. Add lone pairs to complete octets for each O and N.



Azodicarbonamide

methyl cyanoacrylate

Note: NH₂, CH₂ and CH₃ are shorthand for carbon atoms singly bonded to hydrogen atoms.

- b. In azodicarbonamide, the two carbon atoms are sp^2 hybridized, the two nitrogen atoms with hydrogens attached are sp^3 hybridized, and the other two nitrogens are sp^2 hybridized. In methyl cyanoacrylate, the CH₃ carbon is sp^3 hybridized, the carbon with the triple bond is sp hybridized, and the other three carbons are sp^2 hybridized.
- c. Azodicarbonamide contains three π bonds and methyl cyanoacrylate contains four π bonds.

d. a) $\approx 109.5^{\circ}$ b) 120° c) $\approx 120^{\circ}$ d) 120° e) 180° f) 120° g) $\approx 109.5^{\circ}$ h) 120°

38. a. Piperine and capsaicin are molecules classified as organic compounds, i.e., compounds based on carbon. The majority of Lewis structures for organic compounds have all atoms with zero formal charge. Therefore, carbon atoms in organic compounds will usually form four bonds, nitrogen atoms will form three bonds and complete the octet with one lone pair of electrons, and oxygen atoms will form two bonds and complete the octet with two lone pairs of electrons. Using these guidelines, the Lewis structures are:



Note: The ring structures are all shorthand notation for rings of carbon atoms. In piperine the first ring contains six carbon atoms and the second ring contains five carbon atoms (plus nitrogen). Also notice that CH_3 , CH_2 , and CH are shorthand for carbon atoms singly bonded to hydrogen atoms.

- b. piperine: 0 sp, 11 sp² and 6 sp³ carbons; capsaicin: 0 sp, 9 sp², and 9 sp³ carbons
- c. The nitrogens are sp³ hybridized in each molecule.

d.	a)	120°	b)	120°	c)	120°
	d)	120°	e)	≈109.5°	f)	109.5°
	g)	120°	h)	109.5°	i)	120°
	j)	109.5°	k)	120°	1)	109.5°

The Molecular Orbital Model

39. If we calculate a nonzero bond order for a molecule, then we predict that it can exist (is stable).

a.	${\rm H_2}^+$:	$(\sigma_{1s})^1$	B.O. = $(1-0)/2 = 1/2$, stable
	H ₂ :	$(\sigma_{1s})^2$	B.O. = $(2-0)/2 = 1$, stable
	H_2^- :	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	B.O. = $(2-1)/2 = 1/2$, stable
	${\rm H_2}^{2-}$:	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	B.O. = $(2-2)/2 = 0$, not stable

	b.	He ₂ ²⁺ :	$(\sigma_{1s})^2$	B.O. = $(2-0)/2$	= 1, stable
		$\operatorname{He_2}^+$:	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	B.O. = $(2-1)/2$	= 1/2, stable
		He ₂ :	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	B.O. = $(2-2)/2$	= 0, not stable
40.	a.	N2 ²⁻ :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p}$	$)^{2}(\pi_{2p}^{*})^{2}$	B.O. = $(8-4)/2 = 2$, stable
		O_2^{2-} :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi$	$^{4}(\pi_{2p}*)^{4}$	B.O. = $(8-6)/2 = 1$, stable
		F_2^{2-} :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi$	$(\pi_{2p}^{*})^{4}(\sigma_{2p}^{*})^{2}$	B.O. = $(8-8)/2 = 0$, not stable
	b.	Be ₂ :	$(\sigma_{2s})^2(\sigma_{2s}*)^2$		B.O. = $(2-2)/2 = 0$, not stable
		B ₂ :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$		B.O. = $(4-2)/2 = 1$, stable
		Ne ₂ :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2$	$)^{4}(\pi_{2p}^{*})^{4}(\sigma_{2p}^{*})^{2}$	B.O. = $(8-8)/2 = 0$, not stable
41.	Th	e electr	on configurations are:	:	

- a. Li_2 : $(\sigma_{2s})^2$ B.O. = (2-0)/2 = 1, diamagnetic (0 unpaired e⁻)b. C_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$ B.O. = (6-2)/2 = 2, diamagnetic (0 unpaired e⁻)c. S_2 : $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^2$ B.O. = (8-4)/2 = 2, paramagnetic (2 unpaired e⁻)
- 42. There are 14 valence electrons in the MO electron configuration. Also, the valence shell is n = 3. Some possibilities from row 3 having 14 valence electrons are Cl₂, SCl⁻, S₂²⁻, and Ar₂²⁺.

43. O₂:
$$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^2$$
 B.O. = $(8 - 4)/2 = 2$
N₂: $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$ B.O. = $(8 - 2)/2 = 3$

In O₂, an antibonding electron is removed, which will increase the bond order to 2.5 [= (8-3)/2]. The bond order increases as an electron is removed, so the bond strengthens. In N₂, a bonding electron is removed, which decreases the bond order to 2.5 = [(7-2)/2]. So the bond strength weakens as an electron is removed from N₂.

44. The electron configurations are:

$$\begin{array}{ll} F_2^+: \ (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3 & \text{B.O.} = (8-5)/2 = 1.5; \ 1 \text{ unpaired } e^- \\ F_2^-: \ (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4 & \text{B.O.} = (8-6)/2 = 1; \ 0 \text{ unpaired } e^- \\ F_2^-: \ (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^1 & \text{B.O.} = (8-7)/2 = 0.5; \ 1 \text{ unpaired } e^- \\ \end{array}$$

From the calculated bond orders, the order of bond lengths should be $F_2^+ < F_2 < F_2^-$.

45. N₂:
$$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$$
 B.O. = $(8-2)/2 = 3$

We need to decrease the bond order from 3 to 2.5. There are two ways to do this. One is to add an electron to form N_2^- . This added electron goes into one of the π_{2p}^* orbitals, giving a bond order of (8-3)/2 = 2.5. We could also remove a bonding electron to form N_2^+ . The bond order for N_2^+ is also 2.5 [= (7-2)/2].

46. Considering only the 12 valence electrons in O₂, the MO models would be:



It takes energy to pair electrons in the same orbital. Thus the structure with no unpaired electrons is at a higher energy; it is an excited state.

47. The electron configurations are (assuming the same orbital order as that for N_2):

a.	CO: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$	B.O. = $(8-2)/2 = 3$, diamagnetic
b.	CO ⁺ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$	B.O. = $(7-2)/2 = 2.5$, paramagnetic
c.	$\text{CO}^{2+}: \ (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4$	B.O. = $(6-2)/2 = 2$, diamagnetic

Because bond order is directly proportional to bond energy and inversely proportional to bond length:

Shortest \rightarrow longest bond length: $CO < CO^+ < CO^{2+}$

Smallest \rightarrow largest bond energy: $CO^{2+} < CO^{+} < CO$

48. The electron configurations are:

a.	CN^+ :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$	B.O. = $(6-2)/2 = 2$, diamagnetic
b.	CN:	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$	B.O. = $(7-2)/2 = 2.5$, paramagnetic
c.	CN ⁻ :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$	B.O. = 3, diamagnetic

The bond orders are CN⁺, 2; CN, 2.5; CN⁻, 3; because bond order is directly proportional to bond energy and inversely proportional to bond length:

Shortest \rightarrow longest bond length: $CN^- < CN < CN^+$

Smallest \rightarrow largest bond energy: $CN^+ < CN < CN^-$ 49. H₂: $(\sigma_{1s})^2$ B₂: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$ $C_2^{2^-}$: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ OF: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$

The bond strength will weaken if the electron removed comes from a bonding orbital. Of the molecules listed, H_2 , B_2 , and C_2^{2-} would be expected to have their bond strength weaken as an electron is removed. OF has the electron removed from an antibonding orbital, so its bond strength increases.

50. CN: $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^1$ NO: $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2 (\pi_{2p}^*)^1$ $O_2^{2^+}$: $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4$ $N_2^{2^+}$: $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4$

If the added electron goes into a bonding orbital, the bond order would increase, making the species more stable and more likely to form. Between CN and NO, CN would most likely form CN^- since the bond order increases (unlike NO^- , where the added electron goes into an antibonding orbital). Between O_2^{2+} and N_2^{2+} , N_2^+ would most likely form since the bond order increases (unlike O_2^{2+} going to O_2^+).

51. The two types of overlap that result in bond formation for p orbitals are in-phase side-to-side overlap (π bond) and in-phase head-to-head overlap (σ bond).



These molecular orbitals are sigma MOs because the electron density is cylindrically symmetric about the internuclear axis.

- 53. a. The electron density would be closer to F on average. The F atom is more electronegative than the H atom, and the 2p orbital of F is lower in energy than the 1s orbital of H.
 - b. The bonding MO would have more fluorine 2p character since it is closer in energy to the fluorine 2p atomic orbital.
 - c. The antibonding MO would place more electron density closer to H and would have a greater contribution from the higher-energy hydrogen 1s atomic orbital.
- 54. a. The antibonding MO will have more hydrogen 1s character because the hydrogen 1s atomic orbital is closer in energy to the antibonding MO.
 - b. No, the net overall overlap is zero. The p_x orbital does not have proper symmetry to overlap with a 1s orbital. The $2p_x$ and $2p_y$ orbitals are called nonbonding orbitals.



- d. Bond order = (2 0)/2 = 1; *Note*: The 2s, $2p_x$, and $2p_y$ electrons have no effect on the bond order.
- e. To form OH⁺, a nonbonding electron is removed from OH. Because the number of bonding electrons and antibonding electrons is unchanged, the bond order is still equal to one.
- 55. $C_2^{2^-}$ has 10 valence electrons. The Lewis structure predicts sp hybridization for each carbon with two unhybridized p orbitals on each carbon.

$$\begin{bmatrix} :C = C: \end{bmatrix}^{2-}$$

$$\begin{array}{l} \text{sp hybrid orbitals form the } \sigma \text{ bond and the two unhybridized} \\ \text{p atomic orbitals from each carbon form the two } \pi \text{ bonds.} \\ \text{MO: } (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2, \text{ B.O.} = (8-2)/2 = 3 \end{array}$$

c.

Both give the same picture, a triple bond composed of one σ and two π bonds. Both predict the ion will be diamagnetic. Lewis structures deal well with diamagnetic (all electrons paired) species. The Lewis model cannot really predict magnetic properties.

56. Lewis structures:

NO ⁺ :	[:N≡=0:]	NO ⁻ : [<u>N</u> =;;] [−]
NO:	 N़≓Ö or	N

Note: Lewis structures do not handle odd numbered electron species very well.

MO model:

NO ⁺ :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2,$	B.O. = 3, 0 unpaired e^{-} (diamagnetic)
NO:	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^1,$	B.O. = 2.5, 1 unpaired e^{-} (paramagnetic)
NO ⁻ :	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^2$	B.O. = 2, 2 unpaired e^{-} (paramagnetic)

The two models give the same results only for NO^+ (a triple bond with no unpaired electrons). Lewis structures are not adequate for NO and NO^- . The MO model gives a better representation for all three species. For NO, Lewis structures are poor for odd electron species. For NO⁻, both models predict a double bond, but only the MO model correctly predicts that NO^- is paramagnetic.

57. O₃ and NO₂⁻are isoelectronic, so we only need consider one of them since the same bonding ideas apply to both. The Lewis structures for O₃ are:



For each of the two resonance forms, the central O atom is sp² hybridized with one unhybridized p atomic orbital. The sp² hybrid orbitals are used to form the two sigma bonds to the central atom and hold the lone pair of electrons on the central O atom. The localized electron view of the π bond uses unhybridized p atomic orbitals. The π bond resonates between the two positions in the Lewis structures; the actual structure of O₃ is an average of the two resonance structures:



In the MO picture of the π bond, all three unhybridized p orbitals overlap at the same time, resulting in π electrons that are delocalized over the entire surface of the molecule. This is represented as:



In the localized electron view, the central carbon atom is sp² hybridized; the sp² hybrid orbitals are used to form the three sigma bonds in $CO_3^{2^-}$. The central C atom also has one unhybridized p atomic orbital that overlaps with another p atomic orbital from one of the oxygen atoms to form the π bond in each resonance structure. This localized π bond moves (resonates) from one position to another. In the molecular orbital model for $CO_3^{2^-}$, all four atoms in $CO_3^{2^-}$ have a p atomic orbital that is perpendicular to the plane of the ion. All four of these p orbitals overlap at the same time to form a delocalized π bonding system where the π electrons can roam above and below the entire surface of the ion. The π molecular orbital system for $CO_3^{2^-}$ is analogous to that for NO_3^- which is shown in Figure 9.48 of the text.

Connecting to Biochemistry

59. For carbon, nitrogen, and oxygen atoms to have formal charge values of zero, each C atom will form four bonds to other atoms and have no lone pairs of electrons, each N atom will form three bonds to other atoms and have one lone pair of electrons, and each O atom will form two bonds to other atoms and have two lone pairs of electrons. Following these bonding requirements gives the following two resonance structures for vitamin B₆:



- a. 21 σ bonds; 4 π bonds (The electrons in the three π bonds in the ring are delocalized.)
- b. Angles a), c), and g): $\approx 109.5^{\circ}$; angles b), d), e), and f): $\approx 120^{\circ}$
- c. 6 sp² carbons; the five carbon atoms in the ring are sp² hybridized, as is the carbon with the double bond to oxygen.
- d. 4 sp³ atoms; the two carbons that are not sp² hybridized are sp³ hybridized, and the oxygens marked with angles a and c are sp³ hybridized.
- e. Yes, the π electrons in the ring are delocalized. The atoms in the ring are all sp² hybridized. This leaves a p orbital perpendicular to the plane of the ring from each atom. Overlap of all six of these p orbitals results in a π molecular orbital system where the electrons are delocalized above and below the plane of the ring (similar to benzene in Figure 9.47 of the text).
- 60. a. To complete the Lewis structure, add two lone pairs to each sulfur atom.



- b. See the Lewis structure. The four carbon atoms in the ring are all sp² hybridized, and the two sulfur atoms are sp³ hybridized.
- c. 23 σ and 9 π bonds. *Note*: CH₃, CH₂, and CH are shorthand for carbon atoms singly bonded to hydrogen atoms.
- 61. To complete the Lewis structure, just add lone pairs of electrons to satisfy the octet rule for the atoms that have fewer than eight electrons.



a.	6	b.	4	c.	The center N in -N=N=N group
d.	33 σ	e.	5π bonds	f.	180°
g.	≈109.5°	h.	sp ³		

62.

For CO, we will assume the same orbital ordering as that for N_2 .

CO: $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$	B.O. = $(8-2)/2 = 3$; 0 unpaired electrons
$O_2: \ (\sigma_{2s})^2 (\sigma_{2s}*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}*)^2$	B.O. = $(8-4)/2 = 2$; 2 unpaired electrons

The most obvious differences are that CO has a larger bond order than O_2 (3 versus 2) and that CO is diamagnetic, whereas O_2 is paramagnetic.

 a. The CO bond is polar with the negative end at the more electronegative oxygen atom. We would expect metal cations to be attracted to and bond to the oxygen end of CO on the basis of electronegativity.

b. :C=O: FC (carbon) =
$$4 - 2 - 1/2(6) = -1$$

FC (oxygen) = $6 - 2 - 1/2(6) = +1$

From formal charge, we would expect metal cations to bond to the carbon (with the negative formal charge).

- c. In molecular orbital theory, only orbitals with proper symmetry overlap to form bonding orbitals. The metals that form bonds to CO are usually transition metals, all of which have outer electrons in the d orbitals. The only molecular orbitals of CO that have proper symmetry to overlap with d orbitals are the π_{2p}^* orbitals, whose shape is similar to the d orbitals. Because the antibonding molecular orbitals have more carbon character (carbon is less electronegative than oxygen), one would expect the bond to form through carbon.
- 64. Benzoic acid $(C_7H_6O_2)$ has 7(4) + 6(1) + 2(6) = 46 valence electrons. The Lewis structure for benzoic acid is:



The circle in the ring indicates the delocalized π bonding in the benzene ring. The two benzene resonance Lewis structures have three alternating double bonds in the ring (see Figure 9.45).

The six carbons in the ring and the carbon bonded to the ring are all sp² hybridized. The five C–H sigma bonds are formed from overlap of the sp² hybridized carbon atoms with hydrogen 1s atomic orbitals. The seven C–C σ bonds are formed from head to head overlap of sp² hybrid orbitals from each carbon. The C–O single bond is formed from overlap of an sp² hybrid orbital on carbon with an sp³ hybrid orbital from oxygen. The C–O σ bond in the double bond is formed from overlap of carbon sp² hybrid orbital with an oxygen sp² orbital. The π bond in the C–O double bond is formed from overlap of parallel p unhybridized atomic orbitals from C and O. The delocalized π bonding system in the ring is formed from overlap of all six unhybridized p atomic orbitals from the six carbon atoms. See Figure 9.47 for delocalized π bonding system in the benzene ring.

Additional Exercises

65. a.
$$XeO_3$$
, $8 + 3(6) = 26 e^{-}$
b. XeO_4 , $8 + 4(6) = 32 e^{-}$
trigonal pyramid; sp³
c. $XeOF_4$, $8 + 6 + 4(7) = 42 e^{-}$
 $\vdots \overrightarrow{F}, \qquad \overrightarrow{F}, \qquad\overrightarrow{F}, \qquad \overrightarrow{F}, \qquad\overrightarrow{F}, \overrightarrow{F}, \qquad\overrightarrow{F}, \overrightarrow{F}, \qquad\overrightarrow{F}, \overrightarrow{F}, \overrightarrow{F}, \overrightarrow{F}, \overrightarrow{F}, \overrightarrow{F}, \overrightarrow{F$



Note: Similar to Exercise 65c, d, and e, $F_2CIO_2^-$ has two additional Lewis structures that are possible, and F_4CIO^- has one additional Lewis structure that is possible. The predicted hybridization is unaffected.

- 67. a. No, some atoms are in different places. Thus these are not resonance structures; they are different compounds.
 - b. For the first Lewis structure, all nitrogens are sp³ hybridized, and all carbons are sp² hybridized. In the second Lewis structure, all nitrogens and carbons are sp² hybridized.
 - c. For the reaction:



Bonds broken:

Bonds formed:

3 C=O (745 kJ/mol)	3 C=N (615 kJ/mol)
3 C–N (305 kJ/mol)	3 C–O (358 kJ/mol)
3 N-H (391 kJ/mol)	3 O–H (467 kJ/mol)

 $\Delta H = 3(745) + 3(305) + 3(391) - [3(615) + 3(358) + 3(467)]$

 $\Delta H = 4323 \text{ kJ} - 4320 \text{ kJ} = 3 \text{ kJ}$

The bonds are slightly stronger in the first structure with the carbon-oxygen double bonds since ΔH for the reaction is positive. However, the value of ΔH is so small that the best conclusion is that the bond strengths are comparable in the two structures.

68. For carbon, nitrogen, and oxygen atoms to have formal charge values of zero, each C atom will form four bonds to other atoms and have no lone pairs of electrons, each N atom will form three bonds to other atoms and have one lone pair of electrons, and each O atom will form two bonds to other atoms and have two lone pairs of electrons. Following these bonding requirements, a Lewis structure for aspartame is:



Another resonance structure could be drawn having the double bonds in the benzene ring moved over one position.

Atoms that have trigonal planar geometry of electron pairs are assumed to have sp^2 hybridization, and atoms with tetrahedral geometry of electron pairs are assumed to have sp^3 hybridization. All the N atoms have tetrahedral geometry, so they are all sp^3 hybridized (no sp^2 hybridization). The oxygens double bonded to carbon atoms are sp^2 hybridized; the other two oxygens with two single bonds are sp^3 hybridized. For the carbon atoms, the six carbon atoms in the benzene ring are sp^2 hybridized, and the three carbons double bonded to oxygen are also sp^2 hybridized (tetrahedral geometry). Answering the questions:

- 9 sp² hybridized C and N atoms (9 from C's and 0 from N's)
- 7 sp³ hybridized C and O atoms (5 from C's and 2 from O's)
- 39 σ bonds and 6 π bonds (this includes the 3 π bonds in the benzene ring that are delocalized)

69.



In order to rotate about the double bond, the molecule must go through an intermediate stage where the π bond is broken and the sigma bond remains intact. Bond energies are 347 kJ/mol for C–C and 614 kJ/mol for C=C. If we take the single bond as the strength of the σ bond, then the strength of the π bond is (614 – 347 =) 267 kJ/mol. In theory, 267 kJ/mol must be supplied to rotate about a carbon-carbon double bond.

70.
$$CO, 4 + 6 = 10 e^{-};$$
 $CO_2, 4 + 2(6) = 16 e^{-};$ $C_3O_2, 3(4) + 2(6) = 24 e^{-}$
:C==O: $\ddot{O} = C = \ddot{O}$
 $\ddot{O} = C = C = \ddot{O}$

There is no molecular structure for the diatomic CO molecule. The carbon in CO is sp hybridized. CO_2 is a linear molecule, and the central carbon atom is sp hybridized. C_3O_2 is a linear molecule with all the central carbon atoms exhibiting sp hybridization.

71. a. BH₃ has
$$3 + 3(1) = 6$$
 valence electrons.



trigonal planar, nonpolar, 120°, sp²

b. N_2F_2 has 2(5) + 2(7) = 24 valence electrons.





Nonpolar

Can also be:

polar

These are distinctly different molecules.

c. C_4H_6 has 4(4) + 6(1) = 22 valence electrons.



All C atoms are trigonal planar with 120° bond angles and sp² hybridization. Because C and H have about equal electronegativities, the C–H bonds are essentially nonpolar, so the molecule is nonpolar. All neutral compounds composed of only C and H atoms are nonpolar.

d. ICl₃ has 7 + 3(7) = 28 valence electrons.



- 72. a. Yes, both have four sets of electrons about the P. We would predict a tetrahedral structure for both. See part d for the Lewis structures.
 - b. The hybridization is sp³ for P in each structure since both structures exhibit a tetrahedral arrangement of electron pairs.
 - c. P has to use one of its d orbitals to form the π bond since the p orbitals are all used to form the hybrid orbitals.
 - d. Formal charge = number of valence electrons of an atom [(number of lone pair electrons) + 1/2(number of shared electrons)]. The formal charges calculated for the O and P atoms are next to the atoms in the following Lewis structures.



In both structures, the formal charges of the Cl atoms are all zeros. The structure with the P=O bond is favored on the basis of formal charge since it has a zero formal charge for all atoms.

73. a. The Lewis structures for NNO and NON are:



The NNO structure is correct. From the Lewis structures, we would predict both NNO and NON to be linear. However, we would predict NNO to be polar and NON to be nonpolar. Since experiments show N_2O to be polar, NNO is the correct structure.

b. Formal charge = number of valence electrons of atoms – [(number of lone pair electrons) + 1/2(number of shared electrons)].



The formal charges for the atoms in the various resonance structures are below each atom. The central N is sp hybridized in all the resonance structures. We can probably ignore the third resonance structure on the basis of the relatively large formal charges as compared to the first two resonance structures.

c. The sp hybrid orbitals from the center N overlap with atomic orbitals (or appropriate hybrid orbitals) from the other two atoms to form the two sigma bonds. The remaining two unhybridized p orbitals from the center N overlap with two p orbitals from the peripheral N to form the two π bonds.



74. N₂ (ground state): $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$, B.O. = 3, diamagnetic (0 unpaired e⁻) N₂ (1st excited state): $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^1 (\pi_{2p}^*)^1$

B.O. = (7 - 3)/2 = 2, paramagnetic (2 unpaired e⁻)

The first excited state of N₂ should have a weaker bond and should be paramagnetic.

- 75. F_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^4(\pi_{2p}^*)^4$; F_2 should have a lower ionization energy than F. The electron removed from F_2 is in a π_{2p}^* antibonding molecular orbital that is higher in energy than the 2p atomic orbitals from which the electron in atomic fluorine is removed. Because the electron removed from F_2 is higher in energy than the electron removed from F, it should be easier to remove an electron from F_2 than from F.
- 76.



The two orbitals will overlap side to side, so when the orbitals are in phase, a π bonding molecular orbital would form.

- 77. Side-to-side in-phase overlap of these d orbitals would produce a π bonding molecular orbital. There would be no probability of finding an electron on the axis joining the two nuclei, which is characteristic of π MOs.
- 78. Molecule A has a tetrahedral arrangement of electron pairs because it is sp³ hybridized. Molecule B has 6 electron pairs about the central atom, so it is d^2sp^3 hybridized. Molecule C has two σ and two π bonds to the central atom, so it either has two double bonds to the central atom (as in CO₂) or one triple bond and one single bond (as in HCN). Molecule C is consistent with a linear arrangement of electron pairs exhibiting sp hybridization. There are many correct possibilities for each molecule; an example of each is:



Challenge Problems

79. The following Lewis structure has a formal charge of zero for all of the atoms in the molecule.



The three C atoms each bonded to three H atoms are sp^3 hybridized (tetrahedral geometry); the other five C atoms with trigonal planar geometry are sp^2 hybridized. The one N atom with the double bond is sp^2 hybridized, and the other three N atoms are sp^3 hybridized. The answers to the questions are:

- 6 C and N atoms are sp² hybridized
- 6 C and N atoms are sp³ hybridized

- 0 C and N atoms are sp hybridized (linear geometry)
- 25 σ bonds and 4 π bonds
- 80. The complete Lewis structure follows. All but two of the carbon atoms are sp^3 hybridized. The two carbon atoms that contain the double bond are sp^2 hybridized (see *).



No; most of the carbons are not in the same plane since a majority of carbon atoms exhibit a tetrahedral structure (109.5° bond angles). *Note*: HO, H₂C, CH, CH₂, and CH₃ are shorthand for carbon atoms singly bonded to hydrogen atoms.

81. a. NCN^{2-} has 5+4+5+2=16 valence electrons.

$$\left[\begin{array}{c} \ddot{N} = C = \ddot{N} \end{array} \right]^{2} \longleftrightarrow \left[:N \equiv C - \ddot{N} : \right]^{2} \longleftrightarrow \left[:\ddot{N} - C \equiv N : \right]^{2}$$

 H_2NCN has 2(1) + 5 + 4 + 5 = 16 valence electrons.



NCNC(NH₂)₂ has 5 + 4 + 5 + 4 + 2(5) + 4(1) = 32 valence electrons.



favored by formal charge

Melamine $(C_3N_6H_6)$ has 3(4) + 6(5) + 6(1) = 48 valence electrons.



b. NCN²⁻: C is sp hybridized. Each resonance structure predicts a different hybridization for the N atom. Depending on the resonance form, N is predicted to be sp, sp², or sp³ hybridized. For the remaining compounds, we will give hybrids for the favored resonance structures as predicted from formal charge considerations.



Melamine: N in NH₂ groups are all sp³ hybridized; atoms in ring are all sp² hybridized.

- c. NCN²⁻: 2 σ and 2 π bonds; H₂NCN: 4 σ and 2 π bonds; dicyandiamide: 9 σ and 3 π bonds; melamine: 15 σ and 3 π bonds
- d. The π -system forces the ring to be planar, just as the benzene ring is planar.
- e. The structure: $N \equiv C N$

best agrees with experiments because it has three different CN bonds. This structure is also favored on the basis of formal charge.

82. One of the resonance structures for benzene is:



To break $C_6H_6(g)$ into C(g) and H(g) requires the breaking of 6 C–H bonds, 3 C=C bonds, and 3 C–C bonds:

$$C_6H_6(g) \to 6 C(g) + 6 H(g)$$
 $\Delta H = 6D_{C-H} + 3D_{C-C} + 3D_{C-C}$

$$\Delta H = 6(413 \text{ kJ}) + 3(614 \text{ kJ}) + 3(347 \text{ kJ}) = 5361 \text{ kJ}$$

The question asks for ΔH_{f}° for $C_{6}H_{6}(g)$, which is ΔH for the reaction:

$$6 \operatorname{C}(s) + 3 \operatorname{H}_2(g) \to \operatorname{C}_6\operatorname{H}_6(g) \quad \Delta \operatorname{H} = \Delta \operatorname{H}_{f, \operatorname{C}_6\operatorname{H}_6(g)}^{\circ}$$

To calculate ΔH for this reaction, we will use Hess's law along with the value ΔH_{f}° for C(g) and the bond energy value for H₂ (D_{H2} = 432 kJ/mol).

$$\begin{array}{ll} 6 \ C(g) + 6 \ H(g) \rightarrow C_6 H_6(g) & \Delta H_1 = -5361 \ kJ \\ & 6 \ C(s) \rightarrow 6 \ C(g) & \Delta H_2 = \ 6(717 \ kJ) \\ & 3 \ H_2(g) \rightarrow 6 \ H(g) & \Delta H_3 = \ 3(432 \ kJ) \\ \hline & 6 \ C(s) + 3 \ H_2(g) \rightarrow C_6 H_6(g) & \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = 237 \ kJ; \ \Delta H_{f, \ C_6 H_6(g)}^{\circ} = 237 \ kJ/mol \end{array}$$

The experimental ΔH_{f}° for $C_{6}H_{6}(g)$ is more stable (lower in energy) by 154 kJ than the ΔH_{f}° calculated from bond energies (83 – 237 = -154 kJ). This extra stability is related to benzene's ability to exhibit resonance. Two equivalent Lewis structures can be drawn for benzene. The π -bonding system implied by each Lewis structure consists of three localized π bonds. This is not correct because all C–C bonds in benzene are equivalent. We say the π electrons in benzene are delocalized over the entire surface of $C_{6}H_{6}$ (see Section 14.5 of the text). The large discrepancy between ΔH_{f}° values is due to the delocalized π electrons, whose effect was not accounted for in the calculated ΔH_{f}° value. The extra stability associated with benzene can be called resonance stabilization. In general, molecules that exhibit resonance are usually more stable than predicted using bond energies.

83. a.
$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s})}{25 \times 10^{-9} \text{ m}} = 7.9 \times 10^{-18} \text{ J}$$

$$7.9 \times 10^{-18} \text{ J} \times \frac{6.022 \times 10^{23}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 4800 \text{ kJ/mol}$$

Using ΔH values from the various reactions, 25-nm light has sufficient energy to ionize N_2 and N and to break the triple bond. Thus N_2 , N_2^+ , N, and N⁺ will all be present, assuming excess N_2 .

b. To produce atomic nitrogen but no ions, the range of energies of the light must be from 941 kJ/mol to just below 1402 kJ/mol.

$$\frac{941 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 1.56 \times 10^{-18} \text{ J/photon}$$

$$\lambda = \frac{\text{hc}}{\text{E}} = \frac{(6.6261 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s})}{1.56 \times 10^{-18} \text{ J}} = 1.27 \times 10^{-7} \text{ m} = 127 \text{ nm}$$

$$\frac{1402 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.0221 \times 10^{23}} \times \frac{1000 \text{ J}}{\text{kJ}} = 2.328 \times 10^{-18} \text{ J/photon}$$

$$\lambda = \frac{\text{hc}}{\text{E}} = \frac{(6.6261 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m/s})}{2.328 \times 10^{-18} \text{ J}} = 8.533 \times 10^{-8} \text{ m} = 85.33 \text{ nm}$$

Light with wavelengths in the range of 85.33 nm $< \lambda \le 127$ nm will produce N but no ions.

- c. N_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$; the electron removed from N_2 is in the σ_{2p} molecular orbital, which is lower in energy than the 2p atomic orbital from which the electron in atomic nitrogen is removed. Because the electron removed from N_2 is lower in energy than the electron removed from N_2 is greater than that for N.
- 84. The π bonds between S atoms and between C and S atoms are not as strong. The p atomic orbitals do not overlap with each other as well as the smaller p atomic orbitals of C and O overlap.
- 85. O=N-Cl: The bond order of the NO bond in NOCl is 2 (a double bond).

NO: From molecular orbital theory, the bond order of this NO bond is 2.5. (See Figure 9.40 of the text.)

Both reactions apparently involve only the breaking of the N–Cl bond. However, in the reaction ONCl \rightarrow NO + Cl, some energy is released in forming the stronger NO bond, lowering the value of Δ H. Therefore, the apparent N–Cl bond energy is artificially low for this reaction. The first reaction involves only the breaking of the N–Cl bond.

86. The molecular orbitals for BeH_2 are formed from the two hydrogen 1s orbitals and the 2s and one of the 2p orbitals from beryllium. One of the sigma bonding orbitals forms from overlap of the hydrogen 1s orbitals with a 2s orbital from beryllium. Assuming the z axis is the internuclear axis in the linear BeH_2 molecule, then the $2p_z$ orbital from beryllium has proper symmetry to overlap with the 1s orbitals from hydrogen; the $2p_x$ and $2p_y$ orbitals are nonbonding orbitals since they don't have proper symmetry necessary to overlap with 1s orbitals. The type of bond formed from the $2p_z$ and 1s orbitals is a sigma bond since the orbitals overlap head to head. The MO diagram for BeH_2 is:



Bond order = (4 - 0)/2 = 2; the MO diagram predicts BeH₂ to be a stable species and also predicts that BeH₂ is diamagnetic. *Note*: The σ_s MO is a mixture of the two hydrogen 1s orbitals with the 2s orbital from beryllium, and the σ_p MO is a mixture of the two hydrogen 1s orbitals with the $2p_z$ orbital from beryllium. The MOs are not localized between any two atoms; instead, they extend over the entire surface of the three atoms.

87. The ground state MO electron configuration for He₂ is $(\sigma_{1s})^2(\sigma_{1s}^*)^2$, giving a bond order of 0. Therefore, He₂ molecules are not predicted to be stable (and are not stable) in the lowestenergy ground state. However, in a high-energy environment, electron(s) from the antibonding orbitals in He₂ can be promoted into higher-energy bonding orbitals, thus giving a nonzero bond order and a "reason" to form. For example, a possible excited-state MO electron configuration for He₂ would be $(\sigma_{1s})^2(\sigma_{1s}^*)^1(\sigma_{2s})^1$, giving a bond order of (3 - 1)/2 =1. Thus excited He₂ molecules can form, but they spontaneously break apart as the electron(s) fall back to the ground state, where the bond order equals zero.



The order from lowest IE to highest IE is: $O_2^- < O_2 < O_2^+ < O_2$

The electrons for O_2^- , O_2 , and O_2^+ that are highest in energy are in the π^*_{2p} MOs. But for O_2^- , these electrons are paired. O_2^- should have the lowest ionization energy (its paired π_{2p}^* electron is easiest to remove). The species O_2^+ has an overall positive charge, making it harder to remove an electron from O_2^+ than from O_2 . The highest-energy electrons for O (in the 2p atomic orbitals) are lower in energy than the π_{2p}^* electrons for the other species; O will have the highest ionization energy because it requires a larger quantity of energy to remove an electron from O as compared to the other species.

89. The electron configurations are:

N₂: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ O₂: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$ N_2^{2-} : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^2$ $N_2^{-}: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2 (\pi_{2p}^*)^1$ O_2^+ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$

Note: The ordering of the σ_{2p} and π_{2p} orbitals is not important to this question.

The species with the smallest ionization energy has the electron that is easiest to remove. From the MO electron configurations, O_2 , N_2^{2-} , N_2^{-} , and O_2^{+} all contain electrons in the same higher-energy antibonding orbitals (π_{2p}^*) , so they should have electrons that are easier to remove as compared to N₂, which has no π_{2p}^* electrons. To differentiate which has the easiest π_{2p}^{*} to remove, concentrate on the number of electrons in the orbitals attracted to the number of protons in the nucleus.

 N_2^{2-} and N_2^{-} both have 14 protons in the two nuclei combined. Because N_2^{2-} has more electrons, one would expect N_2^{2-} to have more electron repulsions, which translates into having an easier electron to remove. Between O_2 and O_2^+ , the electron in O_2 should be easier to remove. O_2 has one more electron than O_2^+ , and one would expect the fewer electrons in O_2^+ to be better attracted to the nuclei (and harder to remove). Between N_2^{2-} and O_2 , both have 16 electrons; the difference is the number of protons in the nucleus. Because N_2^{2-} has two fewer protons than O_2 , one would expect the N_2^{2-} to have the easiest electron to remove, which translates into the smallest ionization energy.

90. a. $F_2(g) \rightarrow F(g) + F(g)$ $\Delta H = F_2^{-}$ bond energy

Using Hess's law:

 $F_2^{-}(g) \rightarrow F_2(g) + e^{-}$ $\Delta H = 290$. kJ (IE for F_2) $F_2(g) \rightarrow 2 F(g)$ $\Delta H = 154 \text{ kJ}$ (BE for F₂ from Table 13.6) $F(g) + e^- \rightarrow F^-(g)$ $\Delta H = -327.8 \text{ kJ}$ (EA for F from Table12.8)

 $F_2^{-}(g) \rightarrow F(g) + F^{-}(g) \quad \Delta H = 116 \text{ kJ}; \text{ BE for } F_2^{-} = 116 \text{ kJ/mol}$

Note that F_2^- has a smaller bond energy than F_2 .

b. F₂:
$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$$
 B.O. = $(8-6)/2 = 1$
F₂⁻: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^1$ B.O. = $(8-7)/2 = 0.5$

MO theory predicts that F_2 should have a stronger bond than F_2^- because F_2 has the larger bond order. As determined in part a, F_2 indeed has a stronger bond because the F_2 bond energy (154 kJ/mol) is greater than the F_2^- bond energy (116 kJ/mol).

Integrative Problems

91. a. Li₂: $(\sigma_{2s})^2$ B.O. = (2-0)/2 = 1B₂: $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^2$ B.O. = (4-2)/2 = 1

Both have a bond order of 1.

b. B_2 has four more electrons than Li_2 , so four electrons must be removed from B_2 to make it isoelectronic with Li_2 . The isoelectronic ion is B_2^{4+} .

c.
$$1.5 \text{ kg } \text{B}_2 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } \text{B}_2}{21.62 \text{ g } \text{B}_2} \times \frac{6455 \text{ kJ}}{\text{mol } \text{B}_2} = 4.5 \times 10^5 \text{ kJ}$$

92. a. HF,
$$1 + 7 = 8 e^{-1}$$
 SbF₅, $5 + 5(7) = 40 e^{-1}$



linear, sp³ (if F is hybridized)

trigonal bipyramid, dsp³

$$H_2F^+, 2(1) + 7 - 1 = 8 e^-$$

V-shaped, sp³

SbF₆⁻, 5 + 6(7) + 1 = 48 e⁻

$$\begin{bmatrix} \vdots \overleftarrow{F} & \vdots \overleftarrow{F} \\ \vdots \overleftarrow{F} &$$

b.
$$2.93 \text{ mL} \times \frac{0.975 \text{ g HF}}{\text{mL}} \times \frac{1 \text{ mol HF}}{20.01 \text{ g HF}} = 0.143 \text{ mol HF}$$

$$10.0 \text{ mL} \times \frac{3.10 \text{ g SbF}_5}{\text{mL}} \times \frac{1 \text{ mol SbF}_5}{216.8 \text{ g SbF}_5} = 0.143 \text{ mol SbF}_5$$

The balanced equation requires a 2:1 mole ratio between HF and SbF₅. Because we have the same amount (moles) of each reactant, HF is limiting.

$$0.143 \text{ mol } \text{HF} \times \frac{1 \text{ mol } [\text{H}_2\text{F}]^+[\text{SbF}_6]^-}{2 \text{ mol } \text{HF}} \times \frac{256.8 \text{ g}}{\text{mol } [\text{H}_2\text{F}]^+[\text{SbF}_6]^-} = 18.4 \text{ g} [\text{H}_2\text{F}]^+[\text{SbF}_6]^-$$

93. Element X has 36 protons, which identifies it as Kr. Element Y has one less electron than Y^- , so the electron configuration of Y is $1s^22s^22p^5$. This is F.

$$KrF_{3}^{+}$$
, $8 + 3(7) - 1 = 28 e^{-1}$

