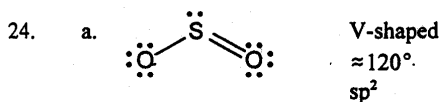


14. C_2H_2 has $2(4) + 2(1) = 10$ valence electrons.



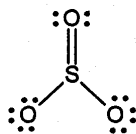
Each carbon atom in C_2H_2 is sp hybridized since each carbon atom is surrounded by two effective pairs of electrons, i.e., each carbon atom has a linear arrangement of the electrons. Since each carbon atom is sp hybridized, then each carbon atom has two unhybridized p atomic orbitals. The two $C-H$ 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 the carbon atoms is formed from overlap of sp hybrid orbitals on each carbon atom. The two π bonds of the triple bond are formed from parallel overlap of the two unhybridized p atomic orbitals on each carbon.

20. All have a tetrahedral arrangement of electron pairs about the central atom so all have central atoms with sp^3 hybridization. See Exercise 8.84 for the Lewis structures.



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.

b.

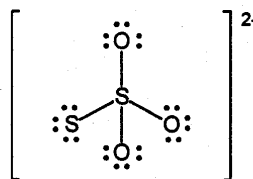


plus two other resonance structures

trigonal planar
 sp^2

120°

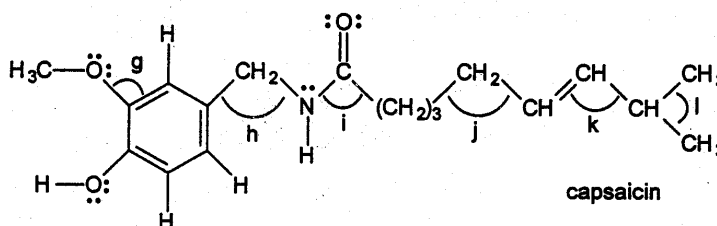
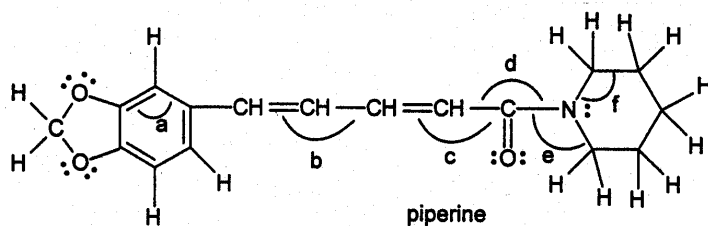
c.



tetrahedral
 sp^3

109.5°

30. 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 6 carbon atoms and the second ring contains 5 carbon atoms (plus nitrogen). Also notice that CH₃, CH₂ and CH are shorthand for carbon atoms singly bonded to hydrogen atoms.

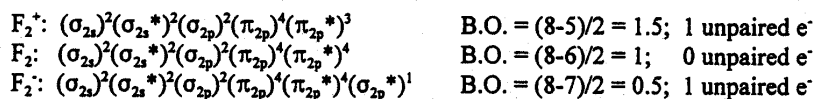
b. piperine: 0 sp, 11 sp² and 6 sp³ carbons; capsaicin: 0 sp, 9 sp² and 9 sp³ carbons

c. The nitrogens are sp³ hybridized in each molecule.

- | | | |
|------------|-------------|-----------|
| d. a. 120° | e. ≈ 109.5° | i. 120° |
| b. 120° | f. 109.5° | j. 109.5° |
| c. 120° | g. 120° | k. 120° |
| d. 120° | h. 109.5° | l. 109.5° |

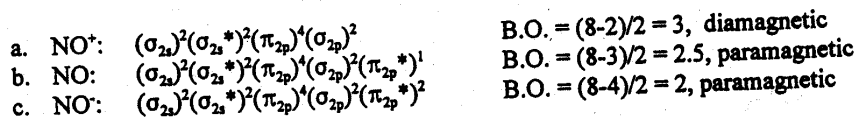
34. a. N₂²⁺: (σ_{2s})²(σ_{2s}^{*})²(π_{2p})⁴(σ_{2p})²(π_{2p}^{*})² B.O. = (8-4)/2 = 2, stable
 O₂²⁺: (σ_{2s})²(σ_{2s}^{*})²(σ_{2p})²(π_{2p})⁴(π_{2p}^{*})⁴ B.O. = (8-6)/2 = 1, stable
 F₂²⁺: (σ_{2s})²(σ_{2s}^{*})²(σ_{2p})²(π_{2p})⁴(π_{2p}^{*})⁴(σ_{2p}^{*})² B.O. = (8-8)/2 = 0, not stable
- b. Be₂: (σ_{2s})²(σ_{2s}^{*})² B.O. = (2-2)/2 = 0, not stable
 B₂: (σ_{2s})²(σ_{2s}^{*})²(π_{2p})² B.O. = (4-2)/2 = 1, stable
 Ne₂: (σ_{2s})²(σ_{2s}^{*})²(σ_{2p})²(π_{2p})⁴(π_{2p}^{*})⁴(σ_{2p}^{*})² B.O. = (8-8)/2 = 0, not stable

38. The electron configurations are:



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

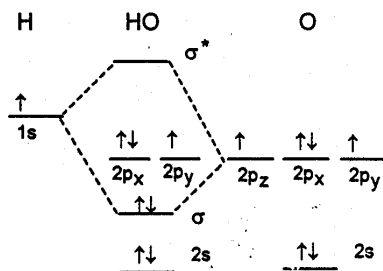
42. The electron configurations are (assuming the same orbital order as that for N_2):



48. a. The antibonding MO will have more hydrogen 1s character since the hydrogen 1s atomic orbital is closer in energy to the antibonding MO.
- b. No, the 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.

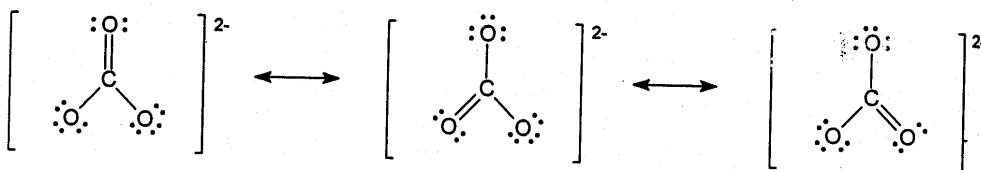


c.



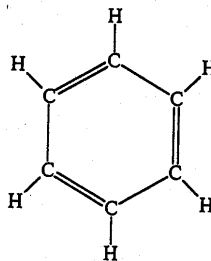
- d. Bond order = $\frac{2-0}{2} = 1$; Note: The 2s, $2p_x$, and $2p_y$ electrons have no effect on the bond order.
- e. To form OH^+ a nonbonding electron is removed from OH. Since the number of bonding electrons and antibonding electrons are unchanged, then the bond order is still equal to one.

50. The Lewis structures for CO_3^{2-} are (24 e⁻):



In the localized electron view, the central carbon atom is sp^2 hybridized which are used to form the three sigma bonds in CO_3^{2-} . The central C atom also has one unhybridized p atomic orbital which 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 which 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 over 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 9.49 of the text.

64. One of the resonance structures for benzene is:

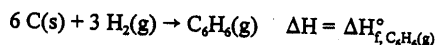


To break $\text{C}_6\text{H}_6(\text{g})$ into $\text{C}(\text{g})$ and $\text{H}(\text{g})$ requires the breaking of 6 C-H bonds, 3 C=C bonds and 3 C-C bonds:

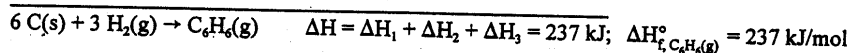
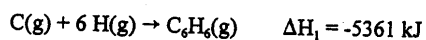


$$\Delta H = 6(413 \text{ kJ}) + 3(614 \text{ kJ}) + 3(347 \text{ kJ}) = 5361 \text{ kJ}$$

The question wants ΔH_f° for $\text{C}_6\text{H}_6(\text{g})$ which is ΔH for the reaction:



To calculate ΔH for this reaction, we will use Hess's law along with the ΔH_f° value for $\text{C}(\text{g})$ and the bond energy value for H_2 ($D_{\text{H}_2} = 432 \text{ kJ/mol}$).



The experimental ΔH_f° for $\text{C}_6\text{H}_6(\text{g})$ is more stable (lower in energy) by 154 kJ as compared to ΔH_f° calculated from bond energies ($87 - 237 = -154 \text{ kJ}$). 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 as all C-C bonds in benzene are equivalent. We say the π electrons in benzene are delocalized over the entire surface of C_6H_6 (see Section 9.5 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.