(e) 
$$\begin{bmatrix} \vdots \ddot{O} \end{bmatrix}^{-} \begin{bmatrix} \ddot{O} & \ddot{O} &$$

$$C \equiv O \qquad \qquad \begin{pmatrix} h \\ \vdots \vdots \vdots \\ \vdots \vdots \vdots \end{pmatrix}^{3^{-}} \qquad \begin{bmatrix} O \\ O - P - O \\ 0 \end{bmatrix}^{3^{-}}$$

# **Extensions**

5. (a) 
$$BCl_{3(g)} + NH_{3(g)} \rightarrow BCl_3NH_3$$
  
(b) :Cl: ... .:Cl: H  
B + H:N:H  $\rightarrow$  :Cl: B:N:H  
:Cl: :Cl: H

6. (a) 
$$\begin{bmatrix} \vdots \\ H : N : H \\ H \end{bmatrix}^{+} \begin{bmatrix} \vdots \vdots \\ \end{bmatrix}^{-}$$

(b) The compound is easy to represent with Lewis structures once you accept the idea of ammonium as a polyatomic positive ion, with nitrogen able to bond four times to hydrogen if an electron is removed.

# 4.2 THE NATURE OF THE CHEMICAL BOND

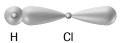
# **PRACTICE**

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# **Understanding Concepts**

- 1. A helium atom has a single orbital containing a pair of electrons. Generally, two half-filled orbitals overlap to form a bond.
- 2. An orbital formed from overlap of two atomic orbitals is like an individual atomic orbital in that it is full when two paired electrons occupy it.
- 3. This overlap is not possible because it would include three electrons occupying one shared orbital.

4. (a)



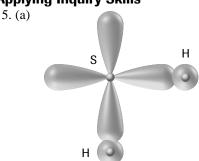
1s and 2p orbitals





2p and 2p orbitals

# **Applying Inquiry Skills**



two 1s and two 2p orbitals

- (b) The angle for the H—S—H bonds is predicted to be  $90^{\circ}$ , since that is the angle between the two p orbitals of the sulfur that are involved in the bonding.
- (c) The prediction is close to the measured angle and therefore inconclusive. The experimental uncertainty of the measured 92° is required to see if the small difference can be explained by the quality of the measurements. If not, then the valence bond theory may require a revision or adjustment.

# **Making Connections**

6. An understanding of covalent bonding allows us to better understand the relationships between properties of substances and their molecular structure. This allows analyses of substances, which is critical in medicine and industry for diagnosing problems, and also allows the prediction and fabrication of new substances with desired properties, like plastics, pharmaceuticals, and alloys.

# **Extension**

7. Molecular orbital theory is an alternative to the valence bond theory for the theoretical description of the bonding in molecules. Both theories use the concept of an orbital and the same rules for filling orbitals with electrons. However, molecular orbital theory constructs orbitals that encompass all of the nuclei in the molecule. (Valence bond theory uses atomic orbitals, such as *s* and *p*, to construct a bonding orbital by an overlap of atomic orbitals.)

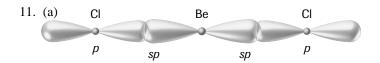
# **PRACTICE**

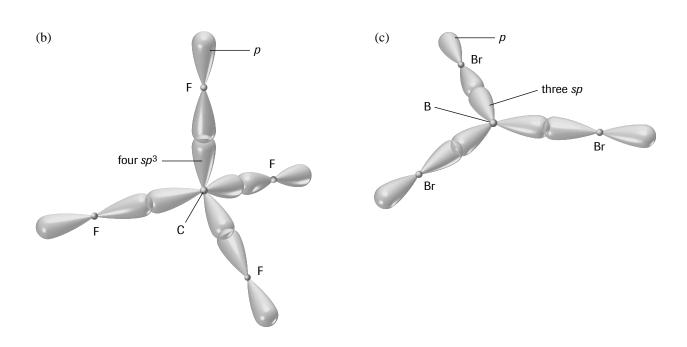
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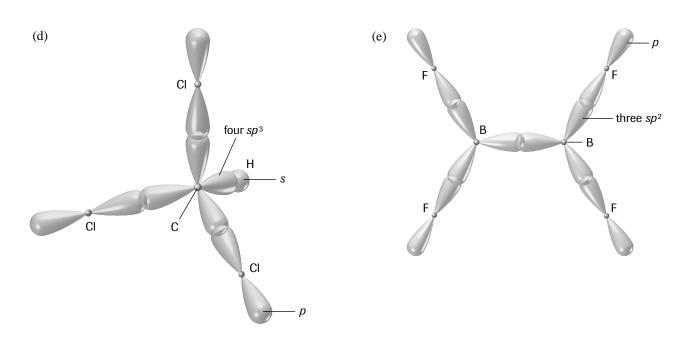
# **Understanding Concepts**

- 8. (a) one 1s orbital
  - (b) one 2p orbital
  - (c) two 3p orbitals
  - (d) one 4p orbital
- 9. Two electrons are present in an orbital formed from overlap.
- 10. (a) ground state— $1s^2 2s^2 2p^2$  promoted state— $1s^2 2s^1 2p^3$  sp<sup>3</sup> hybridization (b) ground state— $1s^2 2s^2 2p^1$  promoted state— $1s^2 2s^1 2p^2$  sp<sup>2</sup> hybridization
  - (c) ground state— $1s^2 2s^2$  promoted state— $1s^2 2s^1 2p^1$  sp hybridization

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- 12. Promoting electrons to higher energy levels uses less energy than is gained by allowing more bonds to form.
- 13. Hybridized orbitals are formed only during bonding—they do not exist in isolated atoms.
- 14. The hybridized orbital concept was necessary to explain the similarity of bonds and the observed bond angles in structures like CH<sub>4</sub>, and to explain the formation of double and triple bonds.

# **Applying Inquiry Skills**

- 15. Two typical examples: Knowledge of empirical formulas preceded and led to the Lewis structure theory, and empirical knowledge of the equivalence of bonding orbitals in carbon preceded and led to the theory of hybridization.
- 16. To determine the hybridization of atomic orbitals in a molecule, we require experimental evidence for the molecular formula, and experimental evidence for the bond angles.

## **Extension**

- 17. (a) PCl<sub>5</sub> requires five hybrid orbitals, and SF<sub>6</sub> requires six, using their valence, from the given formulas for their compounds. Using promotion of electrons in orbital configurations, we obtain the same answer.
  - (b) Using promotion of electrons in orbital configurations: P atom:  $1s^2$   $2s^2$   $2p^6$   $3s^2$   $3p^3$  to  $1s^2$   $2s^2$   $2p^6$   $3s^1$   $3p^3$   $4d^1$  S atom:  $1s^2$   $2s^2$   $2p^6$   $3s^2$   $3p^4$  to  $1s^2$   $2s^2$   $2p^6$   $3s^1$   $3p^3$   $4d^2$
  - (c) Scientists know the directions of hybrid orbitals from the molecular shape, which can be determined by spectroscopy and X-ray diffraction.

## **PRACTICE**

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# **Understanding Concepts**

- 18. Pi bonds are formed by the side-to-side overlap of p orbitals of adjacent atoms.
- 19. The concept of the pi bond was created to explain double and triple bonding between atoms.
- 20. (a)  $C_2Cl_{4(1)}$  molecules have a double bond between the two carbons. Each carbon is  $sp^2$  hybridized, which gives three bonding orbitals in a trigonal planar shape. Two of these  $sp^2$  orbitals form  $\sigma$  bonds with hydrogens, and one with the other carbon. Each carbon also has one more bonding (p) orbital which forms the  $\pi$  bond with the other carbon atom.
  - (b)  $H_2CO_{(g)}$  molecules have a double bond between the carbon and the oxygen. The carbon is  $sp^2$  hybridized, which gives three bonding orbitals in a trigonal planar shape. Two of these  $sp^2$  orbitals form  $\sigma$  bonds with hydrogens, and one with the oxygen. The carbon and the oxygen also each have one more bonding (p) orbital which overlaps side to side to form the  $\pi$  bond.
  - (c)  $CO_{2(g)}$  molecules have double bonds between the carbon and each oxygen. Each carbon is sp hybridized, which gives two bonding orbitals in a linear shape. These two sp orbitals each form  $\sigma$  bonds with an oxygen. The carbon has two more bonding (p) orbitals, and each oxygen has one more bonding (p) orbital; and on each side of the carbon these p orbitals overlap side to side to form the  $\pi$  bond with each oxygen.
- 21. Propene,  $C_3H_{6(g)}$ , has three central carbon atoms bonded in a chain, with a double bond between the first two carbons. Each of these first two carbons is  $sp^2$  hybridized, which gives three bonding orbitals in a trigonal planar shape. On the first carbon, two of these  $sp^2$  orbitals form  $(\sigma)$  bonds with hydrogens, and one  $(\sigma)$  bond with the other carbon. Each of these first two carbons also has one more bonding (p) orbital. These overlap side to side to form the second  $(\pi)$  bond between the carbons. The third carbon is  $sp^3$  hybridized, creating four bonding orbitals in a tetrahedral shape. One of these forms a  $(\sigma)$  bond with the second carbon, and the other three form  $(\sigma)$  bonds with hydrogens.

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# Applying Inquiry Skills 22. H H H 23. (a) H H

- 23. (a) H C = C = C H
  - (b) Propadiene,  $C_3H_{4(g)}$ , has three central carbon atoms bonded in a chain, with double bonds between the carbons. Each of the end two carbons is  $sp^2$  hybridized, which gives three bonding orbitals in a trigonal planar shape. On each end carbon, two of these  $sp^2$  orbitals form  $(\sigma)$  bonds with hydrogens, and one  $(\sigma)$  bond with the middle carbon. Each of these first two carbons also has one more bonding (p) orbital. The middle carbon is sp hybridized, creating two bonding orbitals in a linear shape, which form the  $(\sigma)$  bond with the end carbons. This middle carbon also has two more (p) bonding orbitals. These (p) orbitals overlap side to side to form the second  $(\pi)$  bond between the middle and (each) end carbon.
  - (c) The shape around the end carbon atoms is trigonal planar.

# **Extension**

- 24. (a) Each carbon atom is joined (bonded) to three others.
  - (b) Three bonds for each carbon atom suggest that each carbon is  $sp^2$  hybridized, forming sigma bonds with the three closest other carbons and a pi bond between two of these carbon atoms.
  - (c) Even if we ignore any differences in bond angles between the pentagons and hexagons, the explanation in (b) still cannot be correct. A carbon with  $sp^2$  hybridization would have two single bonds and one double bond. These bonds would not be the same. Therefore, the explanation in (b) is not acceptable.

(The bonds are neither single nor double, if they must all be identical. The electrons in the *p* orbital (that would form a pi bond) are delocalized, meaning all of them are equally shared among all the carbon atoms in each ring. This is similar in concept to the bonding in a benzene ring.)

## **PRACTICE**

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# **Understanding Concepts**

25. The concept of triple bonding was created to explain the properties of compounds like C<sub>2</sub>H<sub>2(g)</sub>.

- 26. (a) C<sub>2</sub>F<sub>2(g)</sub> has molecules that have triple bonds between carbon atoms that have *sp* hybridization, which forms two orbitals on opposite sides of the nucleus, giving a linear shape. Each carbon forms a sigma bond with a fluorine, and a sigma bond and two pi bonds with the other carbon.
  - (b) HCN<sub>(g)</sub> has molecules that have triple bonds between the carbon and the nitrogen. The carbon atom has *sp* hybridization, which forms two orbitals on opposite sides of the nucleus, giving a linear shape. The carbon forms a sigma bond with the hydrogen, and a sigma bond and two pi bonds with the nitrogen.
- 27. Propyne has three central carbon atoms bonded in a chain, with a triple bond between the first two carbons. Each of the first two carbons is sp hybridized, which gives two bonding orbitals in a linear shape. On the first carbon, one of these sp orbitals forms a sigma bond with a hydrogen, and one sigma bond with the middle carbon. Each of these first two carbons also has two more bonding (p) orbitals. These p orbitals overlap side to side to form the two pi bonds. The third carbon is  $sp^3$  hybridized, creating four bonding orbitals in a tetrahedral shape, which form sigma bonds with the second carbon and three hydrogens.
- 28. Quadruple bonds are not likely for a carbon atom because  $sp^3$  hybridization would only allow three orbitals to overlap—the other orbital would be on the opposite sides of the atoms. As well, with  $sp^2$  hybridization, at least one of the  $sp^2$  orbitals would be on the opposite sides of the atoms, and with sp hybridization, one of the sp orbitals would have to be on the opposite sides of the atoms. If we assume no hybridization, the s orbitals could not likely get close enough to overlap because there would be a p orbital in the same direction, extending much farther out.

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# **Applying Inquiry Skills**

# 29. Hypothesis

(a) One might logically hypothesize that double bonds should be longer and stronger than single bonds, and triple bonds longer and stronger yet, because more electron orbital density is between the nuclei. More electron density might make the bonds longer with more space required for more electrons but make the bond stronger because there is more electrostatic attraction of electrons and nuclei.

# **Analysis**

(b) According to the evidence provided, the order of bond length, from shortest to longest is triple, double, and then single bonds. The order of bond strength, from weakest to strongest is single, double, and then triple bonds. Single bonds are the longest but the weakest, and triple bonds are the shortest but the strongest.

## **Evaluation**

(c) The hypothesis is verified for bond strength, but not for bond length. The reasoning based on electron density appears acceptable for bond strength but does not appear correct for bond lengths. (Note that the reasoning did not take into account the shapes and directions of the *p* orbitals forming the pi bonds.)

# **Making Connections**

- 30. (Student reports should contain the following information.)
  - (a) Infrared spectroscopy is based on the frequencies absorbed by the internal vibrations of molecules—that is, the vibration of atoms on either side of a bond.
  - (b) Each type of bond has a specific vibrational frequency which varies slightly depending on the other atoms in the molecule. Therefore, a unique compound has a unique set of frequencies that it will absorb which allow it to be uniquely identified.
  - (c) This technique is used in analysis in medical, pharmaceutical, sports, and industrial chemical laboratories, to name a few.

## CASE STUDY: THE STRANGE CASE OF BENZENE

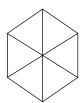
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- (d) Benzene is found in coal tar and also in the combustion products of natural materials. Technologically, benzene is produced by the catalytic re-forming of petroleum and is also made from toluene ( $C_6H_5CH_3$ , or methylbenzene).
- (e) More than half of all benzene is used to produce styrene (phenylethene or vinyl benzene) which is the monomer for the plastic polystyrene. Benzene is also used to make detergents, pharmaceuticals, pesticides, and explosives.
- (f) Couper and Loschmidt proposed the following non-cyclic structure but could not provide any empirical support.

• Ladenburg tried to explain the chemical reactivity of benzene by proposing a prism-type structure.



 Clause also tried to explain the properties of benzene using a hexagon of carbon atoms with diagonal bonds between opposite carbon atoms.



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