

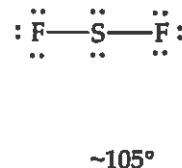
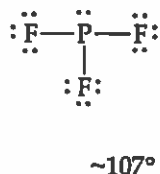
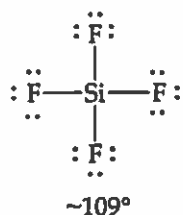
# 9 Molecular Geometry and Bonding Theories

## Visualizing Concepts

- 9.1 Removing an atom from the equatorial plane of trigonal bipyramid in Figure 9.3 creates a seesaw shape. It might appear that you could also obtain a seesaw by removing two atoms from the square plane of the octahedron. However, one of the B-A-B angles in the seesaw is  $120^\circ$ , so it must be derived from a trigonal bipyramid.
- 9.2
- $120^\circ$
  - If the blue balloon expands, the angle between red and green balloons decreases.
  - Nonbonding (lone) electron pairs exert greater repulsive forces than bonding pairs, resulting in compression of adjacent bond angles.
- 9.3 *Analyze/Plan.* Visualize the molecular geometry and the electron domain geometries that could produce it. Confirm your choices with Tables 9.2 and 9.3. On Table 9.3, note that octahedral electron domain geometry results in only 3 possible molecular geometries: octahedral, square pyramidal and square planar (not T-shaped, bent or linear). *Solve.*
2. Molecular geometry: linear. Possible electron domain geometries: linear, trigonal bipyramidal
  1. Molecular geometry, T-shaped. Possible electron domain geometries: trigonal bipyramidal
  1. Molecular geometry, octahedral. Possible electron domain geometries: octahedral
  1. Molecular geometry, square-pyramidal. Possible electron domain geometries: octahedral
  1. Molecular geometry, square planar. Possible electron domain geometries: octahedral
  1. Molecular geometry, triangular pyramid. Possible electron domain geometries: trigonal bipyramidal. This is an unusual molecular geometry which is not listed in Table 9.3. It could occur if the equatorial substituents on the trigonal bipyramid were extremely bulky, causing the nonbonding electron pair to occupy an axial position.
- 9.4
- $4 e^-$  domains
  - The molecule has a non-zero dipole moment, because the C-H and C-F bond dipoles do not cancel each other.
  - The dipole moment vector bisects the F-C-F and H-C-H angles, with the negative end of the vector toward the F atoms.

- 9.5 (a) The reference point for zero energy on the diagram corresponds to a state where the two Cl atoms are separate and not interacting. This corresponds to an infinite Cl-Cl distance beyond the right extreme of the horizontal axis. The point near the left side of the plot where the curve intersects the x-axis at  $E = 0$  has no special meaning.
- (b) According to the valence-bond model, as atoms approach, their valence atomic orbitals overlap, allowing two electrons of opposite spin to mutually occupy space between the two nuclei. Energy decreases as atom separation decreases because the valence electrons of one atom come close enough to the other atom to be stabilized by both nuclei instead of just one nucleus.
- (c) The Cl-Cl distance at the energy minimum on the plot is the Cl-Cl bond length.
- (d) At interatomic separations shorter than the bond distance, the two nuclei begin to repel each other, increasing the overall energy of the system.
- (e) Energy is shown on the y-axis of the plot. The minimum energy for the two atoms represents the stabilization obtained by bringing two Cl atoms together at the optimum (bond) distance. The y-coordinate of the minimum point on the plot corresponds to the Cl-Cl bond energy, or bond strength.

9.6  $\text{SiF}_4$  32  $e^-$ , 16  $e^-$  pr       $\text{PF}_3$  26  $e^-$ , 13  $e^-$  pr       $\text{SF}_2$  20  $e^-$ , 10  $e^-$  pr



In all three molecules, the electron domain geometry is tetrahedral and the approximate bond angle is  $109^\circ$ . But,  $\text{SiF}_4$  has 0 nonbonding electron pairs,  $\text{PF}_3$  has 1 nonbonding pair, and  $\text{SF}_2$  has 2 nonbonding pairs. If nonbonding electron pairs occupy more space than bonding pairs, we expect the bond angles to decrease in the series, perhaps  $109^\circ$ ,  $107^\circ$ ,  $105^\circ$ .

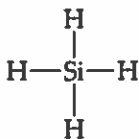
- 9.7 The diagram illustrates mixing of a single s and three p atomic orbitals to form  $sp^3$  hybrids.
- 9.8 (a) Recall that  $\pi$  bonds require p atomic orbitals, so the maximum hybridization of a C atom involved in a double bond is  $sp^2$  and in a triple bond is  $sp$ . There are 6 C atoms in the molecule. Starting on the left, the hybridizations are:  $sp^2$ ,  $sp^2$ ,  $sp^3$ ,  $sp$ ,  $sp$ ,  $sp^3$ .
- (b) All single bonds are  $\sigma$  bonds. Double and triple bonds each contain 1  $\sigma$  bond. This molecule has 8 C-H  $\sigma$  bonds and 5 C-C  $\sigma$  bonds, for a total of 13  $\sigma$  bonds.
- (c) Double bonds have 1  $\pi$  bond and triple bonds have 2  $\pi$  bonds. This molecule has a total of 3  $\pi$  bonds.
- (d) Any central atom with  $sp^2$  hybridization will have bond angles of  $120^\circ$  around it. The two left-most C atoms are  $sp^2$  hybridized, so any angle with one of these C atoms central will be  $120^\circ$ . This amounts to 1 H-C-H, 4 H-C-C and 1 C-C-C angle.

- 9.9 *Analyze/Plan.*  $\sigma$  molecular orbitals (MOs) are symmetric about the internuclear axis,  $\pi$  MOs are not. Bonding MOs have most of their electron density in the area between the nuclei, antibonding MOs have a node between the nuclei.
- (a) (i) Two s atomic orbitals (electron density at each nucleus).  
 (ii) Two p atomic orbitals overlapping end-to-end (node near each nucleus).  
 (iii) Two p atomic orbitals overlapping side-to-side (node near each nucleus).
- (b) (i)  $\sigma$ -type (symmetric about the internuclear axis, s orbitals can produce only  $\sigma$  overlap).  
 (ii)  $\sigma$ -type (symmetric about internuclear axis)  
 (iii)  $\pi$ -type (not symmetric about internuclear axis, side-to-side overlap)
- (c) (i) antibonding (node between nuclei)  
 (ii) bonding (concentration of electron density between nuclei)  
 (iii) antibonding (node between nuclei)
- (d) (i) The nodal plane is between the atom centers, perpendicular to the interatomic axis and equidistant from each atom.  
 (ii) There are two nodal planes; both are perpendicular to the interatomic axis. One is left of the left atom and the second is right of the right atom.  
 (iii) There are two nodal planes; one is between the atom centers, perpendicular to the interatomic axis and equidistant from each atom. The second contains the interatomic axis and is perpendicular to the first.
- 9.10 (a) The diagram has five electrons in MOs formed by 2p atomic orbitals. C has two 2p electrons, so X must have three 2p electrons. X is N.
- (b) The molecule has an unpaired electron, so it is paramagnetic.
- (c) Atom X is N, which is more electronegative than C. The atomic orbitals of the more electronegative N are slightly lower in energy than those of C. The lower energy  $\pi_{2p}$  bonding molecular orbitals will have a greater contribution from the lower energy N atomic orbitals. (Higher energy  $\pi_{2p}^*$  MOs will have a greater contribution from higher energy C atomic orbitals.)

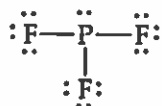
### Molecular Shapes; the VSEPR Model (sections 9.1 and 9.2)

- 9.11 (a) Yes. The stated shape, linear, defines the bond angle ( $180^\circ$ ) and the A-B bond length tells the size.
- (b) No. Atom A could have 0 or 3 nonbonding electron pairs, depending on the total number of electron domains around atom A. Only molecules with 2 or 5 total electron domains about the central atom can possibly result in linear molecular geometry. Refer to Tables 9.2 and 9.3.
- 9.12 (a) In a symmetrical tetrahedron, the four bond angles are equal to each other, with values of  $109.5^\circ$ . The H-C-H angles in  $\text{CH}_4$  and the O-Cl-O angles in  $\text{ClO}_4^-$  will have values close to  $109.5^\circ$ .

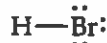
- (b) 'Planar' molecules are flat, so trigonal planar  $\text{BF}_3$  is flat. In the trigonal pyramidal  $\text{NH}_3$  molecule, the central N atom sits out of the plane of the three H atoms; this molecule is not flat.
- 9.13 A molecule with tetrahedral molecular geometry has an atom at each vertex of the tetrahedron. A trigonal pyramidal molecule has one vertex of the tetrahedron occupied by a nonbonding electron pair rather than an atom. That is, a trigonal pyramid is a tetrahedron with one vacant vertex.
- 9.14 (a) three coplanar  $120^\circ$  angles  
 (b) four  $109.5^\circ$  angles  
 (c)  $90^\circ$  angles in the equatorial square plane and between axial atoms and those in the square plane, 12 in all;  $180^\circ$  angles between atoms opposite each other, 3 in all  
 (d) one  $180^\circ$  angle
- 9.15 (a) An *electron domain* is a region in a molecule where electrons are most likely to be found.  
 (b) Each balloon in Figure 9.5 occupies a volume of space. The best arrangement is one where each balloon has its "own" space, where they are as far apart as possible and repulsions are minimized. Electron domains are negatively charged regions, so they also adopt an arrangement where repulsions are minimized.
- 9.16 The negative charge of the electron leads to repulsion between electron domains and causes them to have an effect on molecular structure.
- 9.17 (a) The number of electron domains in a molecule or ion is the number of bonds (double and triple bonds count as one domain) plus the number of nonbonding (lone) electron pairs.  
 (b) A *bonding electron domain* is a region between two bonded atoms that contains one or more pairs of bonding electrons. A *nonbonding electron domain* is localized on a single atom and contains one pair of nonbonding electrons (a lone pair).
- 9.18 We expect the nonbonding electron domain in  $\text{NH}_3$  to occupy a smaller volume than the one in  $\text{PH}_3$ . The electronegativity of N, 3.0, is larger than that of P, 2.1. The nonbonding electrons will be more strongly attracted to N than to P, and the volume of the domain will be smaller. This means that the charge density of the nonbonding domain in  $\text{NH}_3$  will be greater and it will experience stronger repulsions than the nonbonding domain in  $\text{PH}_3$ .
- 9.19 *Analyze/Plan.* Draw the Lewis structure of each molecule and take note of nonbonding (lone) electron pairs about the central atom. *Solve.*
- (a)  $\text{SiH}_4$ , 8 valence  $e^-$ , 4  $e^-$  pr, 0 nonbonding pairs, no effect on molecular shape



- (b)
- $\text{PF}_3$
- , 26 valence
- $e^-$
- , 13
- $e^-$
- pr, 1 nonbonding pair on P, influences molecular shape



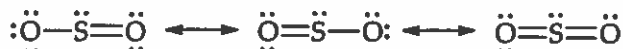
- (c)
- $\text{HBr}$
- , 8 valence
- $e^-$
- , 4
- $e^-$
- pr, 3 nonbonding pairs on Br, no effect on molecular shape because Br is not "central"



- (d)
- $\text{HCN}$
- , 10 valence
- $e^-$
- , 5
- $e^-$
- pr, 0 nonbonding pairs on C, no effect on molecular shape

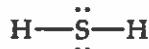


- (e)
- $\text{SO}_2$
- , 18 valence
- $e^-$
- , 9
- $e^-$
- pr, 1 nonbonding pair on S, influences molecular shape

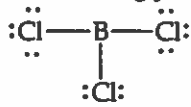


9.20 Draw the Lewis structure of each molecule. If it has nonbonding electron pairs on the central atom, decide whether they will cause to bond angles to deviate from ideal values for the particular electron domain geometry.

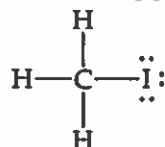
- (a)
- $\text{H}_2\text{S}$
- , 8 valence
- $e^-$
- , 4
- $e^-$
- pr, tetrahedral electron domain geometry with 2 nonbonding electron pairs on S will cause the bond angle to deviate from ideal
- $109.5^\circ$
- angles



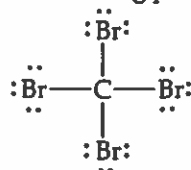
- (b)
- $\text{BCl}_3$
- , 24 valence
- $e^-$
- , 12
- $e^-$
- pr, trigonal planar electron domain geometry with zero nonbonding pairs on B. We confidently predict
- $120^\circ$
- angles.



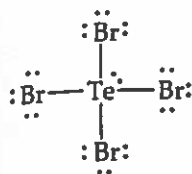
- (c)
- $\text{CH}_3\text{I}$
- , 14 valence
- $e^-$
- , 7
- $e^-$
- pr, tetrahedral electron domain geometry with zero nonbonding pairs on C. We confidently predict
- $109.5^\circ$
- angles.



- (d)
- $\text{CBr}_4$
- , 32 valence
- $e^-$
- , 16
- $e^-$
- pr, tetrahedral electron domain geometry with zero nonbonding pairs on C. We confidently predict
- $109.5^\circ$
- angles.



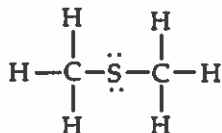
- (e)
- $\text{TeBr}_4$
- , 34 valence
- $e^-$
- , 17
- $e^-$
- pr, trigonal bipyramidal electron domain geometry with one nonbonding pair on Te. The structure is similar to
- $\text{SF}_4$
- shown in Sample Exercise 9.2. The bond angles will deviate from ideal values, but perhaps not as much as in
- $\text{SF}_4$
- . (Structure follows.)



9.21

*Analyze/Plan.* Draw the Lewis structure of each molecule and count the number of nonbonding (lone) electron pairs. Note that the question asks 'in the molecule' rather than just around the central atom. *Solve.*

- (a)
- $(\text{CH}_3)_2\text{S}$
- , 20 valence
- $e^-$
- , 10
- $e^-$
- pr, 2 nonbonding pairs



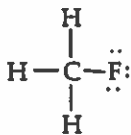
- (b)
- $\text{HCN}$
- , 10 valence
- $e^-$
- , 5
- $e^-$
- pr, 1 nonbonding pair



- (c)
- $\text{H}_2\text{C}_2$
- , 10 valence
- $e^-$
- , 5
- $e^-$
- pr, 0 nonbonding pairs



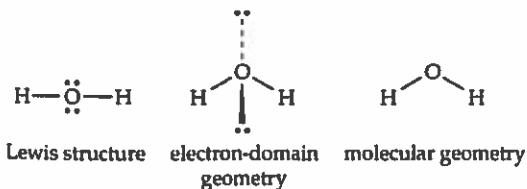
- (d)
- $\text{CH}_3\text{F}$
- , 14 valence
- $e^-$
- , 7
- $e^-$
- pr, 3 nonbonding pairs

9.22 *Analyze/Plan.* See Table 9.1. *Solve.*

- (a) trigonal planar                      (b) tetrahedral  
 (c) trigonal bipyramidal              (d) octahedral

9.23

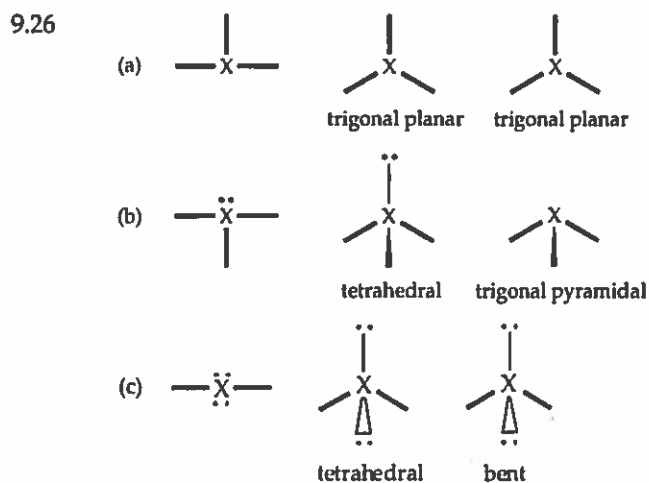
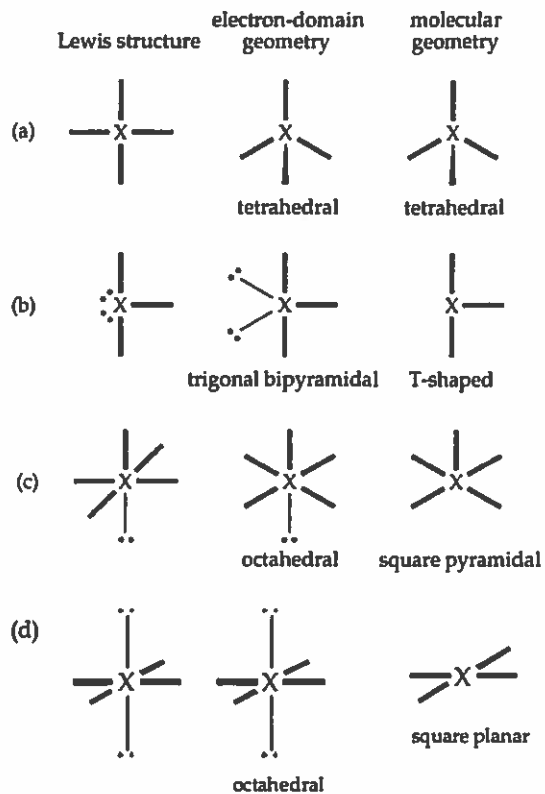
The electron-domain geometry indicated by VSEPR describes the arrangement of all bonding and nonbonding electron domains. The molecular geometry describes just the atomic positions.  $\text{H}_2\text{O}$  has the Lewis structure given below; there are four electron domains around oxygen so the electron-domain geometry is tetrahedral, but the molecular geometry of the three atoms is bent.



We make this distinction because all electron domains must be considered when describing the atomic arrangement and bond angles in a molecule but the molecular geometry or shape is a description of just the atomic positions.

9.24 If the electron-domain geometry is trigonal bipyramidal, there are five total electron domains around the central atom. An  $AB_3$  molecule has three bonding domains, so there must be two nonbonding domains on A.

9.25 *Analyze/Plan.* See Tables 9.2 and 9.3. Solve.



9.27 *Analyze/Plan.* Follow the logic in Sample Exercise 9.1. *Solve.* bent (b), linear (l), octahedral (oh), seesaw (ss), square pyramidal (sp), square planar (spl), tetrahedral (td), trigonal bipyramidal (tbp), trigonal planar (tr), trigonal pyramidal (tp), T-shaped (T)

Molecule or ion	Valence electrons	Lewis structure	Electron-domain geometry	Molecular geometry
(a) HCN	10	$\text{:N}\equiv\text{C}-\text{H}$	$\text{N}\equiv\text{C}-\text{H}$	l
(b) $\text{SO}_3^{2-}$	26	$\left[ \begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\   \\ \text{:}\ddot{\text{S}}\text{:} \\   \\ \text{:}\ddot{\text{O}}\text{:} \\   \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^{2-}$	$\left[ \begin{array}{c} \ddot{\text{O}} \\   \\ \text{S} \\   \\ \text{O} \\   \\ \text{O} \end{array} \right]^{2-}$	td
(c) $\text{SF}_4$	34	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\   \\ \text{:}\ddot{\text{S}}\text{:} \\   \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$	$\begin{array}{c} \text{F} \\   \\ \text{S} \\   \\ \text{F} \end{array}$	tbp
(d) $\text{PF}_6^-$	48	$\left[ \begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\   \\ \text{:}\ddot{\text{P}}\text{:} \\   \\ \text{:}\ddot{\text{F}}\text{:} \end{array} \right]^-$	$\left[ \begin{array}{c} \text{F} \\   \\ \text{P} \\   \\ \text{F} \end{array} \right]^-$	oh
(e) $\text{NH}_3\text{Cl}^+$	14	$\left[ \begin{array}{c} \text{:}\ddot{\text{Cl}}\text{:} \\   \\ \text{H}-\text{N}-\text{H} \\   \\ \text{H} \end{array} \right]^+$	$\left[ \begin{array}{c} \text{Cl} \\   \\ \text{N} \\   \\ \text{H} \end{array} \right]^+$	td
(f) $\text{N}_3^-$	16	$\left[ \text{:}\ddot{\text{N}}-\text{N}\equiv\text{N}\text{:} \right]^-$	$\left[ \text{N}-\text{N}\equiv\text{N} \right]^-$	l

\*More than one resonance structure is possible. All equivalent resonance structures predict the same molecular geometry.

9.28 bent (b), linear (l), octahedral (oh), seesaw (ss) square pyramidal (sp), square planar (spl), tetrahedral (td), trigonal bipyramidal (tbp), trigonal planar (tr), trigonal pyramidal (tp), T-shaped (T)

Molecule or ion	Valence electrons	Lewis structure	Electron-domain Geometry	Molecular geometry
(a) $\text{AsF}_3$	26	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\   \\ \text{:}\ddot{\text{As}}\text{:} \\   \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$	$\begin{array}{c} \ddot{\text{O}} \\   \\ \text{As} \\   \\ \text{F} \end{array}$	td
(b) $\text{CH}_3^+$	6	$\left[ \begin{array}{c} \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array} \right]^+$	$\left[ \begin{array}{c} \text{H} \\   \\ \text{C} \\   \\ \text{H} \end{array} \right]^+$	tr
(c) $\text{BrF}_3$	28	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\   \\ \text{:}\ddot{\text{Br}}\text{:} \\   \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$	$\begin{array}{c} \text{F} \\   \\ \text{Br} \\   \\ \text{F} \end{array}$	tbp



9.28 (Continued). bent (b), linear (l), octahedral (oh), seesaw (ss) square pyramidal (sp), square planar (spl), tetrahedral (td), trigonal bipyramidal (tbp), trigonal planar (tr), trigonal pyramidal (tp), T-shaped (T)

	Molecule or ion	Valence electrons	Lewis structure	Electron-domain Geometry	Molecular geometry
(d)	$\text{ClO}_3^-$	26	$\left[ \begin{array}{c} \text{:}\ddot{\text{O}}\text{---}\ddot{\text{Cl}}\text{---}\ddot{\text{O}}\text{:} \\   \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^-$ $\left[ \begin{array}{c} \ddot{\text{O}} \\   \\ \text{Cl} \\   \\ \ddot{\text{O}} \\ / \quad \backslash \\ \text{O} \quad \text{O} \end{array} \right]^-$	td	tp
(e)	$\text{XeF}_2$	22	$\text{:}\ddot{\text{F}}\text{---}\ddot{\text{Xe}}\text{---}\ddot{\text{F}}\text{:}$ $\begin{array}{c} \text{F} \\   \\ \text{Xe} \\   \\ \text{F} \end{array}$	tbp	l
(f)	$\text{BrO}_2^-$	20	$\left[ \text{:}\ddot{\text{O}}\text{---}\ddot{\text{Br}}\text{---}\ddot{\text{O}}\text{:} \right]^-$ $\left[ \begin{array}{c} \ddot{\text{O}} \\   \\ \text{Br} \\   \\ \ddot{\text{O}} \\ / \quad \backslash \\ \text{O} \quad \text{O} \end{array} \right]^-$	td	b

\*More than one resonance structure is possible. All equivalent resonance structures predict the same molecular geometry.

9.29 *Analyze/Plan.* Work backwards from molecular geometry, using Tables 9.2 and 9.3.  
*Solve.*

- (a) Electron-domain geometries: i, trigonal planar; ii, tetrahedral; iii, trigonal bipyramidal
- (b) nonbonding electron domains: i, 0; ii, 1; iii, 2
- (c) N and P. Shape ii has three bonding and one nonbonding electron domains. Li and Al would form ionic compounds with F, so there would be no nonbonding electron domains. Assuming that F always has three nonbonding domains,  $\text{BF}_3$  and  $\text{ClF}_3$  would have the wrong number of nonbonding domains to produce shape ii.
- (d) Cl (also Br and I, since they have seven valence electrons). This T-shaped molecular geometry arises from a trigonal bipyramidal electron-domain geometry with two nonbonding domains (Table 9.3). Assuming each F atom has three nonbonding domains and forms only single bonds with A, A must have seven valence electrons to produce these electron-domain and molecular geometries. It must be in or below the third row of the periodic table, so that it can accommodate more than four electron domains.

- 9.30 (a) Electron-domain geometries: i, octahedral; ii, tetrahedral; iii, trigonal bipyramidal
- (b) nonbonding electron domains: i, 2; ii, 0; iii, 1
- (c) S or Se. Shape iii has five electron domains, so A must be in or below the third row of the periodic table. This eliminates Be and C. Assuming each F atom has three nonbonding electron domains and forms only single bonds with A, A must

have six valence electrons to produce these electron-domain and molecular geometries.

- (d) Xe. (See Table 9.3) Assuming F behaves typically, A must be in or below the third row and have eight valence electrons. Only Xe fits this description. (Noble gas elements above Xe have not been shown to form molecules of the type  $AF_4$ . See Section 7.8.)

9.31 *Analyze/Plan.* Follow the logic in Sample Exercise 9.3. *Solve.*

- (a) 1 -  $109^\circ$ , 2 -  $109^\circ$  (b) 3 -  $109^\circ$ , 4 -  $109^\circ$   
 (c) 5 -  $180^\circ$  (d) 6 -  $120^\circ$ , 7 -  $109^\circ$ , 8 -  $109^\circ$

9.32 (a) 1 -  $109^\circ$ , 2 -  $120^\circ$  (b) 3 -  $109^\circ$ , 4 -  $120^\circ$

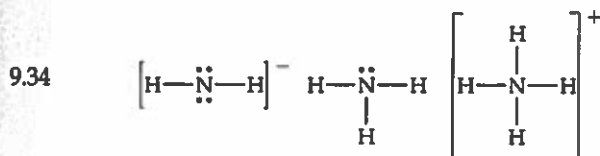
- (c) 5 -  $109^\circ$ , 6 -  $109^\circ$  (d) 7 -  $180^\circ$ , 8 -  $109^\circ$

9.33 *Analyze/Plan.* Given the formula of each molecule or ion, draw the correct Lewis structure and use principles of VSEPR to answer the question. *Solve.*



The three nonbonded electron pairs on each F atom have been omitted for clarity.

The two molecules with trigonal bipyramidal electron domain geometry,  $PF_5$  and  $SF_4$ , have more than one F-A-F bond angle.

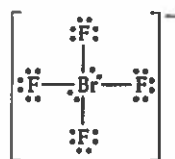


Each species has four electron domains around the N atom, but the number of nonbonding domains decreases from two to zero, going from  $\text{NH}_2^-$  to  $\text{NH}_4^+$ . Since nonbonding domains exert greater repulsive forces on adjacent domains, the bond angles expand as the number of nonbonding domains decreases.

9.35 *Analyze.* Given: molecular formulas. Find: explain features of molecular geometries.

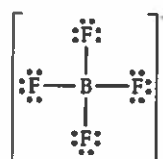
*Plan.* Draw the correct Lewis structures for the molecules and use VSEPR to predict and explain observed molecular geometry. *Solve.*

(a)  $\text{BrF}_4^-$  36  $e^-$ , 18  $e^-$  pr



6  $e^-$  pairs around Br  
 octahedral  $e^-$  domain geometry  
 square planar molecular geometry

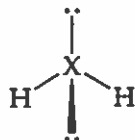
$\text{BF}_4^-$  32  $e^-$ , 16  $e^-$  pr



4  $e^-$  pairs around B,  
 tetrahedral  $e^-$  domain geometry  
 tetrahedral molecular geometry

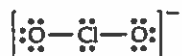
The fundamental feature that determines molecular geometry is the number of electron domains around the central atom, and the number of these that are bonding domains. Although  $\text{BrF}_4^-$  and  $\text{BF}_4^-$  are both of the form  $\text{AX}_4^-$ , the central atoms and thus the number of valence electrons in the two ions are different. This leads to different numbers of  $e^-$  domains about the two central atoms. Even though both ions have four bonding electron domains, the six total domains around Br require octahedral domain geometry and square planar molecular geometry, while the four total domains about B lead to tetrahedral domain and molecular geometry.

(b)  $\text{H}_2\text{X}$ ,  $8 e^-$ ,  $4 e^-$  pr



All molecules in the series have tetrahedral electron domain geometry and bent molecular structure. To a first approximation, the H-X-H angles will be  $109^\circ$ . Any variation will be due to differences in repulsion among the nonbonding and bonding electron domains. The less electronegative the central atom, the larger the nonbonding electron domain, the greater the effect of repulsive forces on adjacent bonding domains. The less electronegative the central atom, the larger the deviation from ideal tetrahedral angles. The angles will vary as  $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se}$ .

9.36 (a)  $\text{ClO}_2^-$   $20 e^-$ ,  $10 e^-$  pr



$4 e^-$  domains around Cl, tetrahedral  $e^-$  domain geometry,  
bent molecular geometry bond angle  $\leq 109.5^\circ$

$\text{NO}_2^-$   $18 e^-$ ,  $9 e^-$  pr



$3 e^-$  domains about N (both resonance structures), trigonal planar  $e^-$  domain geometry bent molecular geometry bond angle  $\leq 120^\circ$

Both molecular geometries are described as "bent" because both molecules have two nonlinear bonding electron domains. The bond angles (the angle between the two bonding domains) in the two ions are different because the total number of electron domains, and thus the electron domain geometries are different.

(b)  $\text{XeF}_2$   $22 e^-$ ,  $11 e^-$  pr



$5 e^-$  domains around Xe, trigonal bipyramidal  $e^-$  domain geometry,  
linear molecular geometry

The question here really is: why do the three nonbonding domains all occupy the equatorial plane of the trigonal bipyramid? In a tbp, there are several different kinds of repulsions, bonding domain-bonding domain (bd-bd), bonding domain-nonbonding domain (bd-nd), and nonbonding domain-nonbonding domain (nd-nd). Each of these can have 90°, 120°, or 180° geometry. Since nonbonding domains occupy more space, 90° nd-nd repulsions are most significant and least desirable. The various electron domains arrange themselves to minimize these 90° nd-nd interactions. The arrangement shown above has no 90° nd-nd repulsions. An arrangement with one or two nonbonding domains in axial positions would lead to at least two 90° nd-nd repulsions, a less stable situation. (To convince yourself, tabulate the number and kinds of repulsions for each possible tbp arrangement of 2bd's and 3nd's.)

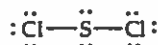
### Shapes and Polarity of Polyatomic Molecules (section 9.3)

9.37 A bond dipole is the asymmetric charge distribution between two bonded atoms with unequal electronegativities. A molecular dipole moment is the three-dimensional sum of all the bond dipoles in a molecule. (A molecular dipole moment is a measurable physical property; a bond dipole is not measurable, unless the molecule is diatomic.)

9.38 For a polar A-X bond in an AX<sub>3</sub> molecule, as the X-A-X bond angle increases from 100° to 120°, the molecular dipole moment decreases. In a symmetrical AX<sub>3</sub> molecule with 120° bond angles, bond dipoles cancel and the molecule is nonpolar. As the bond angle decreases, the resultant of the three bond dipoles becomes larger, and the dipole moment increases.

9.39 *Analyze/plan.* Follow the logic in Sample Exercise 9.4. *Solve.*

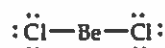
(a) SCl<sub>2</sub>, 20 e<sup>-</sup>, 10 e<sup>-</sup> pr



tetrahedral e<sup>-</sup> domain geometry  
bent molecular geometry

S and Cl have different electronegativities; the S-Cl bonds are polar. The bond dipoles are not opposite each other, so the molecule is polar. The dipole moment vector bisects the Cl-S-Cl bond angle. (A more difficult question is which end of the dipole moment vector is negative. The resultant of the two bond dipoles has its negative end toward the Cl atoms. However, the partial negative charge due to the lone pairs on S points opposite to the negative end of the resultant. A reasonable guess is that the negative end of the dipole moment vector is in the direction of the lone pairs.)

(b) BeCl<sub>2</sub>, 16 e<sup>-</sup>, 8 e<sup>-</sup> pr

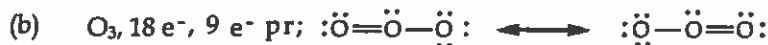


linear electron domain and molecular geometry

(Resonance structures with Be=Cl can be drawn, but electronegativity arguments predict that most electron density will reside on Cl and that the structure above

is the main resonance contributor.) Be and Cl have very different electronegativities, so the Be–Cl bonds are polar. The individual bond dipoles are equal and opposite, so the net molecular dipole moment is zero.

- 9.40 (a) If  $\text{PH}_3$  is polar, it must have a measurable dipole moment. This means that the three P–H bond dipoles do not cancel. If  $\text{PH}_3$  were planar, the P–H bond dipoles would cancel, and the molecule would be nonpolar. The measurable dipole moment of  $\text{PH}_3$  is experimental evidence that the molecule cannot be planar.



trigonal planar  $e^-$  domain geometry  
bent molecular geometry

Since all atoms are the same, the individual bond dipoles are zero. However, the central O atom has a lone pair of electrons which cause an unequal electron (and charge) distribution in the molecule. This lone pair is the source of the dipole moment in  $\text{O}_3$ .

- 9.41 (a) In Exercise 9.29, molecules ii and iii will have nonzero dipole moments. Molecule i has zero nonbonding electron pairs on A, and the 3 A–F dipoles are oriented so that the sum of their vectors is zero (the bond dipoles cancel). Molecules ii and iii have nonbonding electron pairs on A and their bond dipoles do not cancel. A nonbonding electron pair (or pairs) on a central atom almost guarantees at least a small molecular dipole moment, because no bond dipole exactly cancels a nonbonding pair. (Exceptions are molecular geometries with nonbonding electron domains  $180^\circ$  apart.)

- (b)  $\text{AF}_4$  molecules will have a zero dipole moment if the 4 A–F bond dipoles are arranged (symmetrically) so that they cancel, and any nonbonding pairs are arranged so that they cancel. Therefore, in Exercise 9.30, molecules i and ii have zero dipole moments and are nonpolar.

- 9.42 (a) For a molecule with polar bonds to be nonpolar, the polar bonds must be (symmetrically) arranged so that the bond dipoles cancel. And, any nonbonding pairs about the central atom must be arranged so that they cancel. In most cases, nonbonding  $e^-$  domains will be absent from the central atom.

- (b)  $\text{AB}_2$ : linear  $e^-$  domain geometry (edg), linear molecular geometry (mg), trigonal bipyramidal edg, linear mg

$\text{AB}_3$ : trigonal planar edg, trigonal planar mg

$\text{AB}_4$ : tetrahedral edg, tetrahedral mg; octahedral edg, square planar mg

- 9.43 *Analyze/Plan.* Given molecular formulas, draw correct Lewis structures, determine molecular structure and polarity. *Solve.*

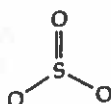
- (a) Polar,  $\Delta\text{EN} > 0$

I–F

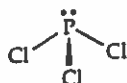
- (b) Nonpolar, the molecule is linear and the bond dipoles cancel.

$\text{S}=\text{C}=\text{S}$

- (c) Nonpolar, in a symmetrical trigonal planar structure, the bond dipoles cancel.



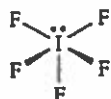
- (d) Polar, although the bond dipoles are essentially zero, there is an unequal charge distribution due to the nonbonded electron pair on P.



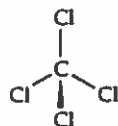
- (e) Nonpolar, symmetrical octahedron



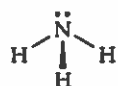
- (f) Polar, square pyramidal molecular geometry, bond dipoles do not cancel.



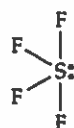
- 9.44 (a) Nonpolar, in a symmetrical tetrahedral structure (Figure 9.1) the bond dipoles cancel.



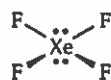
- (b) Polar, there is an unequal charge distribution due to the nonbonded electron pair on N.



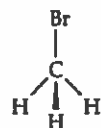
- (c) Polar, there is an unequal charge distribution due to the nonbonded electron pair on S.



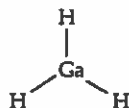
- (d) Nonpolar, the bond dipoles and the nonbonded electron pairs cancel.



- (e) Polar, the C-H and C-Br bond dipoles are not equal and do not cancel.

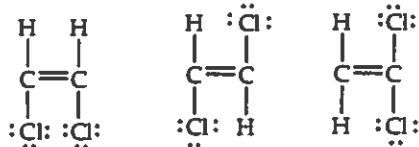


- (f) Nonpolar, in a symmetrical trigonal planar structure, the bond dipoles cancel.

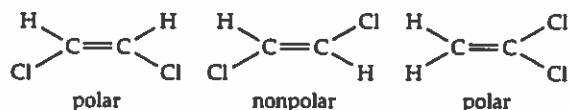


- 9.45 *Analyze/Plan.* Given molecular formulas, draw correct Lewis structures, analyze molecular structure and determine polarity. *Solve.*

- (a)  $C_2H_2Cl_2$ , each isomer has 24  $e^-$ , 12  $e^-$  pr. Lewis structures:

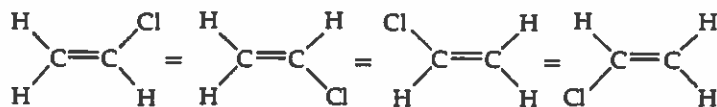


Molecular geometries:



- (b) All three isomers are planar. The molecules on the left and right are polar because the C-Cl bond dipoles do not point in opposite directions. In the middle isomer, the C-Cl bonds and dipoles are pointing in opposite directions (as are the C-H bonds), the molecule is nonpolar and has a measured dipole moment of zero.
- (c)  $C_2H_3Cl$  (lone pairs on Cl omitted for clarity)

There are four possible placements for Cl:



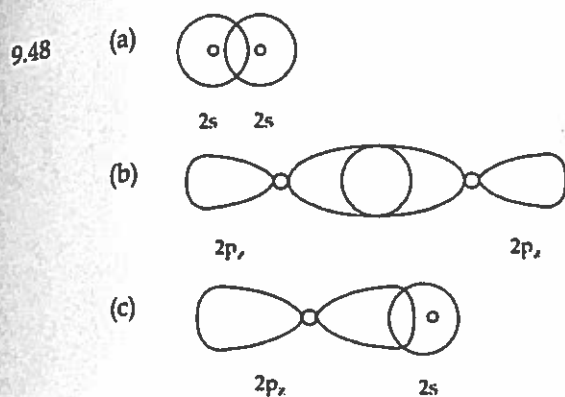
By rotating each of these structures in various directions, it becomes clear that the four structures are equivalent;  $C_2H_3Cl$  has only one isomer. Because  $C_2H_3Cl$  has only one C-Cl bond, the bond dipoles do not cancel, and the molecule has a dipole moment.

- 9.46 Each C-Cl bond is polar. The question is whether the vector sum of the C-Cl bond dipoles in each molecule will be nonzero. In the *ortho* and *meta* isomers, the C-Cl vectors are at  $60^\circ$  and  $120^\circ$  angles, respectively, and their resultant dipole moments are nonzero. In the *para* isomer, the C-Cl vectors are opposite, at an angle of  $180^\circ$ , with a resultant dipole moment of zero. The *ortho* and *meta* isomers are polar, the *para* isomer is nonpolar.

### Orbital Overlap; Hybrid Orbitals (sections 9.4 and 9.5)

- 9.47 (a) *Orbital overlap* occurs when a valence atomic orbital on one atom shares the same region of space with a valence atomic orbital on an adjacent atom.

- (b) A chemical bond is a concentration of electron density between the nuclei of two atoms. This concentration can take place because orbitals on the two atoms overlap.

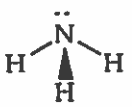


- 9.49 (a) 4 valence  $e^-$ , 2  $e^-$  pairs  
 $H-Mg-H$   
 2 bonding  $e^-$  domains, linear  $e^-$  domain and molecular geometry
- (b) The linear electron domain geometry in  $MgH_2$  requires  $sp$  hybridization.



- 9.50 By analogy to the  $H_2$  molecule shown in Figure 9.14, as the distance between the atoms decreases, the overlap between their bonding orbitals increases. According to Figure 7.6, the bonding atomic radius for the halogens is in the order  $F < Cl < Br < I$ . The order of bond lengths in the molecules is  $I-F < I-Cl < I-Br < I-I$ . If the extent of orbital overlap increases as the distance between atoms decreases,  $I-F$  has the greatest overlap and  $I_2$  the least. The order for extent of orbital overlap is  $I-I < I-Br < I-Cl < I-F$ .

- 9.51 *Analyze/Plan.* For entries where the molecule is listed, follow the logic in Sample Exercises 9.4 and 9.5. For entries where no molecule is listed, decide electron domain geometry from hybridization (or vice-versa). If the molecule is nonpolar, the terminal atoms will be identical. If the molecule is polar, the terminal atoms will be different, or the central atom will have one or more lone pairs, or both. *Solve.*

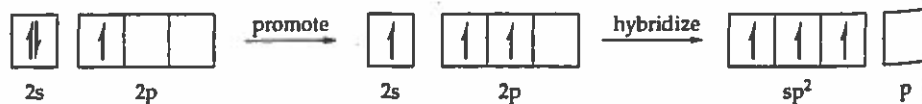
Molecule	Molecular Structures	Electron Domain Geometry	Hybridization of Central Atom	Dipole Moment Yes or No
$CO_2$	$O=C=O$	linear	$sp$	no
$NH_3$		tetrahedral	$sp^3$	yes



CH <sub>4</sub>		tetrahedral	sp <sup>3</sup>	no
BH <sub>3</sub>		trigonal planar	sp <sup>2</sup>	no
SF <sub>4</sub>		trigonal bipyramidal	not applicable	yes
SF <sub>6</sub>		octahedral	not applicable	no
H <sub>2</sub> CO		trigonal planar	sp <sup>2</sup>	yes
PF <sub>5</sub>		trigonal bipyramidal	not applicable	no
XeF <sub>2</sub>		trigonal bipyramidal	not applicable	no

9.52 In order for atomic orbitals to mix or hybridize, they must have the same principal quantum number. In each principal quantum level, there are a maximum of three *p* orbitals. Any hybrid orbital can have contribution from a maximum of three *p* orbitals. Hybrid orbitals designated sp<sup>4</sup> or sp<sup>5</sup> would require contribution from four or five *p* orbitals, which is not possible.

9.53 (a) B: [He]2s<sup>2</sup>2p<sup>1</sup>



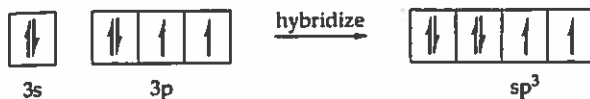
(b) The hybrid orbitals are called sp<sup>2</sup>.



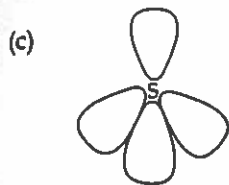
(d) A single 2p orbital is unhybridized. It lies perpendicular to the trigonal plane of the  $sp^2$  hybrid orbitals.

9.54

(a) S:  $[\text{Ne}]3s^23p^4$



(b) The hybrid orbitals are called  $sp^3$ .

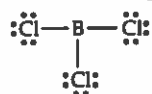


(d) The hybrid orbitals formed in (a) would not be appropriate for  $\text{SF}_4$ . There are five electron domains in  $\text{SF}_4$ , four bonding and one nonbonding. A set of four  $sp^3$  hybrid orbitals could not accommodate all the electron pairs around S.

9.55

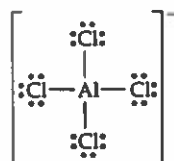
*Analyze/Plan.* Given the molecular (or ionic) formula, draw the correct Lewis structure and determine the electron domain geometry, which determines hybridization. *Solve.*

(a)  $24 e^-$ ,  $12 e^-$  pairs



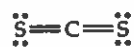
$3 e^-$  pairs around B, trigonal planar  $e^-$  domain geometry,  $sp^2$  hybridization

(b)  $32 e^-$ ,  $16 e^-$  pairs



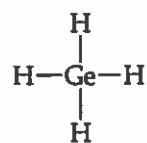
$4 e^-$  domains around Al, tetrahedral  $e^-$  domain geometry,  $sp^3$  hybridization

(c)  $16 e^-$ ,  $8 e^-$  pairs

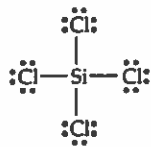
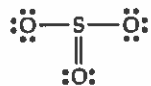


$2 e^-$  domains around C, linear  $e^-$  domain geometry,  $sp$  hybridization

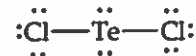
(d)  $8 e^-$ ,  $4 e^-$  pairs



$4 e^-$  pairs around Ge, tetrahedral  $e^-$  domain geometry,  $sp^3$  hybridization

9.56 (a) 32 e<sup>-</sup>, 16 e<sup>-</sup> pairs4 e<sup>-</sup> pairs around Si, tetrahedral e<sup>-</sup> domain geometry, sp<sup>3</sup> hybridization(b) 10 e<sup>-</sup>, 5 e<sup>-</sup> pairs2 e<sup>-</sup> domains around C, linear e<sup>-</sup> domain geometry, sp hybridization(c) 24 e<sup>-</sup>, 12 e<sup>-</sup> pairs

(other resonance structures are possible)

3 e<sup>-</sup> domains around S, trigonal planar e<sup>-</sup> domain geometry, sp<sup>2</sup> hybridization(d) 20 e<sup>-</sup>, 10 e<sup>-</sup> pairs4 e<sup>-</sup> domains around Te, tetrahedral e<sup>-</sup> domain geometry, sp<sup>3</sup> hybridization

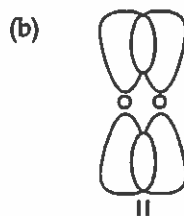
9.57 (a) No hybrid orbitals discussed in this chapter have angles of 90°; p atomic orbitals are perpendicular to each other.

(b) Angles of 109.5° are characteristic of sp<sup>3</sup> hybrid orbitals.(c) Angles of 120° can be formed by sp<sup>2</sup> hybrids.9.58 (a) The three moieties, BH<sub>4</sub><sup>-</sup>, CH<sub>4</sub>, and NH<sub>4</sub><sup>+</sup>, each have 8 valence e<sup>-</sup>, 4 e<sup>-</sup> pairs, 4 bonding e<sup>-</sup> domains, tetrahedral e<sup>-</sup> domain and molecular geometry and sp<sup>3</sup> hybridization at the central atom.

(b) The electronegativity of the central atoms decreases in the series N &gt; C &gt; B. The question is: where does the electronegativity of H lie in this series? By examination of electronegativity values in Figure 8.7, H is slightly less electronegative than C, and almost the same as B. The magnitude of the bond dipole decreases in the series N-H &gt; C-H &gt; B-H. The negative end of the dipole is toward N, C, and H, respectively.

(c) AlH<sub>4</sub><sup>-</sup>, SiH<sub>4</sub>, and PH<sub>4</sub><sup>+</sup>. By the same arguments used in part (a), we expect these three moieties to have the same tetrahedral e<sup>-</sup> domain and molecular geometry and sp<sup>3</sup> hybridization at the central atom as the species in part (a).

## Multiple Bonds (section 9.6)

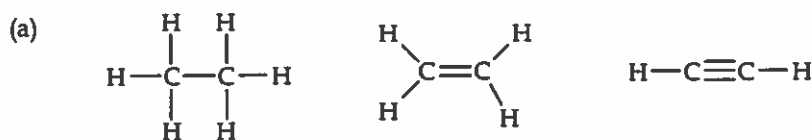


- (c) A  $\sigma$  bond is generally stronger than a  $\pi$  bond, because there is more extensive orbital overlap.
- (d) Two  $s$  orbitals cannot form a  $\pi$  bond. A  $\pi$  bond has no electron density along the internuclear axis. Overlap of  $s$  orbitals results in electron density along the internuclear axis. (Another way to say this is that  $s$  orbitals have the wrong symmetry to form a  $\pi$  bond.)

- 9.60 (a) Two unhybridized  $p$  orbitals remain, and the atom can form two  $\pi$  bonds.
- (b) It would be much easier to twist or rotate around a single sigma bond. Sigma bonds are formed by end-to-end overlap of orbitals and the bonding electron density is symmetric about the internuclear axis. Rotating (twisting) around a sigma bond can be done without disrupting either the orbital overlap or bonding electron density, without breaking the bond.

The  $\pi$  part of a double bond is formed by side-to-side overlap of  $p$  atomic orbitals perpendicular to the internuclear axis. This  $\pi$  overlap locks the atoms into position and makes twisting difficult. Also, only a small twist (rotation) destroys overlap of the  $p$  orbitals and breaks the  $\pi$  bond.

- 9.61 *Analyze/Plan.* Draw the correct Lewis structures, count electron domains and decide hybridization. Molecules with  $\pi$  bonds that require all bonded atoms to be in the same plane are planar. For bond-type counting, single bonds are  $\sigma$  bonds, double bonds consist of one  $\sigma$  and one  $\pi$  bond, triple bonds consist of one  $\sigma$  and two  $\pi$  bonds. *Solve.*



- (b)  $sp^3$                        $sp^2$                        $sp$
- (c) nonplanar                      planar                      planar
- (d)  $7\sigma, 0\pi$                        $5\sigma, 1\pi$                        $3\sigma, 2\pi$

- (e) Since Si has the same valence electron configuration as C, the structures of the Si analogs would be the same as the C-based molecules. The hybridization at Si is then the same as the hybridization at C. This argument assumes that the Si analogs exist.

Silicon, which lies in the row below C, has a larger bonding atomic radius and larger atomic orbitals than C. In the analogous compounds, Si-Si distances will

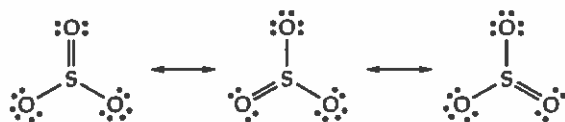
be greater than C–C distances. This means that the close approach of Si atoms required to form strong, stable  $\pi$  bonds in  $\text{Si}_2\text{H}_4$  and  $\text{Si}_2\text{H}_2$  is not possible and these Si analogs do not readily form.

- 9.62 (a)  $\begin{array}{c} \text{H}-\ddot{\text{N}}-\ddot{\text{N}}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \quad \text{:N}\equiv\text{N:}$
- (b) The N atoms in  $\text{N}_2\text{H}_4$  are  $sp^3$  hybridized; there are no unhybridized p orbitals available for  $\pi$  bonding. In  $\text{N}_2$ , the N atoms are  $sp$  hybridized, with two unhybridized p orbitals on each N atom available to form the two  $\pi$  bonds in the  $\text{N}\equiv\text{N}$  triple bond.
- (c) The N–N triple bond in  $\text{N}_2$  is significantly stronger than the N–N single bond in  $\text{N}_2\text{H}_4$ , because it consists of one  $\sigma$  and two  $\pi$  bonds, rather than a 'plain' sigma bond. Generally, bond strength increases as the extent of orbital overlap increases. The additional overlap from the two  $\pi$  bonds adds to the strength of the N–N bond in  $\text{N}_2$ .
- 9.63 *Analyze/Plan.* Single bonds are  $\sigma$  bonds, double bonds consist of 1  $\sigma$  and 1  $\pi$  bond. Each bond is formed by a pair of valence electrons. *Solve.*
- (a)  $\text{C}_3\text{H}_6$  has  $3(4) + 6(1) = 18$  valence electrons
- (b) 8 pairs or 16 total valence electrons form  $\sigma$  bonds
- (c) 1 pair or 2 total valence electrons form  $\pi$  bonds
- (d) no valence electrons are nonbonding
- (e) The left and central C atoms are  $sp^2$  hybridized; the right C atom is  $sp^3$  hybridized.
- 9.64 (a) The C with a double bond to O has three electron domains and is  $sp^2$  hybridized; the other three C atoms are  $sp^3$  hybridized.
- (b)  $\text{C}_4\text{H}_8\text{O}_2$  has  $4(4) + 8(1) + 2(6) = 36$  valence electrons.
- (c) 13 pairs or 26 total valence electrons form  $\sigma$  bonds
- (d) 1 pair or 2 total valence electrons form  $\pi$  bonds
- (e) 4 pairs or 8 total valence electrons are nonbonding
- 9.65 *Analyze/Plan.* Given the correct Lewis structure, analyze the electron domain geometry at each central atom. This determines the hybridization and bond angles at that atom. *Solve.*
- (a)  $\sim 109^\circ$  bond angles about the left most C,  $sp^3$ ;  $\sim 120^\circ$  bond angles about the right-hand C,  $sp^2$
- (b) The doubly bonded O can be viewed as  $sp^2$ , the other as  $sp^3$ ; the nitrogen is  $sp^3$  with approximately  $109^\circ$  bond angles.
- (c) 9  $\sigma$  bonds, 1  $\pi$  bond
- 9.66 (a) 1,  $120^\circ$ ; 2,  $120^\circ$ ; 3,  $109^\circ$
- (b) 1,  $sp^2$ ; 2,  $sp^2$ ; 3,  $sp^3$
- (c) 21  $\sigma$  bonds

- 9.67 (a) In a localized  $\pi$  bond, the electron density is concentrated strictly between the two atoms forming the bond. In a delocalized  $\pi$  bond, parallel p orbitals on more than two adjacent atoms overlap and the electron density is spread over all the atoms that contribute p orbitals to the network. There are still two regions of overlap, above and below the  $\sigma$  framework of the molecule.
- (b) The existence of more than one resonance form is a good indication that a molecule will have delocalized  $\pi$  bonding.
- (c)  $\left[ \begin{array}{c} \cdot\ddot{\text{O}}::\ddot{\text{N}}::\ddot{\text{O}}\cdot \\ \cdot\ddot{\text{O}}::\ddot{\text{N}}::\ddot{\text{O}}\cdot \end{array} \right]^- \longleftrightarrow \left[ \begin{array}{c} \cdot\ddot{\text{O}}::\ddot{\text{N}}::\ddot{\text{O}}\cdot \\ \cdot\ddot{\text{O}}::\ddot{\text{N}}::\ddot{\text{O}}\cdot \end{array} \right]^-$

The existence of more than one resonance form for  $\text{NO}_2$  indicates that the  $\pi$  bond is delocalized. From an orbital perspective, the electron-domain geometry around N is trigonal planar, so the hybridization at N is  $sp^2$ . This leaves a p orbital on N and one on each O atom perpendicular to the trigonal plane of the molecule, in the correct orientation for delocalized  $\pi$  overlap. Physically, the two N-O bond lengths are equal, indicating that the two N-O bonds are equivalent, rather than one longer single bond and one shorter double bond.

- 9.68 (a)  $24 e^-$ ,  $12 e^-$  pairs (b)



3 electron domains around S, trigonal planar electron-domain geometry,  $sp^2$  hybrid orbitals

- (c) The multiple resonance structures indicate delocalized  $\pi$  bonding. All four atoms lie in the trigonal plane of the  $sp^2$  hybrid orbitals. On each atom there is a p atomic orbital perpendicular to this plane in the correct orientation for  $\pi$  overlap. The resulting delocalized  $\pi$  electron cloud is Y-shaped (the shape of the molecule) and has electron density above and below the plane of the molecule.

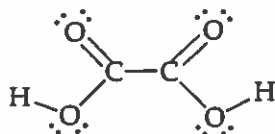
- 9.69 *Analyze/Plan.* Count valence  $e^-$  and  $e^-$  pairs in each molecule. Complete the Lewis structure by placing nonbonding electron pairs. Analyze the electron domain geometry at each central atom; visualize and describe the molecular structure. *Solve.*

- (a)  $26 e^-$ ,  $13 e^-$  pairs



The molecule is linear. Each C atom has 2 bonding  $e^-$  domains, linear geometry and  $sp$  hybridization. This requires that all atoms not only lie in the same plane, but in a line.

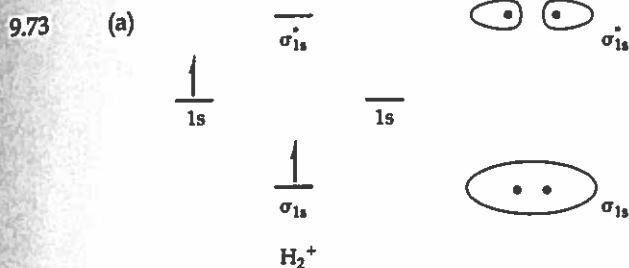
- (b)  $34 e^-$ ,  $17 e^-$  pairs





### Molecular Orbitals and Second Row Diatomic Molecules (sections 9.7 and 9.8)

- 9.71 (a) Hybrid orbitals are mixtures (linear combinations) of atomic orbitals from a single atom; the hybrid orbitals remain localized on that atom. Molecular orbitals are combinations of atomic orbitals from two or more atoms. They are associated with the entire molecule, not a single atom.
- (b) Each MO, like each AO or hybrid, can hold a maximum of two electrons.
- (c) Antibonding MOs can have electrons in them.
- 9.72 (a) An MO, since the AOs come from two different atoms.
- (b) A hybrid orbital, since the AOs are on the same atom.
- (c) Yes. The Pauli principle, that no two electrons can have the same four quantum numbers, means that an orbital can hold at most two electrons. (Since  $n$ ,  $l$ , and  $m_l$  are the same for a particular orbital and  $m_s$  has only two possible values, an orbital can hold at most two electrons). This is true for atomic and molecular orbitals.



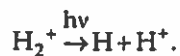
- (b) There is one electron in  $H_2^+$ .



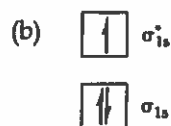
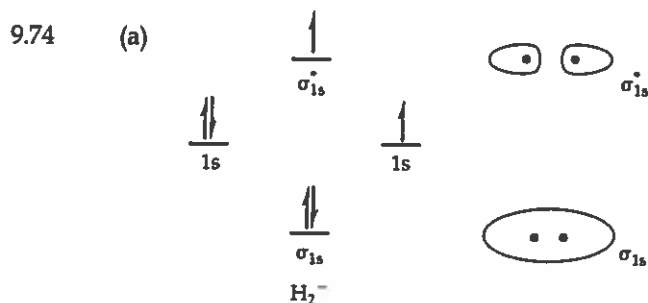
- (c)



- (d) Bond order =  $1/2 (1-0) = 1/2$
- (e) Fall apart. The stability of  $H_2^+$  is due to the lower energy state of the  $\sigma$  bonding molecular orbital relative to the energy of a H 1s atomic orbital. If the single electron in  $H_2^+$  is excited to the  $\sigma_{1s}^*$  orbital, its energy is higher than the energy of an H 1s atomic orbital and  $H_2^+$  will decompose into a hydrogen atom and a hydrogen ion.

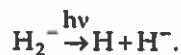




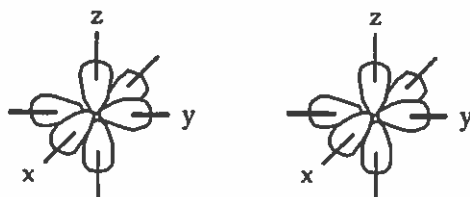


(c) Bond order =  $1/2 (2-1) = 1/2$

(d) If one electron moves from  $\sigma_{1s}$  to  $\sigma_{1s}^*$ , the bond order becomes  $-1/2$ . There is a net increase in energy relative to isolated H atoms, so the ion will decompose.



9.75



(a) One. With three mutually perpendicular p orbitals on each atom, only one set can be oriented for end-to-end, sigma overlap.

(b) Two. The 2 p orbitals on each atom not involved in  $\sigma$  bonding can be aligned for side-to-side  $\pi$  overlap.

(c) Three, 1  $\sigma^*$  and 2  $\pi^*$ . There are a total of 6 p orbitals on the two atoms. When combining AOs to form MOs, total number of orbitals is conserved. If 3 of the 6 MOs are bonding MOs, as described in (a) and (b), then the remaining 3 MOs must be antibonding. They will have the same symmetry as the bonding MOs, 1  $\sigma^*$  and 2  $\pi^*$ .

9.76

(a) Zero

(b) The two  $\pi_{2p}$  molecular orbitals are degenerate; they have the same energy, but they have different spatial orientations  $90^\circ$  apart.

(c) In the bonding MO the electrons are stabilized by both nuclei. In an antibonding MO, the electrons are directed away from the nuclei, so the  $\pi_{2p}$  bonding MO is lower in energy than the  $\pi_{2p}^*$  antibonding MO.

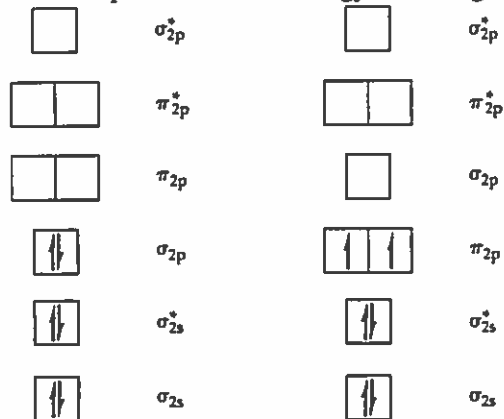
- 9.77 (a) When comparing the same two bonded atoms, the greater the bond order, the shorter the bond length and the greater the bond energy. That is, bond order and bond energy are directly related, while bond order and bond length are inversely related. When comparing different bonded nuclei, there are no simple relationships (see Solution 8.100).



$\text{Be}_2$  has a bond order of zero and is not energetically favored over isolated Be atoms; it is not expected to exist.  $\text{Be}_2^+$  has a bond order of 0.5 and is slightly lower in energy than isolated Be atoms. It will probably exist under special experimental conditions, but be unstable.

- 9.78 (a)  $\text{O}_2^{2-}$  has a bond order of 1.0, while  $\text{O}_2^-$  has a bond order of 1.5. For the same bonded atoms, the greater the bond order the shorter the bond, so  $\text{O}_2^-$  has the shorter bond.

- (b) The two possible orbital energy level diagrams are:



The magnetic properties of a molecule reveal whether it has unpaired electrons. If the  $\sigma_{2p}$  MOs are lower in energy,  $\text{B}_2$  has no unpaired electrons. If the  $\pi_{2p}$  MOs are lower in energy than the  $\sigma_{2p}$  MO, there are two unpaired electrons. The magnetic properties of  $\text{B}_2$  must indicate that it has unpaired electrons.

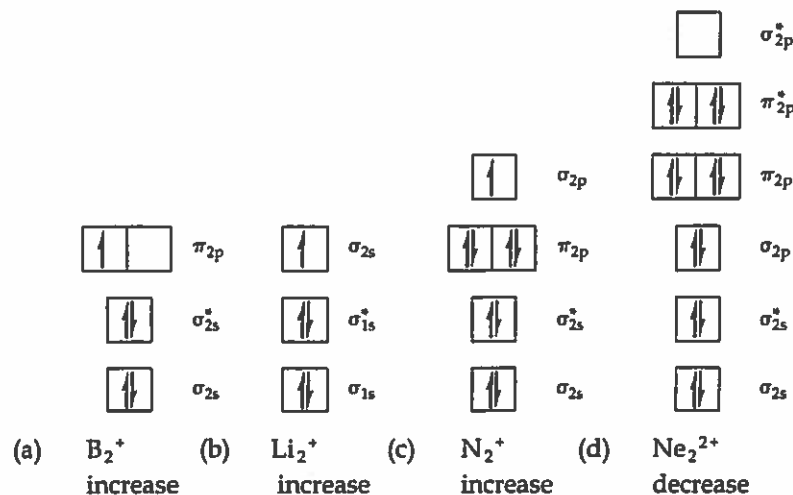
- (c) According to Figure 9.43, the two highest-energy electrons of  $\text{O}_2$  are in antibonding  $\pi_{2p}^*$  MOs and  $\text{O}_2$  has a bond order of 2.0. Removing these two electrons to form  $\text{O}_2^{2+}$  produces an ion with bond order 3.0.  $\text{O}_2^{2+}$  has a stronger O–O bond than  $\text{O}_2$ , because  $\text{O}_2^{2+}$  has a greater bond order.

- 9.79 (a), (b) Substances with no unpaired electrons are weakly repelled by a magnetic field. This property is called *diamagnetism*.

- (c)  $\text{O}_2^{2-}, \text{Be}_2^{2+}$  [see Figure 9.43 and Solution 9.77(b)]

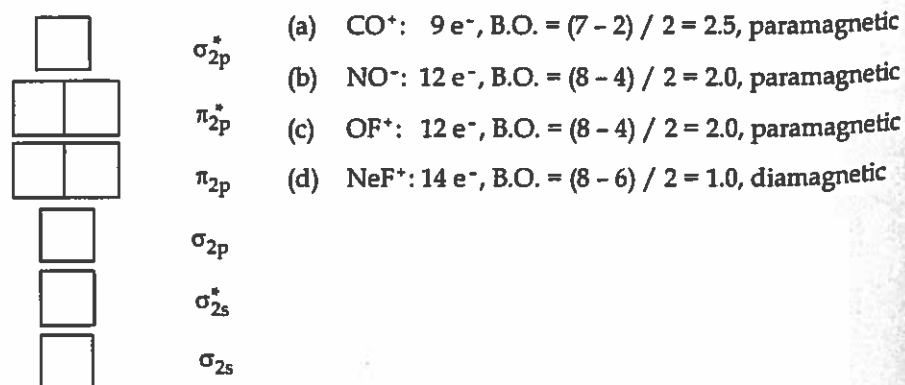
- 9.80 (a) Substances with unpaired electrons are attracted into a magnetic field. This property is called *paramagnetism*.
- (b) Weigh the substance normally and in a magnetic field, as shown in Figure 9.44. Paramagnetic substances appear to have a larger mass when weighed in a magnetic field.
- (c) See Figures 9.35 and 9.43.  $O_2^+$ , one unpaired electron;  $N_2^{2-}$ , two unpaired electrons;  $Li_2^+$ , one unpaired electron

9.81



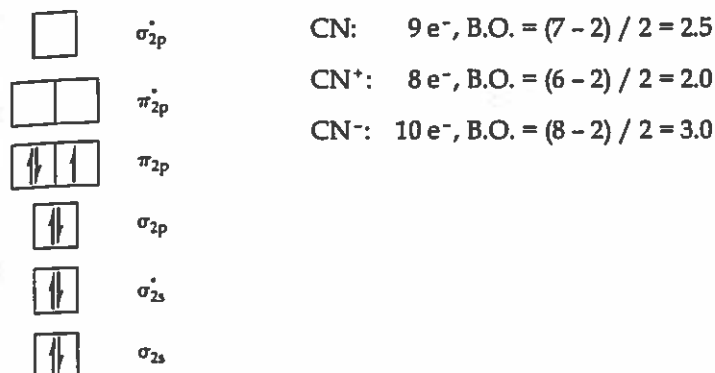
Addition of an electron increases bond order if it occupies a bonding MO and decreases stability if it occupies an antibonding MO.

- 9.82 Determine the number of "valence" (non-core) electrons in each molecule or ion. Use the homonuclear diatomic MO diagram from Figure 9.43 (shown below) to calculate bond order and magnetic properties of each species. The electronegativity difference between heteroatomics increases the energy difference between the 2s AO on one atom and the 2p AO on the other, rendering the "no interaction" MO diagram in Figure 9.43 appropriate.



- 9.83 *Analyze/Plan.* Determine the number of "valence" (non-core) electrons in each molecule or ion. Use the homonuclear diatomic MO diagram from Figure 9.43 (shown below) to calculate bond order and magnetic properties of each species. The electronegativity

difference between heteroatoms increases the energy difference between the 2s AO on one atom and the 2p AO on the other, rendering the "no interaction" MO diagram in Figure 9.43 appropriate. *Solve.*



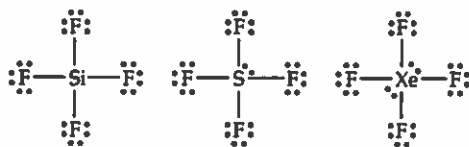
- (a) CN<sup>-</sup> has the highest bond order and therefore the strongest C–N bond.
- (b) CN and CN<sup>+</sup>. CN has an odd number of valence electrons, so it must have an unpaired electron. The electron configuration for CN is shown in the diagram. Removing one electron from the  $\pi_{2p}$  MOs to form CN<sup>+</sup> produces an ion with two unpaired electrons. Adding one electron to the  $\pi_{2p}$  MOs of CN to form CN<sup>-</sup> produces an ion with all electrons paired.
- 9.84 (a) The bond order of NO is  $[1/2 (8 - 3)] = 2.5$ . The electron that is lost is in an antibonding molecular orbital, so the bond order in NO<sup>+</sup> is 3.0. The increase in bond order is the driving force for the formation of NO<sup>+</sup>.
- (b) To form NO<sup>-</sup>, an electron is added to an antibonding orbital, and the new bond order is  $[1/2 (8 - 4)] = 2$ . The order of increasing bond order and bond strength is: NO<sup>-</sup> < NO < NO<sup>+</sup>. NO<sup>-</sup> and NO are paramagnetic with two and one unpaired electrons, respectively. NO<sup>+</sup> is diamagnetic.
- (c) NO<sup>+</sup> is isoelectronic with N<sub>2</sub>, and NO<sup>-</sup> is isoelectronic with O<sub>2</sub>.
- 9.85 (a) 3s, 3p<sub>x</sub>, 3p<sub>y</sub>, 3p<sub>z</sub>                      (b)  $\pi_{3p}$
- (c) Two. Note that there are two degenerate  $\pi_{3p}$  bonding molecular orbitals; each holds two electrons. A total of 4 electrons can be designated as  $\pi_{3p}$ , but no single molecular orbital can hold more than two electrons.
- (d) If the MO diagram for P<sub>2</sub> is similar to that of N<sub>2</sub>, P<sub>2</sub> will have no unpaired electrons and be diamagnetic.
- 9.86 (a) I: 5s, 5p<sub>x</sub>, 5p<sub>y</sub>, 5p<sub>z</sub>; Br: 4s, 4p<sub>x</sub>, 4p<sub>y</sub>, 4p<sub>z</sub>
- (b) By analogy to F<sub>2</sub>, the BO of IBr will be 1.
- (c) I and Br have valence atomic orbitals with different principal quantum numbers. This means that the radial extensions (sizes) of the valence atomic orbital that contribute to the MO are different. The n = 5 valence AOs on I are larger than the n = 4 valence AOs on Br.

- (d)  $\sigma_{np}^*$   
 (e) None

## Additional Exercises

- 9.87 (a) The physical basis of VSEPR is the electrostatic repulsion of like-charged particles, in this case groups or domains of electrons. That is, owing to electrostatic repulsion, electron domains will arrange themselves to be as far apart as possible.
- (b) The  $\sigma$ -bond electrons are localized in the region along the internuclear axes. The positions of the atoms and geometry of the molecule are thus closely tied to the locations of these electron pairs. Because the  $\pi$ -bond electrons are distributed above and below the plane that contains the  $\sigma$  bonds, these electron pairs do not, in effect, influence the geometry of the molecule. Thus, all  $\sigma$ - and  $\pi$ -bond electrons localized between two atoms are located in the same electron domain.
- 9.88 The Pauli exclusion principle is the fundamental basis for assigning pairs of electrons with their spins paired to electron domains. The Pauli principle states that no two electrons can have the same four quantum numbers. This means that the maximum occupancy of an orbital, be it atomic, hybrid, molecular, or whatever, is two electrons. And, if two electrons occupy the same orbital, their spins must be paired.

9.89

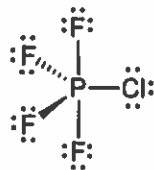


e<sup>-</sup> domain geometry td  
 molecular shape td

tbp  
 seesaw (ss)

octahedral (oh)  
 square planar (s)

Although there are four bonding electron domains in each molecule, the number of nonbonding domains is different in each case. The bond angles and thus the molecular shape are influenced by the total number of electron domains.

9.90 (a) 40 e<sup>-</sup>, 20 e<sup>-</sup> pairs5 e<sup>-</sup> domains

trigonal bipyramidal electron domain geometry

- (b) The greater the electronegativity of the terminal atom, the larger the negative charge centered on the atom, the smaller the effective size of the P-X bonding electron domain. A P-F bond will produce a smaller (and shorter) electron domain than a P-Cl bond.

- (c) The molecular geometry (shape) is also trigonal bipyramidal, because all five electron domains are bonding domains. Because we predicted the P-F electron domain to be smaller, the larger P-Cl bonding domain will occupy the equatorial plane of the molecule, minimizing the number of  $90^\circ$  P-Cl to P-F repulsions. This is the same argument that places a "larger" nonbonding domain in the equatorial position of a molecule like  $\text{SF}_4$ .
- (d) The molecular geometry is distorted from a perfect trigonal bipyramid because not all electron domains are alike. The  $90^\circ$  P-Cl to P-F repulsions will be greater than the  $90^\circ$  P-F to P-F repulsions, so the F(axial)-P-Cl angles will be greater than  $90^\circ$ . The equatorial F-P-F angles may distort slightly to "make room" for the axial F atoms that are "pushed away" from the equatorial Cl atom.

9.91 For any triangle, the law of cosines gives the length of side  $c$  as  $c^2 = a^2 + b^2 - 2ab \cos \theta$ .

Let the edge length of the cube ( $uy = vy = vz$ ) =  $X$

The length of the face diagonal ( $uv$ ) is

$$(uv)^2 = (uy)^2 + (vy)^2 - 2(uy)(vy) \cos 90$$

$$(uv)^2 = X^2 + X^2 - 2(X)(X) \cos 90$$

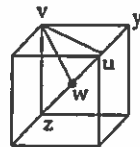
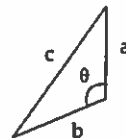
$$(uv)^2 = 2X^2; uv = \sqrt{2}X$$

The length of the body diagonal ( $uz$ ) is

$$(uz)^2 = (vz)^2 + (uv)^2 - 2(vz)(uv) \cos 90$$

$$(uz)^2 = X^2 + (\sqrt{2}X)^2 - 2(X)(\sqrt{2}X) \cos 90$$

$$(uz)^2 = 3X^2; uz = \sqrt{3}X$$



$\updownarrow$   
 $X$

For calculating the characteristic tetrahedral angle, the appropriate triangle has vertices  $u$ ,  $v$ , and  $w$ . Theta,  $\theta$ , is the angle formed by sides  $wu$  and  $wv$  and the hypotenuse is side  $uv$ .

$$wu = wv = uz/2 = \sqrt{3}/2X; uv = \sqrt{2}X$$

$$(\sqrt{2}X)^2 = (\sqrt{3}/2X)^2 + (\sqrt{3}/2X)^2 - 2(\sqrt{3}/2X)(\sqrt{3}/2X) \cos \theta$$

$$2X^2 = 3/4 X^2 + 3/4 X^2 - 3/2 X^2 \cos \theta$$

$$2X^2 = 3/2 X^2 - 3/2 X^2 \cos \theta$$

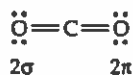
$$1/2 X^2 = -3/2 X^2 \cos \theta$$

$$\cos \theta = -(1/2 X^2) / (3/2 X^2) = -1/3 = -0.3333$$

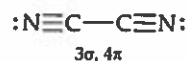
$$\theta = 109.47^\circ$$

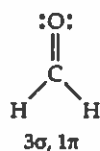
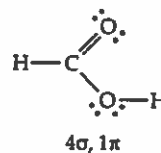
9.92

(a)  $\text{CO}_2$ , 16 valence  $e^-$

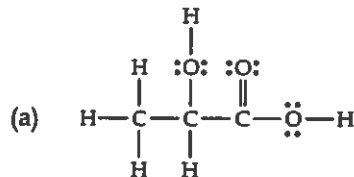


(b)  $(\text{CN})_2$ , 18 valence  $e^-$



(c)  $\text{H}_2\text{CO}$ , 12 valence  $e^-$ (d)  $\text{HCOOH}$ , 18 valence  $e^-$ 

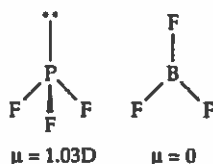
9.93



$$3(4) + 3(6) + 6(1) = 36 e^-, 18 e^- \text{ pr}$$

(b) There are 11  $\sigma$  and 1  $\pi$  bonds.(c) The  $\text{C}=\text{O}$  on the right-hand C atom is shortest. For the same bonded atoms, in this case C and O, the greater the bond order, the shorter the bond.(d, e) The right-most C has three  $e^-$  domains, so the hybridization is  $sp^2$ ; bond angles about this C atom are approximately  $120^\circ$ . The middle and left-hand C atoms both have four  $e^-$  domains, are  $sp^3$  hybridized, and have bond angles of approximately  $109^\circ$ .

9.94



$\text{BF}_3$  is a trigonal planar molecule with the central B atom symmetrically surrounded by the three F atoms (Figure 9.12). The individual B-F bond dipoles cancel, and the molecule has a net dipole moment of zero.  $\text{PF}_3$  has tetrahedral electron-domain geometry with one of the positions in the tetrahedron occupied by a nonbonding electron pair. The individual P-F bond dipoles do not cancel and the presence of a nonbonding electron pair ensures an asymmetrical electron distribution; the molecule is polar.

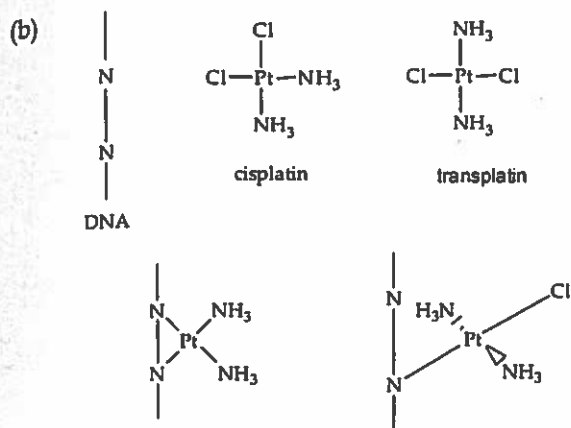
9.95

(a) Square pyramidal

(b) Yes, there is one nonbonding electron domain on A. If there were only five bonding domains, the shape would be trigonal bipyramidal. With five bonding and one nonbonding electron domains, the molecule has octahedral domain geometry.

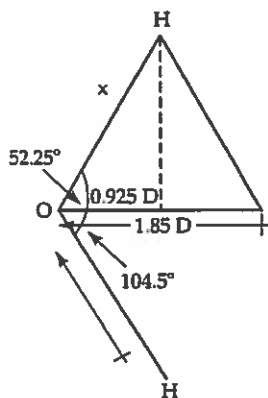
(c) Yes. If the B atoms are halogens, each will have three nonbonding electron pairs; there are five bonding pairs, and A has one nonbonded pair, for a total of  $[5(3) + 5 + 1] = 21 e^-$  pairs and 42 electrons in the Lewis structure. If the five halogens contribute  $35 e^-$ , A must contribute seven valence electrons. A is also a halogen.

- 9.96 (a) The compound on the right has a dipole moment. In the square planar trans structure on the left, all equivalent bond dipoles can be oriented opposite each other, for a net dipole moment of zero.



The cis orientation of the Cl atoms in cisplatin means that when they leave, the Pt can bind two adjacent N sites on DNA. This "chelate" orientation (see Chapter 24) tightly binds cisplatin to DNA. Transplatin can bind only one DNA N atom at a time. Thus, to avoid bumping by transplatin NH<sub>3</sub> groups and DNA, the plane of transplatin must rotate away from the DNA backbone. This is a much looser bonding situation than for cisplatin.

9.97



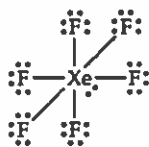
- (a) The bond dipoles in H<sub>2</sub>O lie along the O-H bonds with the positive end at H and the negative end at O. The dipole moment vector of the H<sub>2</sub>O molecule is the resultant (vector sum) of the two bond dipoles. This vector bisects the H-O-H angle and has a magnitude of 1.85 D with the negative end pointing toward O.
- (b) Since the dipole moment vector bisects the H-O-H bond angle, the angle between one H-O bond and the dipole moment vector is 1/2 the H-O-H bond angle, 52.25°. Dropping a perpendicular line from H to the dipole moment vector creates the right triangle pictured. If  $x$  = the magnitude of the O-H bond dipole,  $x \cos(52.25) = 0.925 \text{ D}$ .  $x = 1.51 \text{ D}$ .
- (c) The X-H bond dipoles (Table 8.3) and the electronegativity values of X (Figure 8.7) are



	Electronegativity	Bond dipole
F	4.0	1.82
O	3.5	1.51
Cl	3.0	1.08

Since the electronegativity of O is midway between the values for F and Cl, the O-H bond dipole should be approximately midway between the bond dipoles of HF and HCl. The value of the O-H bond dipole calculated in part (b) is consistent with this prediction.

- 9.98 (a)  $\text{XeF}_6$ , 50  $e^-$ , 25  $e^-$  pairs



- (b) There are seven electron domains around Xe, and the maximum number of  $e^-$  domains in Table 9.3 is six.
- (c) Tie seven balloons together and see what arrangement they adopt (seriously! see Figure 9.5). Alternatively, go to the chemical literature where VSEPR was first proposed and see if there is a preferred orientation for seven  $e^-$  domains.
- (d) One of the seven  $e^-$  domains is a nonbonded domain. The question is whether it occupies an axial or equatorial position. The equatorial plane of a pentagonal bipyramid has F-Xe-F angles of  $72^\circ$ . Placing the nonbonded domain in the equatorial plane would create severe repulsions between it and the adjacent bonded domains. Thus, the nonbonded domain will reside in the axial position. The molecular structure is a pentagonal pyramid.

- 9.99



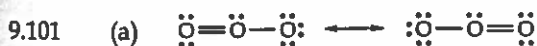
- (a) The molecule is not planar. The  $\text{CH}_2$  planes at each end are twisted  $90^\circ$  from one another.
- (b) Allene has no dipole moment.
- (c) The bonding in allene would not be described as delocalized. The  $\pi$  electron clouds of the two adjacent  $\text{C}=\text{C}$  are mutually perpendicular. The mechanism for delocalization of  $\pi$  electrons is mutual overlap of parallel p atomic orbitals on adjacent atoms. If adjacent  $\pi$  electron clouds are mutually perpendicular, there is no overlap and no delocalization of  $\pi$  electrons.

- 9.100 (a) 16  $e^-$ , 8  $e^-$  pairs



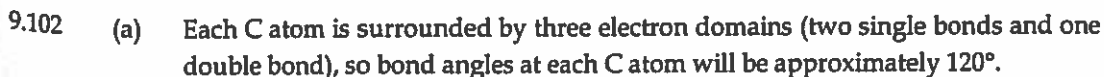
- (b) The observed bond length of 1.16 Å is intermediate between the values for N=N, 1.24 Å, and N≡N, 1.10 Å. This is consistent with the resonance structures, which indicate contribution from formally double and triple bonds to the true bonding picture in N<sub>3</sub><sup>-</sup>.
- (c) In each resonance structure, the central N has two electron domains, so it must be sp hybridized. It is difficult to predict the hybridization of terminal atoms in molecules where there are resonance structures because there are a different number of electron domains around the terminal atoms in each structure. Since the "true" electronic arrangement is a combination of all resonance structures, we will assume that the terminal N-N bonds have some triple bond character and that the terminal N atoms are sp hybridized. (There is no experimental measure of hybridization at terminal atoms, since there are no bond angles to observe.)
- (d) In each resonance structure, N-N σ bonds are formed by sp hybrids and π bonds are formed by unhybridized p orbitals. Nonbonding e<sup>-</sup> pairs can reside in sp hybrids or p atomic orbitals.
- (e) Recall that electrons in 2s orbitals are on the average closer to the nucleus than electrons in 2p orbitals. Since sp hybrids have greater s orbital character, it is reasonable to expect the radial extension of sp orbitals to be smaller than that of sp<sup>2</sup> or sp<sup>3</sup> orbitals and σ bonds formed by sp orbitals to be slightly shorter than those formed by other hybrid orbitals, assuming the same bonded atoms.

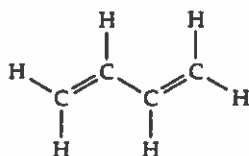
There are no solitary σ bonds in N<sub>3</sub><sup>-</sup>. That is, the two σ bonds in N<sub>3</sub><sup>-</sup> are each accompanied by at least one π bond between the bonding pair of atoms. Sigma bonds that are part of a double or triple bond must be shorter so that the p orbitals can overlap enough for the π bond to form. Thus, the observation is not applicable to this molecule. (Comparison of C-H bond lengths in C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and related molecules would confirm or deny the observation.)



To accommodate the π bonding by all 3 O atoms indicated in the resonance structures above, all O atoms are sp<sup>2</sup> hybridized.

- (b) For the first resonance structure, both sigma bonds are formed by overlap of sp<sup>2</sup> hybrid orbitals, the π bond is formed by overlap of atomic p orbitals, one of the nonbonded pairs on the right terminal O atom is in a p atomic orbital, and the remaining five nonbonded pairs are in sp<sup>2</sup> hybrid orbitals.
- (c) Only unhybridized p atomic orbitals can be used to form a delocalized π system.
- (d) The unhybridized p orbital on each O atom is used to form the delocalized π system, and in both resonance structures one nonbonded electron pair resides in a p atomic orbital. The delocalized π system then contains four electrons, two from the π bond and two from the nonbonded pair in the p orbital.

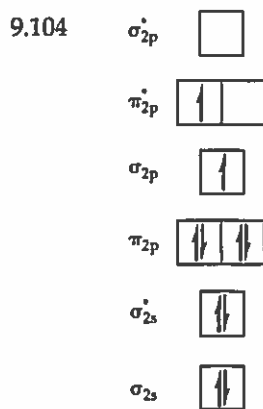




Since there is free rotation around the central C-C single bond, other conformations are possible.

- (b) According to Table 8.5, the average C-C length is 1.54 Å, and the average C=C length is 1.34 Å. While the C=C bonds in butadiene appear "normal," the central C-C is significantly shorter than average. Examination of the bonding in butadiene reveals that each C atom is  $sp^2$  hybridized and the  $\pi$  bonds are formed by the remaining unhybridized 2p orbital on each atom. If the central C-C bond is rotated so that all four C atoms are coplanar, the four 2p orbitals are parallel, and some delocalization of the  $\pi$  electrons occurs.

- 9.103 (a) The diagram shows two s atomic orbitals with opposite phases. Because they are spherically symmetric, the interaction of s orbitals can only produce a  $\sigma$  molecular orbital. Because the two orbitals in the diagram have opposite phases, the interaction excludes electron density from the region between the nuclei. The resulting MO has a node between the two nuclei and is labeled  $\sigma_{2s}^*$ . The principal quantum number designation is arbitrary, because it defines only the size of the pertinent AOs and MOs. Shapes and phases of MOs depend only on these same characteristics of the interacting AOs.
- (b) The diagram shows two p atomic orbitals with oppositely phased lobes pointing at each other. End-to-end overlap produces a  $\sigma$ -type MO; opposite phases mean a node between the nuclei and an antibonding MO. The interaction results in a  $\sigma_{2p}^*$  MO.
- (c) The diagram shows parallel p atomic orbitals with like-phased lobes aligned. Side-to-side overlap produces a  $\pi$ -type MO; overlap of like-phased lobes concentrates electron density between the nuclei and a bonding MO. The interaction results in a  $\pi_{2p}$  MO.



(a)  $N_2$  in the first excited state has two unpaired electrons and is paramagnetic.

(b)  $N_2$  in the ground state has a B.O. of 3; in the first excited state (at left) it has a B.O. of 2. Owing to the reduction in bond order,  $N_2$  in the first excited state has a weaker (and longer) N-N bond than  $N_2$  in the ground state.

9.105 We will refer to azo benzene (on the left) as A and hydrazobenzene (on the right) as H.

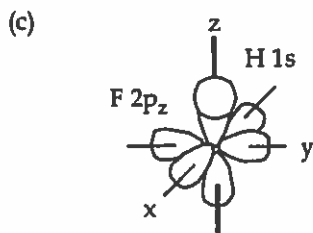
- (a) A:  $sp^2$ ; H:  $sp^3$

- (b) A: Each N and C atom has one unhybridized p orbital. H: Each C atom has one unhybridized p orbital, but the N atoms have no unhybridized p orbitals.
- (c) A:  $120^\circ$ ; H:  $109^\circ$
- (d) Since all C and N atoms in A have unhybridized p orbitals, all can participate in delocalized  $\pi$  bonding. The delocalized  $\pi$  system extends over the entire molecule, including both benzene rings and the azo "bridge." In H, the N atoms have no unhybridized p orbitals, so they cannot participate in delocalized  $\pi$  bonding. Each of the benzene rings in H is delocalized, but the network cannot span the N atoms in the bridge.
- (e) This is consistent with the answer to (d). In order for the unhybridized p orbitals in A to overlap, they must be parallel. This requires a planar  $\sigma$  bond framework where all atoms in the molecule are coplanar.
- (f) For a molecule to be useful in a solar energy conversion device, it must absorb visible light. This requires a HOMO-LUMO energy gap in the visible region. For organic molecules, the size of the gap is related to the number of conjugated  $\pi$  bonds; the more conjugated  $\pi$  bonds, the smaller the gap and the more likely the molecule is to be colored. Azobenzene has seven conjugated  $\pi$  bonds ( $\pi$  network delocalized over the entire molecule) and appears red-orange. Hydrazobenzene has only three conjugated  $\pi$  bonds ( $\pi$  network on benzene rings only) and appears white. Thus, the smaller HOMO-LUMO energy gap in A causes it to be both intensely colored and a more useful molecule for solar energy conversion.

9.106 (a) H:  $1s^1$ ; F:  $[\text{He}]2s^22p^5$

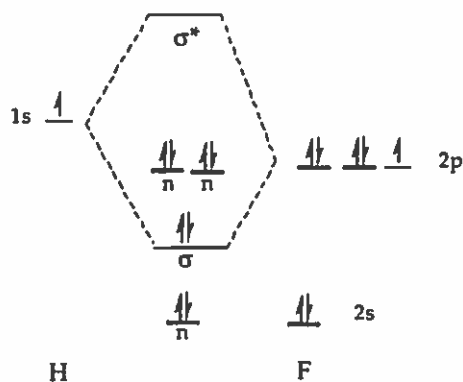
When molecular orbitals are formed from atomic orbitals, the total number of orbitals is conserved. Since H and F have a total of five valence AOs ( $H_{1s} + F_{2s} + 3F_{2p}$ ), the MO diagram for HF has five MOs.

- (b) H and F have a total of eight valence electrons. Since each MO can hold a maximum of two electrons, four of the five MOs would be occupied.



If H and F lie on the  $z$  axis, then the  $2p_z$  orbital of F will overlap with the  $1s$  orbital of H.

- (d) Since F is more electronegative than H, the valence orbitals on F are at lower energy than those on H.



The HF MO diagram has 6 nonbonding, 2 bonding and 0 antibonding electrons. The BO =  $[2 - 0]/2 = 1$ . (Nonbonding electrons do not "count" toward bond order.)



In the Lewis structure for HF, the nonbonding electrons are on the (more electronegative) F atom, as they are in the MO diagram.

9.107 (a) CO, 10  $e^-$ , 5  $e^-$  pair

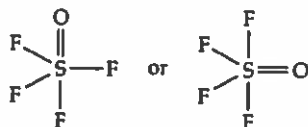


- (b) The bond order for CO, as predicted by the MO diagram in Figure 9.46, is  $1/2[8 - 2] = 3.0$ . A bond order of 3.0 agrees with the triple bond in the Lewis structure.
- (c) Applying the MO diagram in Figure 9.46 to the CO molecule, the highest energy electrons would occupy the  $\pi_{2p}$  MOs. That is,  $\pi_{2p}$  would be the HOMO, highest occupied molecular orbital. If the true HOMO of CO is a  $\sigma$ -type MO, the order of the  $\pi_{2p}$  and  $\sigma_{2p}$  orbitals must be reversed. Figure 9.42 shows how the interaction of the 2s orbitals on one atom and the 2p orbitals on the other atom can affect the relative energies of the resulting MOs. This 2s-2p interaction in CO is significant enough so that the  $\sigma_{2p}$  MO is higher in energy than the  $\pi_{2p}$  MOs, and the  $\sigma_{2p}$  is the HOMO. This is the same energy order of MOs shown for large 2s-2p interaction in homonuclear diatomic molecules in Figure 9.43.
- (d) We expect the atomic orbitals of the more electronegative element to have lower energy than those of the less electronegative element. When atoms of the two elements combine, the lower energy atomic orbitals make a greater contribution to the bonding MOs and the higher energy atomic orbitals make a larger contribution to the antibonding orbitals. Thus, the  $\pi_{2p}$  bonding MOs will have a greater contribution from the more electronegative O atom.

9.108 (a) The carbon-carbon bond order in ethylene is two. This means that there are two more bonding  $e^-$  pairs (4 bonding  $e^-$ ) than antibonding  $e^-$  pairs. If one  $e^-$  is promoted from a bonding to an antibonding MO, there is one fewer bonding  $e^-$  and one more antibonding  $e^-$ ; there is now an excess of two bonding  $e^-$  or one bonding  $e^-$  pair. The electron transition reduces the carbon-carbon bond order from two to one.

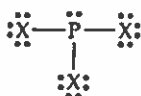


- (d) trigonal bipyramidal electron-domain geometry



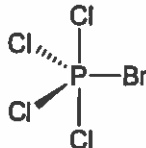
- (e) Because F is more electronegative than O, S-F bonding domains are smaller than the S=O domain. The structure that minimizes S=O repulsions is more likely (see Solution 9.90). That is, the structure with fewer 90° F-S=O angles and more 120° F-S=O angles is favored. The structure on the right, with O in the equatorial position is more likely. Note that a double bond involving an atom with an expanded octet of electrons, such as the S=O in this molecule, does not have the same geometric implications as a double bond to a first row element.

- 9.111 (a)
- $PX_3$
- , 26 valence
- $e^-$
- , 13
- <sup>-</sup>
- pairs

4 electron domains around P, tetrahedral  $e^-$  domain geometry,

If all bonding and nonbonding electron domains are the same size, perfect tetrahedral angles are 109.5°. If all bonding electron domains are the same size but the nonbonding domain is larger, bond angles are somewhat less than 109°.

- (b) As electronegativity increases ( $I < Br < Cl < F$ ), the X-P-X angles decrease
- (c) The greater the electronegativity of X, the larger the magnitude of negative charge centered on X. The more negative charge centered on X, the smaller the P-X bonding domains, the greater the effect of the nonbonding domain and the smaller the bond angle. Also, as the electronegativity of X decreases and the bonding domain size increases, the effect of the large nonbonding domain decreases.
- (d)  $PBrCl_4$ , 40 valence electrons, 20  $e^-$  pairs. The molecule will have trigonal bipyramidal electron-domain geometry (similar to  $PCl_5$  in Table 9.3.) Based on the argument in part (c), the P-Br bond will have greater repulsions with P-Cl bonds than P-Cl bonds have with each other. Therefore, the Br will occupy an equatorial position in the trigonal bipyramid, so that the more unfavorable P-Br to P-Cl repulsions can be situated at larger angles in the equatorial plane.



- 9.112 (a) Three electron domains around each central C atom,
- $sp^2$
- hybridization

- (b) A 180° rotation around the C=C double bond is required to convert the
- trans*
- isomer into the
- cis*
- isomer. A 90° rotation around the bond eliminates all overlap of the p orbitals that form the
- $\pi$
- bond and it is broken.

(c) average bond enthalpy

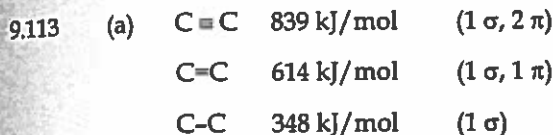


The difference in these values, 266 kJ/mol, is the average bond enthalpy of a C-C  $\pi$  bond. This is the amount of energy required to break 1 mol of C-C  $\pi$  bonds. The energy per molecule is

$$266 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} = 4.417 \times 10^{-19} \\ = 4.42 \times 10^{-19} \text{ J/molecule}$$

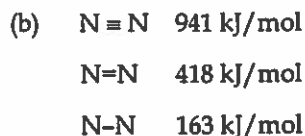
$$(d) \lambda = hc/E = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.998 \times 10^8 \text{ m/s}}{4.417 \times 10^{-19} \text{ J}} = 4.50 \times 10^{-7} \text{ m} = 450 \text{ nm}$$

(e) Yes, 450 nm light is in the visible portion of the spectrum. A cis-trans isomerization in the retinal portion of the large molecule rhodopsin is the first step in a sequence of molecular transformations in the eye that leads to vision. The sequence of events enables the eye to detect visible photons, in other words, to see.



The contribution from 1  $\pi$  bond would be (614-348) 266 kJ/mol. From a second  $\pi$  bond, (839 - 614), 225 kJ/mol. An average  $\pi$  bond contribution would be (266 + 225)/2 = 246 kJ/mol.

$$\text{This is } \frac{246 \text{ kJ}/\pi \text{ bond}}{348 \text{ kJ}/\sigma \text{ bond}} \times 100 = 71\% \text{ of the average enthalpy of a } \sigma \text{ bond.}$$



$$\text{first } \pi = (418 - 163) = 255 \text{ kJ/mol}$$

$$\text{second } \pi = (941 - 418) = 523 \text{ kJ/mol}$$

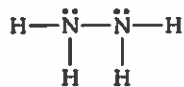
$$\text{average } \pi \text{ bond enthalpy} = (255 + 523)/2 = 389 \text{ kJ/mol}$$

$$\text{This is } \frac{389 \text{ kJ}/\pi \text{ bond}}{163 \text{ kJ}/\sigma \text{ bond}} \times 100 = 240\% \text{ of the average enthalpy of a } \sigma \text{ bond.}$$

N-N  $\sigma$  bonds are weaker than C-C  $\sigma$  bonds, while N-N  $\pi$  bonds are stronger than C-C  $\pi$  bonds. The relative energies of C-C  $\sigma$  and  $\pi$  bonds are similar, while N-N  $\pi$  bonds are much stronger than N-N  $\sigma$  bonds.



- (c)
- $\text{N}_2\text{H}_4$
- , 14 valence
- $e^-$
- , 7
- $e^-$
- pairs

4 electron domains around N,  $sp^3$  hybridization

- $\text{N}_2\text{H}_2$
- , 12 valence
- $e^-$
- , 6
- $e^-$
- pairs

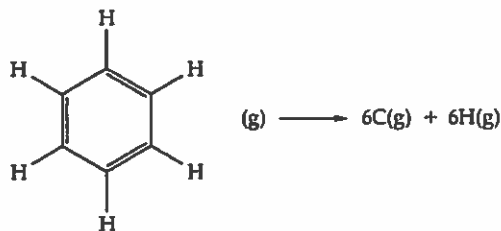
3 electron domains around N,  $sp^2$  hybridization

- $\text{N}_2$
- , 10 valence
- $e^-$
- , 5
- $e^-$
- pairs

2 electron domains around N,  $sp$  hybridization

- (d) In the three types of N-N bonds, each N atom has a nonbonding or lone pair of electrons. The lone pair to bond pair repulsions are minimized going from
- $109^\circ$
- to
- $120^\circ$
- to
- $180^\circ$
- bond angles, making the
- $\pi$
- bonds stronger relative to the
- $\sigma$
- bond. In the three types of C-C bonds, no lone-pair to bond-pair repulsions exist, and the
- $\sigma$
- and
- $\pi$
- bonds have more similar energies.

9.114



$$\begin{aligned} \Delta H &= 6D(\text{C}-\text{H}) + 3D(\text{C}-\text{C}) + 3D(\text{C}=\text{C}) - 0 \\ &= 6(413 \text{ kJ}) + 3(348 \text{ kJ}) + 3(614 \text{ kJ}) \\ &= 5364 \text{ kJ} \end{aligned}$$

(The products are isolated atoms; there is no bond making.)

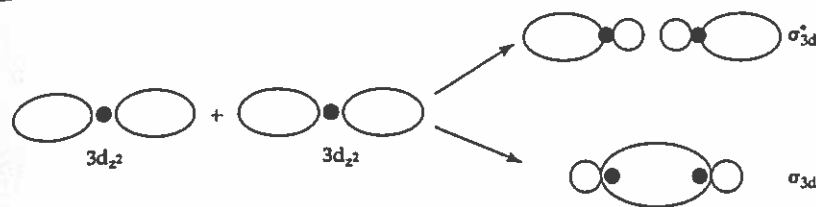
According to Hess' law:

$$\begin{aligned} \Delta H^\circ &= 6\Delta H_f^\circ \text{C}(\text{g}) + 6\Delta H_f^\circ \text{H}(\text{g}) - \Delta H_f^\circ \text{C}_6\text{H}_6(\text{g}) \\ &= 6(718.4 \text{ kJ}) + 6(217.94 \text{ kJ}) - (82.9 \text{ kJ}) \\ &= 5535 \text{ kJ} \end{aligned}$$

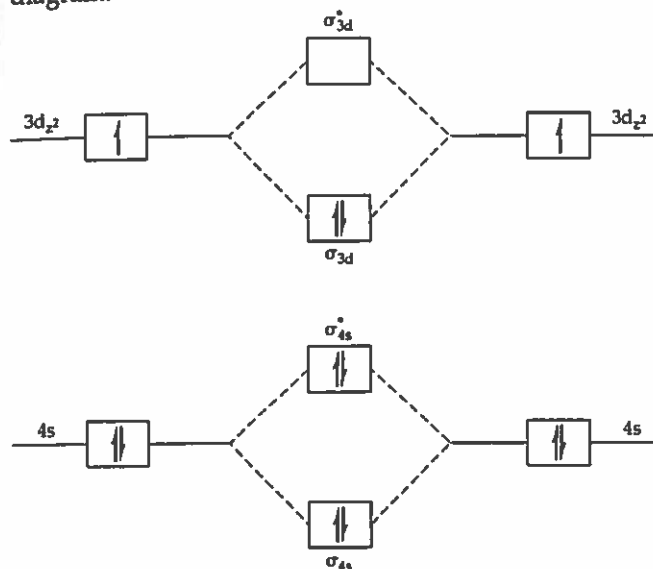
The difference in the two results, 171 kJ/mol  $\text{C}_6\text{H}_6$  is due to the resonance stabilization in benzene. That is, because the  $\pi$  electrons are delocalized, the molecule has a lower overall energy than that predicted for the presence of 3 localized C-C and C=C bonds. Thus, the amount of energy actually required to decompose 1 mole of  $\text{C}_6\text{H}_6(\text{g})$ , represented by the Hess' law calculation, is greater than the sum of the localized bond enthalpies (not taking resonance into account) from the first calculation above.

9.115

- (a)  $3d_{z^2}$   
 (b) Ignoring the donut of the  $d_{z^2}$  orbital



- (c) A node is generated in  $\sigma_{3d}^*$  because antibonding MOs are formed when AO lobes with opposite phases interact. Electron density is excluded from the internuclear region and a node is formed in the MO.
- (d) Sc:  $[\text{Ar}]4s^23d^1$  Omitting the core electrons, there are six  $e^-$  in the energy level diagram.



- (e) The bond order in  $\text{Sc}_2$  is  $1/2(4 - 2) = 1.0$ .

9.116

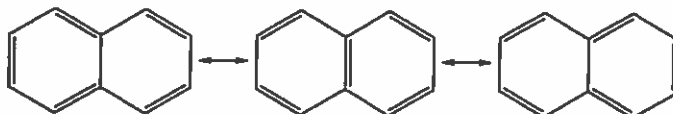
- (a) The molecular and empirical formulas of the four molecules are:  
 benzene: molecular,  $\text{C}_6\text{H}_6$ ; empirical, CH  
 naphthalene: molecular,  $\text{C}_{10}\text{H}_8$ ; empirical,  $\text{C}_5\text{H}_4$   
 anthracene: molecular,  $\text{C}_{14}\text{H}_{10}$ ; empirical,  $\text{C}_7\text{H}_5$   
 tetracene: molecular,  $\text{C}_{18}\text{H}_{12}$ ; empirical,  $\text{C}_3\text{H}_2$

- (b) Yes. Since the compounds all have different empirical formulas, combustion analysis could in principle be used to distinguish them. In practice, the mass % of C in the four compounds is not very different, so the data would have to be precise to at least 3 decimal places and 4 would be better.



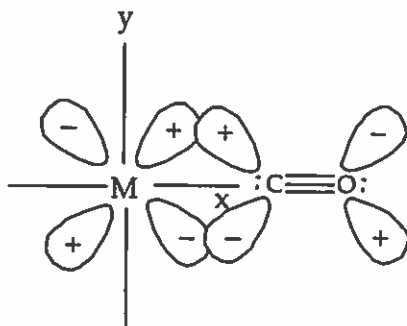
- (d)  $\Delta H_{\text{comb}} = 5D(\text{C}=\text{C}) + 6D(\text{C}-\text{C}) + 8D(\text{C}-\text{H}) + 12D(\text{O}=\text{O}) - 20D(\text{C}=\text{O}) - 8D(\text{O}-\text{H})$   
 $= 5(614) + 6(348) + 8(413) + 12(495) - 20(799) - 8(463)$   
 $= -5282 \text{ kJ/mol C}_{10}\text{H}_8$

- (e) Yes. For example, the resonance structures of naphthalene are:

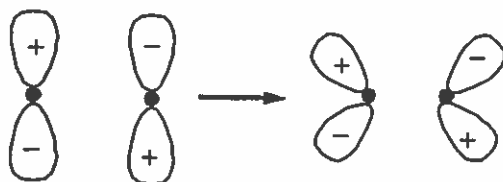


- (f) Colored compounds absorb visible light and appear the color of the visible light that they reflect. Colorless compounds typically absorb shorter wavelength, higher energy light. The energy of light absorbed corresponds to the energy gap between the HOMO and LUMO of the molecule. That tetracene absorbs longer wavelength, lower energy visible light indicates that it has the smallest HOMO-LUMO energy gap of the four molecules. Tetracene also has the most conjugated double bonds of the four molecules. We might conclude that the more conjugated double bonds in an organic molecule, the smaller the HOMO-LUMO energy gap. More information about the absorption spectra of anthracene, naphthalene and benzene is needed to confirm this conclusion.

9.117 (a) - (e)



- (c) The two lobes of a p AO have opposite phases. These are shown on the diagram as + and -. An antibonding MO is formed when p AOs with opposite phases interact.



- (d) Note that the  $d_{xy}$  AO has lobes that lie between, not on, the x and y axes.
- (e) A  $\pi$  bond forms by overlap of orbitals on M and C. There is electron density above and below, but not along, the M-C axis.
- (f) According to Exercise 9.107, the HOMO of CO is a  $\sigma$ -type MO. So the appropriate MO diagram is shown on the left side of Figure 9.43. A lone CO molecule has 10 valence electrons, the HOMO is  $\sigma_{2p}$  and the bond order is 3.0. The LUMO is  $\pi_{2p}^*$ .

When M and CO interact as shown in the  $\pi_{2p}^*$  diagram, d- $\pi$  back bonding causes the  $\pi_{2p}^*$  to become partially occupied. Electron density in the  $\pi_{2p}^*$  decreases

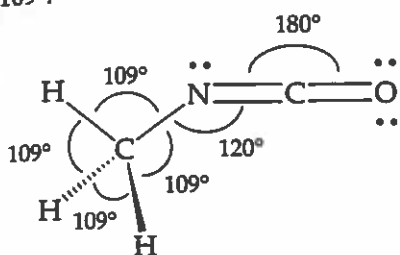
electron density in the bonding molecular orbitals and decreases the BO of the bound CO. The strength of the C–O bond in a metal–CO complex decreases relative to the strength of the C–O bond in an isolated CO molecule.

- 9.118 (a) 22 valence  $e^-$ , 11  $e^-$  pairs



(The structure on the right does not minimize formal charges and will make a minor contribution to the true structure.)

- (b) Both resonance structures predict the same bond angles. All H–C–N angles are  $109^\circ$ .



- (c) The two extreme Lewis structures predict different bond lengths. As the true bonding model is some blend of the extreme Lewis structures, the true bond lengths are a blend of the extreme values. Our bond length estimates take into account that the structure minimizing formal charge makes a larger contribution to the true structure.

According to Exercise 9.97, the O–H bond length in water is  $0.96 \text{ \AA}$ . According to Figure 7.6, the covalent radius of C is  $0.04 \text{ \AA}$  greater than that of O, so we expect the C–H bond length to be approximately  $0.04 \text{ \AA}$  greater than the O–H distance, about  $1.00 \text{ \AA}$ .

Bond	Length ( $\text{\AA}$ ) N=C=O	Length ( $\text{\AA}$ ) N $\equiv$ C–O	Length ( $\text{\AA}$ ) estimated
C–H	1.00	1.00	1.00
C–N	1.43	1.43	1.43
N–C	1.38	1.16	1.33
C–O	1.23	1.43	1.28

- (d) The molecule will have a dipole moment. The N–C and C–O bond dipoles are opposite each other, but they are not equal. And, there are nonbonding electron pairs which are not directly opposite each other (in either structure) and will not cancel. There will be a resulting dipole.