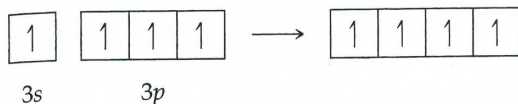
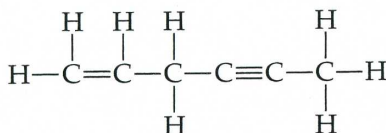


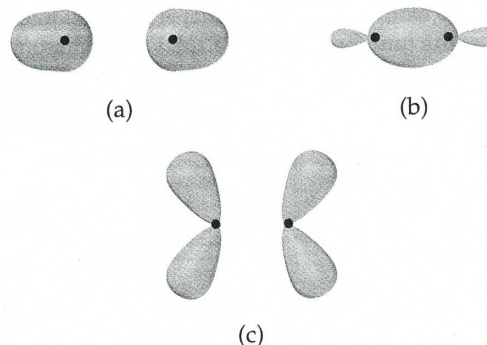
- 9.7 The orbital diagram below presents the final step in the formation of hybrid orbitals by a silicon atom. (a) Do you think one or more electrons have been promoted? Why or why not? (b) What type of hybrid orbitals are being produced in this hybridization? [Section 9.5]



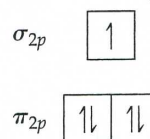
- 9.8 Consider the hydrocarbon drawn below. (a) What is the hybridization at each carbon atom in the molecule? (b) How many σ bonds are there in the molecule? (c) How many π bonds? [Section 9.6]



- 9.9 For each of the following contour representations of molecular orbitals, identify (i) the atomic orbitals (s or p) used to construct the MO, (ii) the type of MO (σ or π), and (iii) whether the MO is bonding or antibonding. [Sections 9.7 and 9.8]



- 9.10 The diagram below shows the highest occupied MOs of a neutral molecule CX, where element X is in the same row of the periodic table as C. (a) Based on the number of electrons, can you determine the identity of X? (b) Would the molecule be diamagnetic or paramagnetic? (c) Consider the π_{2p} MOs of the molecule. Would you expect them to have a greater atomic orbital contribution from C, have a greater atomic orbital contribution from X, or be an equal mixture of atomic orbitals from the two atoms? [Section 9.8]



EXERCISES

Molecular Shapes; the VSEPR Model

- 9.11 (a) An AB_2 molecule is described as linear, and the A—B bond length is specified. Does this information completely describe the geometry of the molecule? (b) The molecules BF_3 and SO_3 are both described as trigonal planar. Does this information completely define the bond angles of these molecules?
- 9.12 (a) Methane (CH_4) and the perchlorate ion (ClO_4^-) are both described as tetrahedral. What does this indicate about their bond angles? (b) The NH_3 molecule is trigonal pyramidal. How many parameters need to be specified to define its geometry completely?
- 9.13 (a) What is meant by the term *electron domain*? (b) Explain in what way electron domains behave like the balloons in Figure 9.5. Why do they do so?
- 9.14 (a) How does one determine the number of electron domains in a molecule or ion? (b) What is the difference between a *bonding electron domain* and a *nonbonding electron domain*?
- 9.15 Describe the characteristic electron-domain geometry of each of the following numbers of electron domains about a central atom: (a) 3, (b) 4, (c) 5, (d) 6.
- 9.16 Indicate the number of electron domains about a central atom, given the following angles between them: (a) 120° , (b) 180° , (c) 109.5° , (d) 90° .
- 9.17 What is the difference between the electron-domain geometry and the molecular geometry of a molecule? Use the water molecule as an example in your discussion.

- 9.18 An AB_3 molecule is described as having a trigonal-bipyramidal electron-domain geometry. How many nonbonding domains are on atom A? Explain.

- 9.19 Give the electron-domain and molecular geometries of a molecule that has the following electron domains on its central atom: (a) four bonding domains and no nonbonding domains, (b) three bonding domains and two nonbonding domains, (c) five bonding domains and one nonbonding domain.

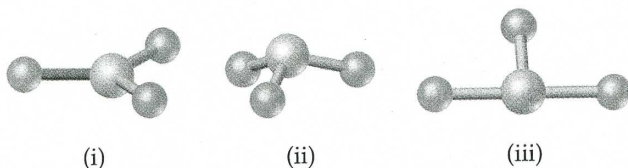
- 9.20 What are the electron-domain and molecular geometries of a molecule that has the following electron domains on its central atom? (a) Three bonding domains and no nonbonding domains, (b) three bonding domains and one nonbonding domain, (c) two bonding domains and three nonbonding domains.

- 9.21 Draw the Lewis structure for each of the following molecules or ions, and predict their electron-domain and molecular geometries: (a) PF_3 , (b) CH_3^+ , (c) BrF_3 , (d) ClO_4^- , (e) XeF_2 , (f) BrO_2^- .

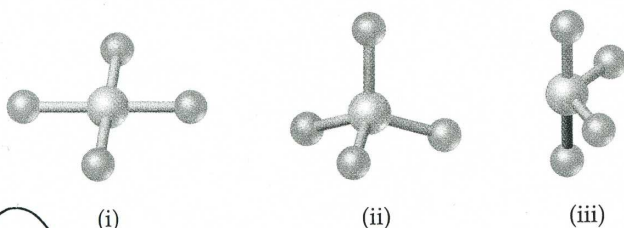
- 9.22 Give the electron-domain and molecular geometries for the following molecules and ions: (a) HCN , (b) SO_3^{2-} , (c) SF_4 , (d) PF_6^- , (e) NH_3Cl^+ , (f) N_3^- .

- 9.23 The figure that follows shows ball-and-stick drawings of three possible shapes of an AF_3 molecule. (a) For each shape, give the electron-domain geometry on which the molecular geometry is based. (b) For each shape, how many nonbonding electron domains are there on atom A? (c) Which of the following elements will lead to an AF_3 molecule with the shape in (ii): Li, B, N, Al, P, Cl?

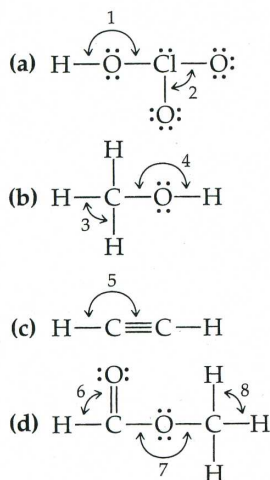
(d) Name an element A that is expected to lead to the AF_3 structure shown in (iii). Explain your reasoning.



9.24 The figure that follows contains ball-and-stick drawings of three possible shapes of an AF_4 molecule. (a) For each shape, give the electron-domain geometry on which the molecular geometry is based. (b) For each shape, how many nonbonding electron domains are there on atom A? (c) Which of the following elements will lead to an AF_4 molecule with the shape in (iii): Be, C, S, Se, Si, Xe? (d) Name an element A that is expected to lead to the AF_4 structure shown in (i).



9.25 Give the approximate values for the indicated bond angles in the following molecules:



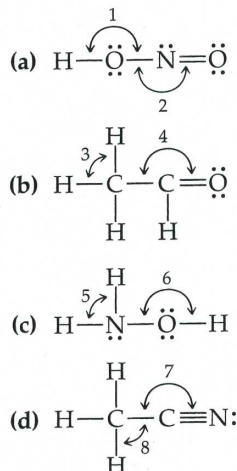
Polarity of Polyatomic Molecules

9.31 Does SO_2 have a dipole moment? If so, in which direction does the net dipole point?

9.32 The PH_3 molecule is polar. How does this offer experimental proof that the molecule cannot be planar?

9.33 (a) Consider the AF_3 molecules in Exercise 9.23. Which of these will have a nonzero dipole moment? Explain. (b) Which of the AF_4 molecules in Exercise 9.24 will have a zero dipole moment?

9.26 Give approximate values for the indicated bond angles in the following molecules:



9.27 The three species NH_2^- , NH_3 , and NH_4^+ have $\text{H}-\text{N}-\text{H}$ bond angles of 105° , 107° , and 109° , respectively. Explain this variation in bond angles.

9.28 Predict the trend in the $\text{F(axial)}-\text{A}-\text{F(equatorial)}$ bond angle in the following AF_n molecules: PF_5 , SF_4 , and ClF_3 .

9.29 (a) Explain why BrF_4^- is square planar, whereas BF_4^- is tetrahedral. (b) In which of these molecules, CF_4 or SF_4 , do you think the actual bond angle is closest to the ideal angle predicted by the VSEPR model? Explain briefly.

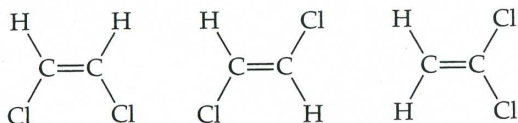
9.30 (a) Explain why the following ions have different bond angles: ClO_2^- and NO_2^- . Predict the bond angle in each case. (b) Given that the spatial requirement of a nonbonding pair of electrons is greater than that of a bonding pair, explain why the XeF_2 molecule is linear and not bent.

9.34 (a) What conditions must be met if a molecule with polar bonds is nonpolar? (b) What geometries will give nonpolar molecules for AB_2 , AB_3 , and AB_4 geometries?

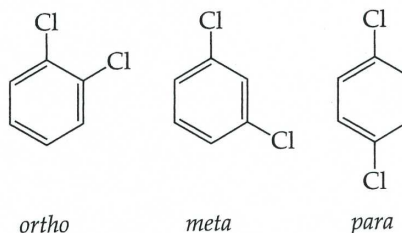
9.35 Predict whether each of the following molecules is polar or nonpolar: (a) CCl_4 , (b) NH_3 , (c) SF_4 , (d) XeF_4 , (e) CH_3Br , (f) GaH_3 .

9.36 Predict whether each of the following molecules is polar or nonpolar: (a) IF , (b) CS_2 , (c) SO_3 , (d) PCl_3 , (e) SF_6 , (f) IF_5 .

- 9.37 **CQ** Dichloroethylene ($C_2H_2Cl_2$) has three forms (isomers), each of which is a different substance. A pure sample of one of these substances is found experimentally to have a dipole moment of zero. Can we determine which of the three substances was measured?



- 9.38 Dichlorobenzene, $C_6H_4Cl_2$, exists in three forms (isomers), called *ortho*, *meta*, and *para*:



Which of these would have a nonzero dipole moment? Explain.

Orbital Overlap; Hybrid Orbitals

- 9.39 **CQ** (a) What is meant by the term *orbital overlap*? (b) What is the significance of overlapping orbitals in valence-bond theory? (c) What two fundamental concepts are incorporated in valence-bond theory?
- 9.40 **CQ** Draw sketches illustrating the overlap between the following orbitals on two atoms: (a) the $2s$ orbital on each, (b) the $2p_z$ orbital on each (assume that the atoms are on the z -axis), (c) the $2s$ orbital on one and the $2p_z$ orbital on the other.
- 9.41 **CQ** Consider the bonding in an MgH_2 molecule. (a) Draw a Lewis structure for the molecule, and predict its molecular geometry. (b) Why is it necessary to promote an electron before forming hybrid orbitals for the Mg atom? (c) What hybridization scheme is used in MgH_2 ? (d) Sketch one of the two-electron bonds between an Mg hybrid orbital and an H $1s$ atomic orbital.
- 9.42 **CQ** (a) Draw a Lewis structure for silane (SiH_4), and predict its molecular geometry. (b) Is it necessary to promote an electron before forming hybrid orbitals for the Si atom? (c) What type of hybridization exists in SiH_4 ? (d) In one diagram, sketch two of the two-electron bonds formed between a hybrid orbital on Si and an H $1s$ orbital. How would the other Si—H bonds be oriented relative to your sketch?
- 9.43 **CQ** Indicate the hybridization and bond angles associated with each of the following electron-domain geometries:

(a) linear, (b) tetrahedral, (c) trigonal planar, (d) octahedral, (e) trigonal bipyramidal.

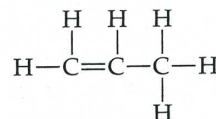
- 9.44 **CQ** What is the designation for the hybrid orbitals formed from each of the following combinations of atomic orbitals: (a) one s and two p ; (b) one s , three p , and one d ; (c) one s , three p , and two d ? What characteristic bond angles are associated with each?
- 9.45 (a) Starting with the orbital diagram of a boron atom, describe the steps needed to construct hybrid orbitals appropriate to describe the bonding in BF_3 . (b) What is the name given to the hybrid orbitals constructed in (a)? (c) On one origin, sketch the large lobes of the hybrid orbitals constructed in part (a). (d) Are there any valence atomic orbitals of B that are left unhybridized? If so, how are they oriented relative to the hybrid orbitals?
- 9.46 (a) Starting with the orbital diagram of a sulfur atom, describe the steps needed to construct hybrid orbitals appropriate to describe the bonding in SF_2 . (b) What is the name given to the hybrid orbitals constructed in (a)? (c) On one origin, sketch the large lobes of the hybrid orbitals constructed in part (a). (d) Would the hybridization scheme in part (a) be appropriate for SF_4 ? Explain.
- 9.47 **CQ** Indicate the hybridization of the central atom in (a) BCl_3 , (b) $AlCl_4^-$, (c) CS_2 , (d) KrF_2 , (e) PF_6^- .
- 9.48 What set of hybrid orbitals is used by the central atom in (a) $SiCl_4$, (b) HCN , (c) SO_3 , (d) ICl_2^- , (e) BrF_4^- ?

Multiple Bonds

- 9.49 **CQ** (a) Sketch a σ bond that is constructed from p orbitals. (b) Sketch a π bond that is constructed from p orbitals. (c) Which is generally the stronger, a σ bond or a π bond? Explain.
- 9.50 **CQ** (a) If the valence atomic orbitals of an atom are sp hybridized, how many unhybridized p orbitals remain in the valence shell? How many π bonds can the atom form? (b) How many σ and π bonds are generally part of a triple bond? (c) How do multiple bonds introduce rigidity into molecules?
- 9.51 **CQ** (a) Draw Lewis structures for methane (CH_4) and formaldehyde (H_2CO). (b) What is the hybridization at the carbon atom in CH_4 and H_2CO ? (c) The carbon atom

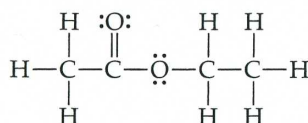
in CH_4 cannot participate in multiple bonding, whereas that in H_2CO can. Explain this observation by using the hybridization at the carbon atom.

- 9.52 **CQ** The nitrogen atoms in N_2 participate in multiple bonding, whereas those in hydrazine, N_2H_4 , do not. How can you explain this observation in light of the hybridization at the nitrogen atoms in the two molecules?
- 9.53 **CQ** Propylene, C_3H_6 , is a gas that is used to form the important polymer called polypropylene. Its Lewis structure is



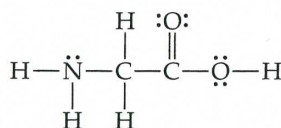
(a) What is the total number of valence electrons in the propylene molecule? (b) How many valence electrons are used to make σ bonds in the molecule? (c) How many valence electrons are used to make π bonds in the molecule? (d) How many valence electrons remain in nonbonding pairs in the molecule? (e) What is the hybridization at each carbon atom in the molecule?

- 9.54 Ethyl acetate, $C_4H_8O_2$, is a fragrant substance used both as a solvent and as an aroma enhancer. Its Lewis structure is



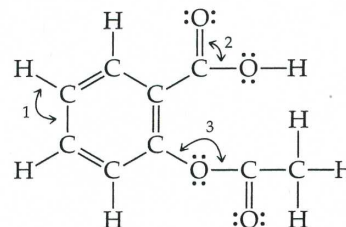
(a) What is the hybridization at each of the carbon atoms of the molecule? (b) What is the total number of valence electrons in ethyl acetate? (c) How many of the valence electrons are used to make σ bonds in the molecule? (d) How many valence electrons are used to make π bonds? (e) How many valence electrons remain in nonbonding pairs in the molecule?

- 9.55 Consider the Lewis structure for glycine, the simplest amino acid:



(a) What are the approximate bond angles about each of the two carbon atoms, and what are the hybridizations of the orbitals on each of them? (b) What are the hybridizations of the orbitals on the two oxygens and the nitrogen atom, and what are the approximate bond angles at the nitrogen? (c) What is the total number of σ bonds in the entire molecule, and what is the total number of π bonds?

- 9.56 The compound with the following Lewis structure is acetylsalicylic acid, better known as aspirin:



(a) What are the approximate values of the bond angles labeled 1, 2, and 3? (b) What hybrid orbitals are used about the central atom of each of these angles? (c) How many σ bonds are in the molecule?

- 9.57 (a) What is the difference between a localized π bond and a delocalized one? (b) How can you determine whether a molecule or ion will exhibit delocalized π bonding? (c) Is the π bond in NO_2^- localized or delocalized?

- 9.58 (a) Write a single Lewis structure for SO_3 , and determine the hybridization at the S atom. (b) Are there other equivalent Lewis structures for the molecule? (c) Would you expect SO_3 to exhibit delocalized π bonding? Explain.

Molecular Orbitals

- 9.59 (a) What are the similarities and differences between atomic orbitals and molecular orbitals? (b) Why is the bonding molecular orbital of H_2 at lower energy than the electron in a hydrogen atom? (c) How many electrons can be placed into each MO of a molecule?

- 9.60 (a) Why is the antibonding molecular orbital of H_2 at higher energy than the electron in a hydrogen atom? (b) Does the Pauli exclusion principle (Section 6.7) apply to MOs? Explain. (c) If two p orbitals of one atom combine with two p orbitals of another atom, how many MOs result? Explain.

- 9.61 Consider the H_2^+ ion. (a) Sketch the molecular orbitals of the ion, and draw its energy-level diagram. (b) How many electrons are there in the H_2^+ ion? (c) Write the electron configuration of the ion in terms of its MOs. (d) What is the bond order in H_2^+ ? (e) Suppose that the ion is excited by light so that an electron moves from a lower-energy to a higher-energy MO. Would you expect the excited-state H_2^+ ion to be stable or to fall apart? Explain.

- 9.62 (a) Sketch the molecular orbitals of the H_2^- ion, and draw its energy-level diagram. (b) Write the electron configuration of the ion in terms of its MOs. (c) Calculate the bond order in H_2^- . (d) Suppose that the ion is

excited by light, so that an electron moves from a lower-energy to a higher-energy molecular orbital. Would you expect the excited-state H_2^- ion to be stable? Explain.

- 9.63 (a) Sketch the σ and σ^* molecular orbitals that can result from the combination of two $2p_z$ atomic orbitals. (b) Sketch the π and π^* MOs that result from the combination of two $2p_x$ atomic orbitals. (c) Place the MOs from parts (a) and (b) in order of increasing energy, assuming no mixing of $2s$ and $2p$ orbitals.

- 9.64 (a) What is the probability of finding an electron on the internuclear axis if the electron occupies a π molecular orbital? (b) For a homonuclear diatomic molecule, what similarities and differences are there between the π_{2p} MO made from the $2p_x$ atomic orbitals and the π_{2p} MO made from the $2p_y$ atomic orbitals? (c) Why are the π_{2p} MOs lower in energy than the π_{2p}^* MOs?

- 9.65 (a) What are the relationships among bond order, bond length, and bond energy? (b) According to molecular orbital theory, would either Be_2 or Be_2^+ be expected to exist? Explain.

- 9.66 Explain the following: (a) The peroxide ion, O_2^{2-} , has a longer bond than the superoxide ion, O_2^- . (b) The magnetic properties of B_2 are consistent with the π_{2p} MOs being lower in energy than the σ_{2p} MO.

9.67 (a) What is meant by the term *diamagnetism*? (b) How does a diamagnetic substance respond to a magnetic field? (c) Which of the following ions would you expect to be diamagnetic: N_2^{2-} , O_2^{2-} , Be_2^{2+} , C_2^{-} ?

9.68 (a) What is meant by the term *paramagnetism*? (b) How can one determine experimentally whether a substance is paramagnetic? (c) Which of the following ions would you expect to be paramagnetic: O_2^{+} , N_2^{2-} , Li_2^{+} , O_2^{2-} ? If the ion is paramagnetic, how many unpaired electrons does it possess?

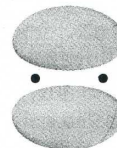
9.69 Using Figures 9.37 and 9.45 as guides, give the molecular orbital electron configuration for (a) B_2^{+} , (b) Li_2^{+} , (c) N_2^{+} , (d) Ne_2^{2+} . In each case indicate whether the addition of an electron to the ion would increase or decrease the bond order of the species.

9.70 If we assume that the energy-level diagrams for homonuclear diatomic molecules shown in Figure 9.42 can be applied to heteronuclear diatomic molecules and ions, predict the bond order and magnetic behavior of (a) CO^{+} , (b) NO^{-} , (c) OF^{+} , (d) NeF^{+} .

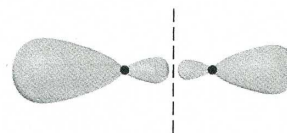
9.71 Determine the electron configurations for CN^{+} , CN , and CN^{-} . Calculate the bond order for each, and indicate which ones are paramagnetic.

9.72 (a) The nitric oxide molecule, NO , readily loses one electron to form the NO^{+} ion. Why is this consistent with the electronic structure of NO ? (b) Predict the order of the $\text{N}-\text{O}$ bond strengths in NO , NO^{+} , and NO^{-} , and describe the magnetic properties of each. (c) With what neutral homonuclear diatomic molecules are the NO^{+} and NO^{-} ions isoelectronic (same number of electrons)?

9.73 Consider the molecular orbitals of the P_2 molecule. (Assume that the MOs of diatomics from the third row of the periodic table are analogous to those from the second row.) (a) Which valence atomic orbitals of P are used to construct the MOs of P_2 ? (b) The figure below shows a sketch of one of the MOs for P_2 . What is the label for this MO? (c) For the P_2 molecule, how many electrons occupy the MO in the figure? (d) Is P_2 expected to be diamagnetic or paramagnetic? Explain.



9.74 The iodine bromide molecule, IBr , is an *interhalogen compound*. Assume that the molecular orbitals of IBr are analogous to the homonuclear diatomic molecule F_2 . (a) Which valence atomic orbitals of I and of Br are used to construct the MOs of IBr ? (b) What is the bond order of the IBr molecule? (c) One of the valence MOs of IBr is sketched below. Why are the atomic orbital contributions to this MO different in size? (d) What is the label for the MO? (e) For the IBr molecule, how many electrons occupy the MO?



Additional Exercises

9.75 (a) What is the physical basis for the VSEPR model? (b) When applying the VSEPR model, we count a double or triple bond as a single electron domain. Why is this justified?

9.76 The molecules SiF_4 , SF_4 , and XeF_4 all have molecular formulas of the type AF_4 , but the molecules have different molecular geometries. Predict the shape of each molecule, and explain why the shapes differ.

9.77 The vertices of a tetrahedron correspond to four alternating corners of a cube. By using analytical geometry, demonstrate that the angle made by connecting two of the vertices to a point at the center of the cube is 109.5° , the characteristic angle for tetrahedral molecules.

9.78 Consider the molecule PF_4Cl . (a) Draw a Lewis structure for the molecule, and predict its electron-domain geometry. (b) Which would you expect to produce a larger electron domain, a $\text{P}-\text{F}$ bond or a $\text{P}-\text{Cl}$ bond? Explain. (c) Predict the molecular geometry of PF_4Cl . How did your answer for part (b) influence your answer here in part (c)? (d) Would you expect the molecule to distort from its ideal electron domain geometry? If so, how would it distort?

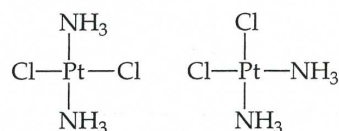
9.79 From their Lewis structures, determine the number of σ and π bonds in each of the following molecules or ions:

(a) CO_2 ; (b) thiocyanate ion, NCS^{-} ; (c) formaldehyde, H_2CO ; (d) formic acid, $\text{HCO}(\text{OH})$, which has one H and two O atoms attached to C.

9.80 The lactic acid molecule, $\text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH})$, gives sour milk its unpleasant, sour taste. (a) Draw the Lewis structure for the molecule, assuming that carbon always forms four bonds in its stable compounds. (b) How many π and how many σ bonds are in the molecule? (c) Which CO bond is shortest in the molecule? (d) What is the hybridization of atomic orbitals around each carbon atom associated with that short bond? (e) What are the approximate bond angles around each carbon atom in the molecule?

9.81 The PF_3 molecule has a dipole moment of 1.03 D, but BF_3 has a dipole moment of zero. How can you explain the difference?

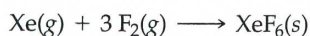
9.82 There are two compounds of the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$:



The compound on the right, *cisplatin*, is used in cancer therapy. Both compounds have a square-planar geometry. Which compound has a nonzero dipole moment?

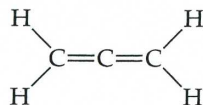
- [9.83] The O—H bond lengths in the water molecule (H_2O) are 0.96 Å, and the H—O—H angle is 104.5°. The dipole moment of the water molecule is 1.85 D. (a) In what directions do the bond dipoles of the O—H bonds point? In what direction does the dipole moment vector of the water molecule point? (b) Calculate the magnitude of the bond dipole of the O—H bonds. (Note: You will need to use vector addition to do this.) (c) Compare your answer from part (b) to the dipole moments of the hydrogen halides (Table 8.3). Is your answer in accord with the relative electronegativity of oxygen?

- [9.84] The reaction of three molecules of fluorine gas with an Xe atom produces the substance xenon hexafluoride, XeF_6 :



- (a) Draw a Lewis structure for XeF_6 . (b) If you try to use the VSEPR model to predict the molecular geometry of XeF_6 , you run into a problem. What is it? (c) What could you do to resolve the difficulty in part (b)? (d) Suggest a hybridization scheme for the Xe atom in XeF_6 . (e) The molecule IF_7 has a pentagonal-bipyramidal structure (five equatorial fluorine atoms at the vertices of a regular pentagon and two axial fluorine atoms). Based on the structure of IF_7 , suggest a structure for XeF_6 .

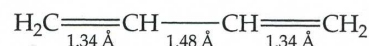
- [9.85] The Lewis structure for allene is



Make a sketch of the structure of this molecule that is analogous to Figure 9.27. In addition, answer the following three questions: (a) Is the molecule planar? (b) Does it have a nonzero dipole moment? (c) Would the bonding in allene be described as delocalized? Explain.

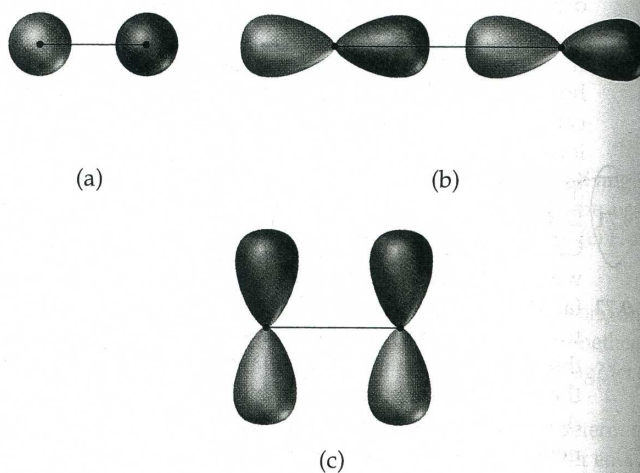
- [9.86] The azide ion, N_3^- , is linear with two N—N bonds of equal length, 1.16 Å. (a) Draw a Lewis structure for the azide ion. (b) With reference to Table 8.5, is the observed N—N bond length consistent with your Lewis structure? (c) What hybridization scheme would you expect at each of the nitrogen atoms in N_3^- ? (d) Show which hybridized and unhybridized orbitals are involved in the formation of σ and π bonds in N_3^- . (e) It is often observed that σ bonds that involve an sp hybrid orbital are shorter than those that involve only sp^2 or sp^3 hybrid orbitals. Can you propose a reason for this? Is this observation applicable to the observed bond lengths in N_3^- ?
- [9.87] In ozone, O_3 , the two oxygen atoms on the ends of the molecule are equivalent to one another. (a) What is the best choice of hybridization scheme for the atoms of ozone? (b) For one of the resonance forms of ozone, which of the orbitals are used to make bonds and which are used to hold nonbonding pairs of electrons? (c) Which of the orbitals can be used to delocalize the π electrons? (d) How many electrons are delocalized in the π system of ozone?

- 9.88 Butadiene, C_4H_6 , is a planar molecule that has the following carbon-carbon bond lengths:



- (a) Predict the bond angles around each of the carbon atoms, and sketch the molecule. (b) Compare the bond lengths to the average bond lengths listed in Table 8.5. Can you explain any differences?

- [9.89] The sketches below show the atomic orbital wave functions (with phases) used to construct some of the MOs of a homonuclear diatomic molecule. For each sketch, determine the MO that will result from mixing the atomic orbital wave functions as drawn. Use the same labels for the MOs as in Figure 9.42.

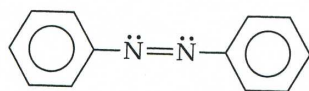


- [9.90] The cyclopentadienide ion has the formula C_5H_5^- . The ion consists of a regular pentagon of C atoms, each bonded to two C neighbors, with a hydrogen atom bonded to each C atom. All the atoms lie in the same plane. (a) Draw a Lewis structure for the ion. According to your structure, do all five C atoms have the same hybridization? Explain. (b) Chemists generally view this ion as having sp^2 hybridization at each C atom. Is that view consistent with your answer to part (a)? (c) Your Lewis structure should show one nonbonding pair of electrons. Under the assumption of part (b), in what type of orbital must this nonbonding pair reside? (d) Are there resonance structures equivalent to the Lewis structure you drew in part (a)? If so, how many? (e) The ion is often drawn as a pentagon enclosing a circle. Is this representation consistent with your answer to part (d)? Explain. (f) Both benzene and the cyclopentadienide ion are often described as systems containing six π electrons. What do you think is meant by this description?

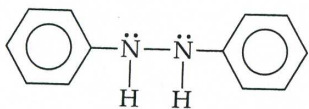
- 9.91 Write the electron configuration for the first excited state for N_2 (that is, the state with the highest-energy electron moved to the next available energy level). What differences do you expect in the properties of N_2 in its ground state and its first excited state?

- 9.92 Figure 9.46 shows how the magnetic properties of a compound can be measured experimentally. When such measurements are made, the sample is generally covered by an atmosphere of pure nitrogen gas rather than air. Why do you suppose this is done?

- [9.93] Azo dyes are organic dyes that are used for many applications, such as the coloring of fabrics. Many azo dyes are derivatives of the organic substance *azobenzene*, $C_{12}H_{10}N_2$. A closely related substance is *hydrazobenzene*, $C_{12}H_{12}N_2$. The Lewis structures of these two substances are



Azobenzene



Hydrazobenzene

(Recall the shorthand notation used for organic molecules.) (a) What is the hybridization at the N atom in each of the substances? (b) How many unhybridized atomic orbitals are there on the N and the C atoms in each of the substances? (c) Predict the N—N—C angles in each of the substances. (d) Azobenzene is said to have greater delocalization of its π electrons than hydrazobenzene. Discuss this statement in light of your answers to (a) and (b). (e) All the atoms of azobenzene lie

in one plane, whereas those of hydrazobenzene do not. Is this observation consistent with the statement in part (d)? (f) Azobenzene is an intense red-orange color, whereas hydrazobenzene is nearly colorless. Discuss this observation with reference to the "Chemistry at Work" box on organic dyes.

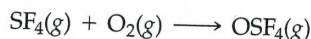
- 9.94 (a) Using only the valence atomic orbitals of a hydrogen atom and a fluorine atom, how many MOs would you expect for the HF molecule? (b) How many of the MOs from part (a) would be occupied by electrons? (c) Do you think the MO diagram shown in Figure 9.48 could be used to describe the MOs of the HF molecule? Why or why not?

- [9.95] Carbon monoxide, CO, is isoelectronic to N_2 . (a) Draw a Lewis structure for CO that satisfies the octet rule. (b) Assume that the diagram in Figure 9.48 can be used to describe the MOs of CO. What is the predicted bond order for CO? Is this answer in accord with the Lewis structure you drew in part (a)? (c) Experimentally, it is found that the highest-energy electrons in CO reside in a σ -type MO. Is that observation consistent with Figure 9.48? If not, what modification needs to be made to the diagram? How does this modification relate to Figure 9.44? (d) Would you expect the π_{2p} MOs of CO to have equal atomic orbital contributions from the C and O atoms? If not, which atom would have the greater contribution?

Integrative Exercises

- 9.96 A compound composed of 2.1% H, 29.8% N, and 68.1% O has a molar mass of approximately 50 g/mol. (a) What is the molecular formula of the compound? (b) What is its Lewis structure if H is bonded to O? (c) What is the geometry of the molecule? (d) What is the hybridization of the orbitals around the N atom? (e) How many σ and how many π bonds are there in the molecule?

- 9.97 Sulfur tetrafluoride (SF_4) reacts slowly with O_2 to form sulfur tetrafluoride monoxide (OSF_4) according to the following unbalanced reaction:

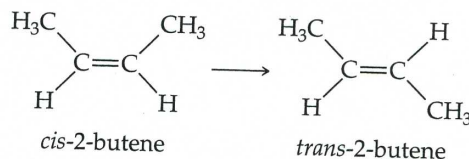


The O atom and the four F atoms in OSF_4 are bonded to a central S atom. (a) Balance the equation. (b) Write a Lewis structure of OSF_4 in which the formal charges of all atoms are zero. (c) Use average bond enthalpies (Table 8.4) to estimate the enthalpy of the reaction. Is it endothermic or exothermic? (d) Determine the electron-domain geometry of OSF_4 , and write two possible molecular geometries for the molecule based on this electron-domain geometry. (e) Which of the molecular geometries in part (d) is more likely to be observed for the molecule? Explain.

- [9.98] The phosphorus trihalides (PX_3) show the following variation in the bond angle $X-P-X$: PF_3 , 96.3° ; PCl_3 , 100.3° ; PBr_3 , 101.0° ; PI_3 , 102° . The trend is generally attributed to the change in the electronegativity of the halogen. (a) Assuming that all electron domains exhibit the same repulsion, what value of the $X-P-X$ angle is predicted by the VSEPR model? (b) What is the general

trend in the $X-P-X$ angle as the electronegativity increases? (c) Using the VSEPR model, explain the observed trend in $X-P-X$ angle as the electronegativity of X changes. (d) Based on your answer to part (c), predict the structure of $PBrCl_4$.

- [9.99] The molecule 2-butene, C_4H_8 , can undergo a geometric change called *cis-trans isomerization*:



As discussed in the "Chemistry and Life" box on the chemistry of vision, such transformations can be induced by light and are the key to human vision. (a) What is the hybridization at the two central carbon atoms of 2-butene? (b) The isomerization occurs by rotation about the central C—C bond. With reference to Figure 9.32, explain why the π bond between the two central carbon atoms is destroyed halfway through the rotation from *cis*- to *trans*-2-butene. (c) Based on average bond enthalpies (Table 8.4), how much energy per molecule must be supplied to break the C—C π bond? (d) What is the longest wavelength of light that will provide photons of sufficient energy to break the C—C π bond and cause the isomerization? (e) Is the wavelength in your answer to part (d) in the visible portion of the electromagnetic spectrum? Comment on the importance of this result for human vision.

- 9.100 (a) Compare the bond enthalpies (Table 8.4) of the carbon-carbon single, double, and triple bonds to deduce