

Unit 7 includes the following OpenStax Sections

- 7.1 Ionic Bonding
- 7.2 Covalent Bonding
- 7.3 Lewis Symbols and Structures
- 7.4 Formal Charges and Resonance
- 7.5 Strengths of Ionic and Covalent Bonds
- 7.6 Molecular Structure and Polarity
- 8.1 Valence Bond Theory
- 8.2 Hybrid Atomic Orbitals
- 8.3 Multiple Bonds
- 8.4 Molecular Orbital Theory

Figure 7.1



Nicknamed “buckyballs,” buckminsterfullerene molecules (C_{60}) contain only carbon atoms. Here they are shown in a ball-and-stick model (left). These molecules have single and double carbon-carbon bonds arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (center). This unconventional molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit middle: modification of work by “Petey21”/Wikimedia Commons; credit right: modification of work by Bill Morrow)

Learning Objectives

- 7.1 Ionic Bonding
 - Explain the formation of cations, anions, and ionic compounds
 - Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

Figure 7.2



(a)



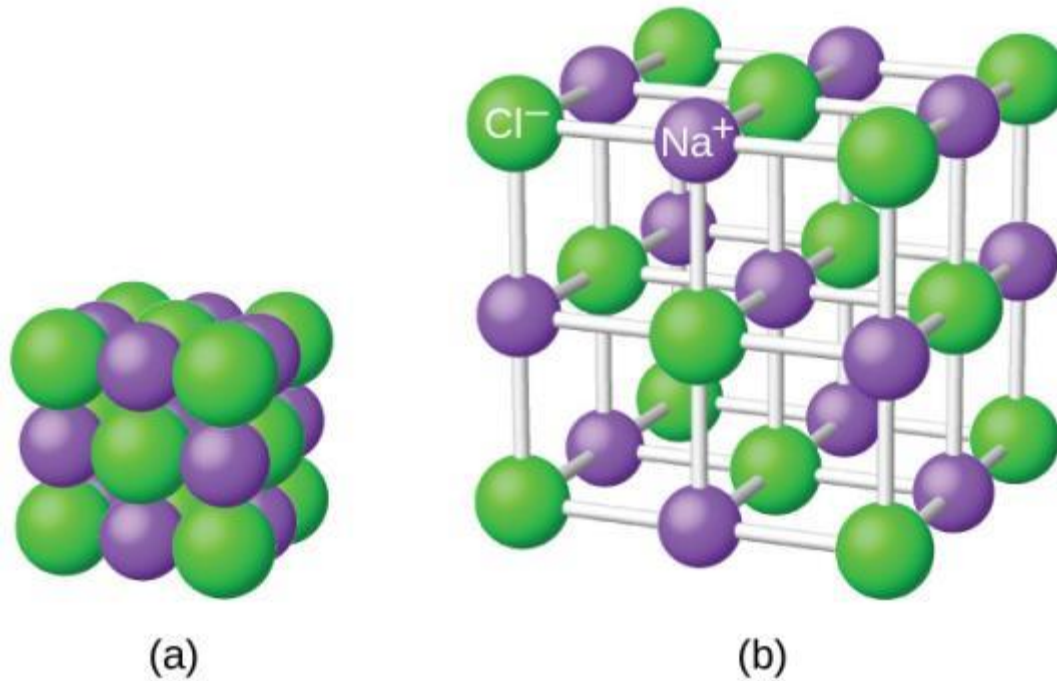
(b)



(c)

(a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by “Jurii”/Wikimedia Commons)

Figure 7.3

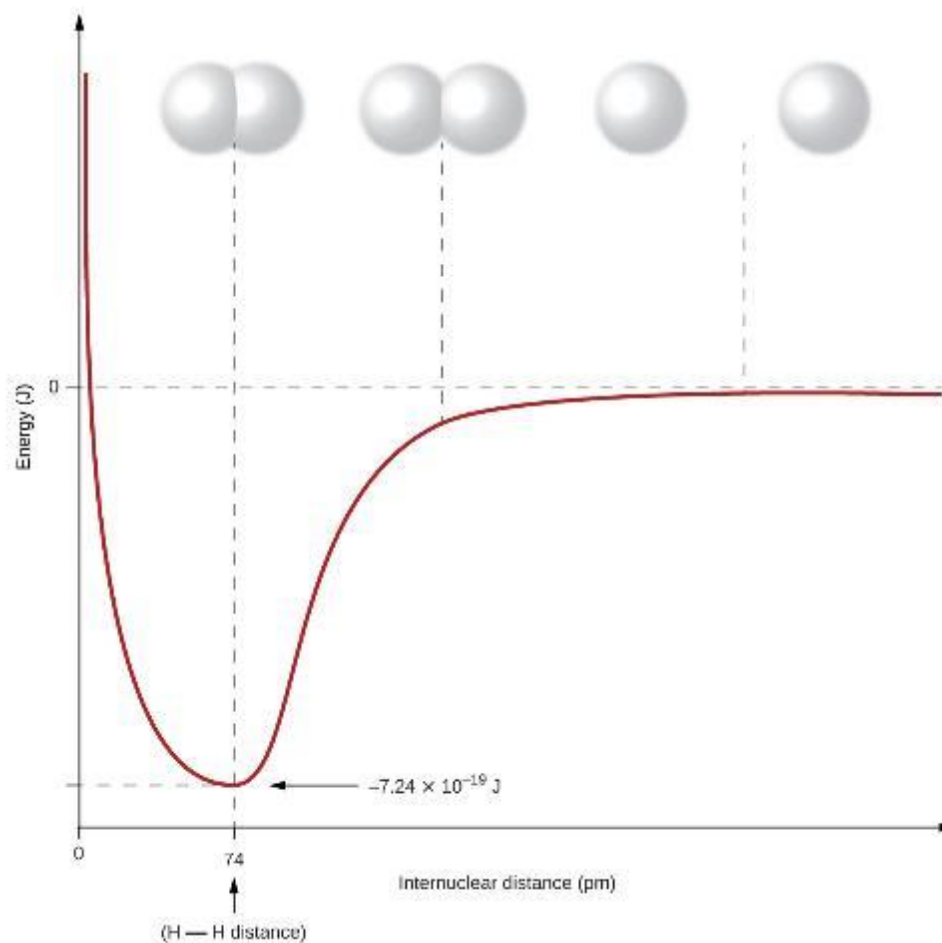


The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is “bonded” to all of the surrounding ions—six in this case.

Learning Objectives

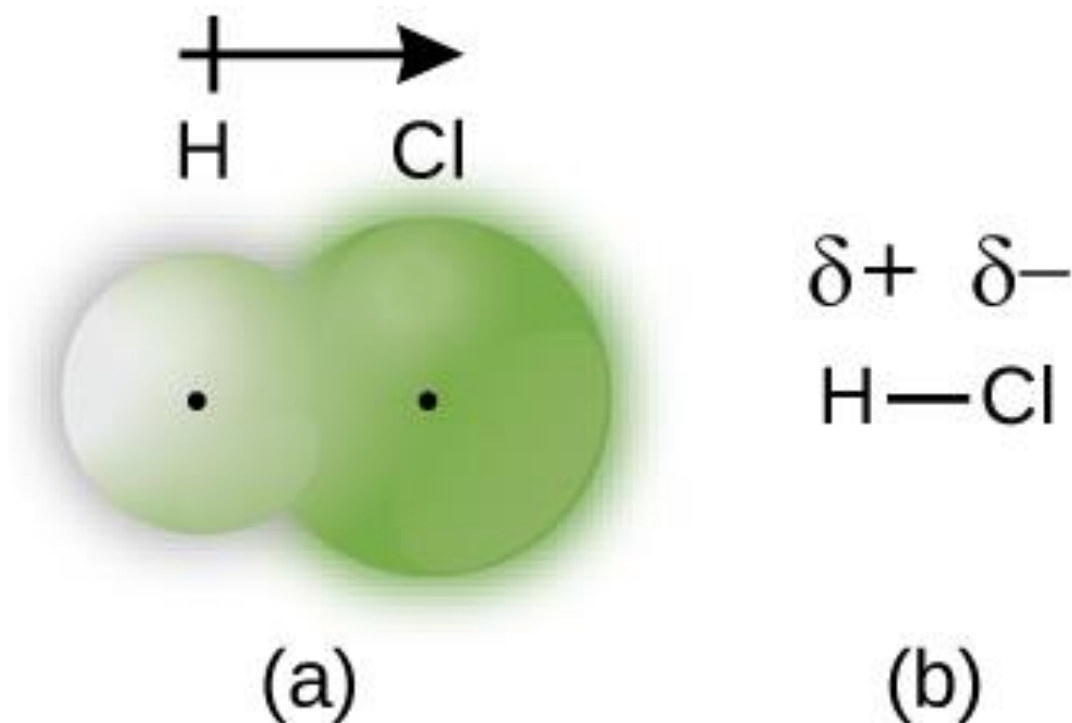
- 7.2 Covalent Bonding
 - Describe the formation of covalent bonds
 - Define electronegativity and assess the polarity of covalent bonds

Figure 7.4



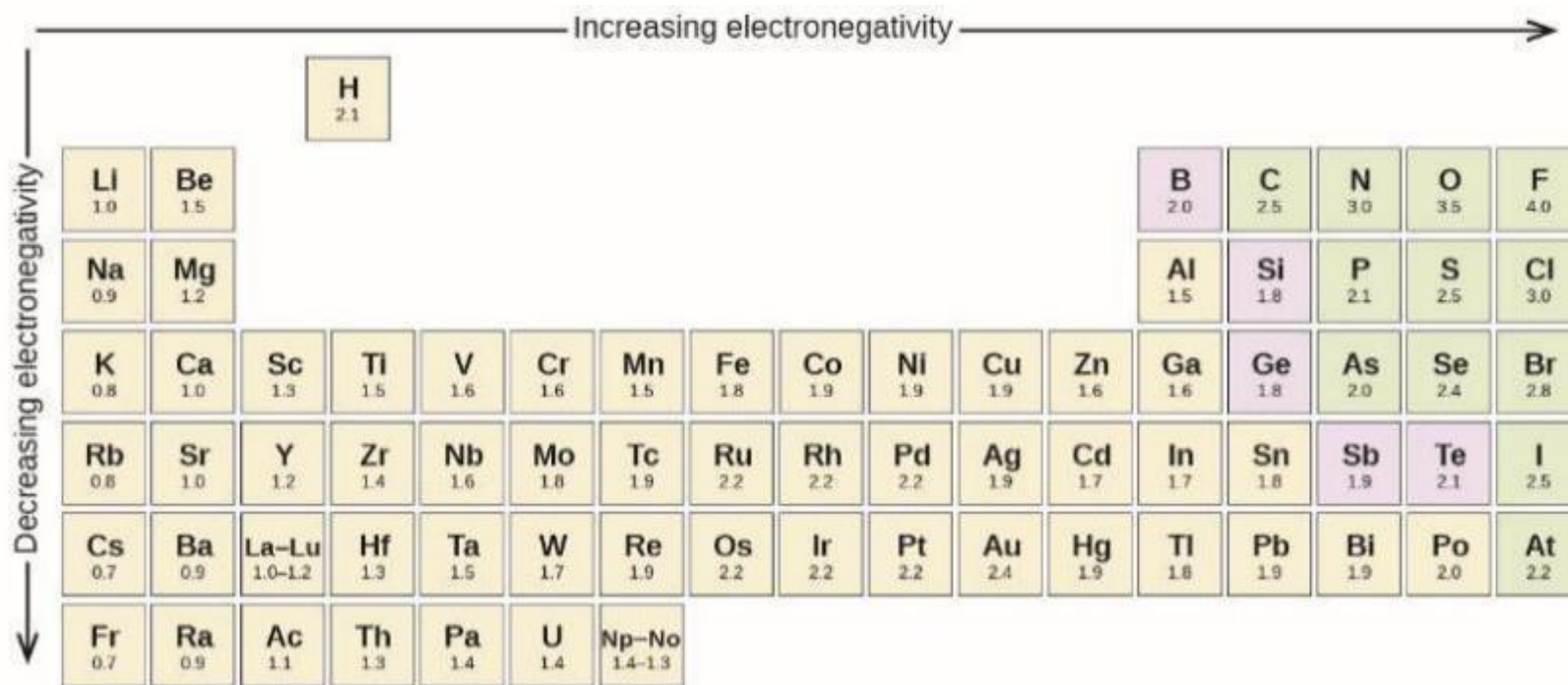
The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

Figure 7.5



(a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols $\delta+$ and $\delta-$ indicate the polarity of the H-Cl bond.

Figure 7.6



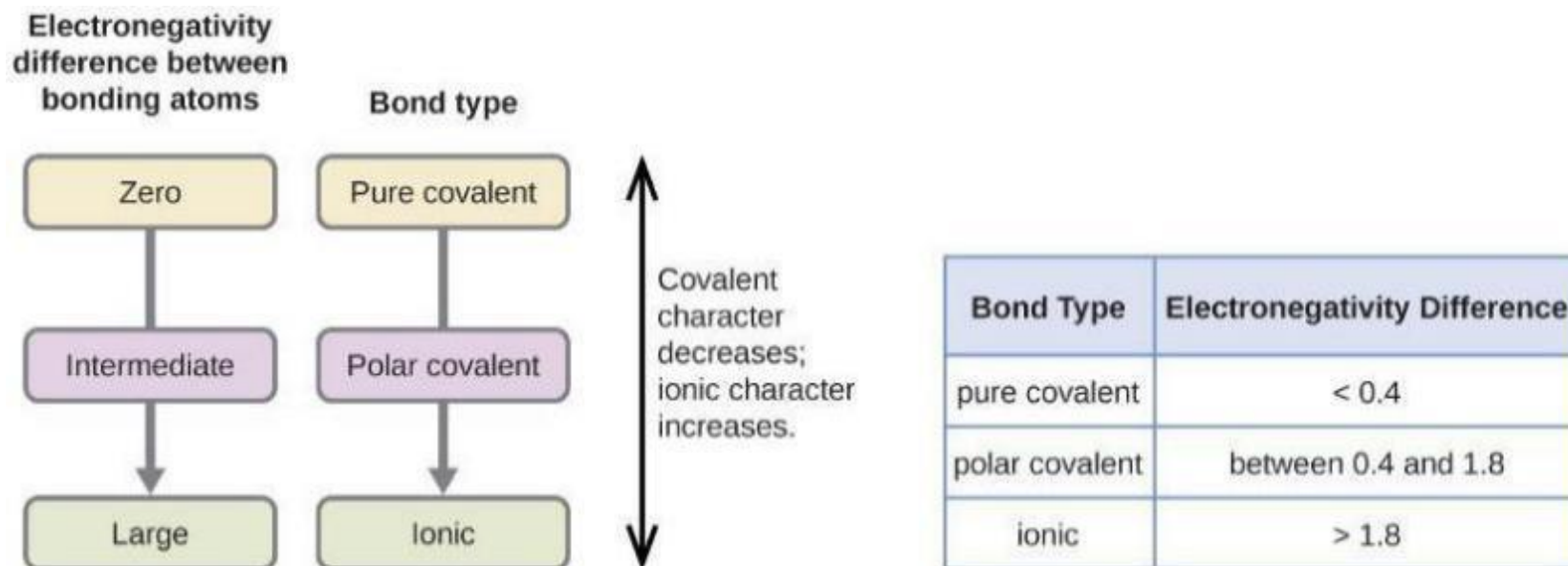
The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Figure 7.7



Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Figure 7.8



As the electronegativity difference increases between two atoms, the bond becomes more ionic.

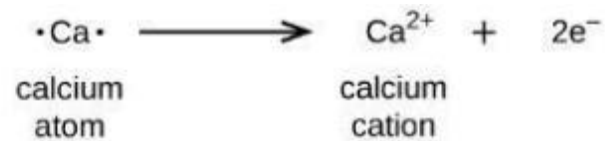
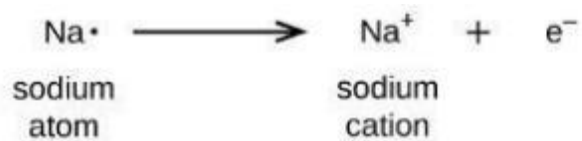
Learning Objectives

- 7.3 Lewis Symbols and Structures
 - Write Lewis symbols for neutral atoms and ions
 - Draw Lewis structures depicting the bonding in simple molecules

Figure 7.9

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[\text{Ne}]3s^1$	Na •
magnesium	$[\text{Ne}]3s^2$	•Mg•
aluminum	$[\text{Ne}]3s^23p^1$	•Al•
silicon	$[\text{Ne}]3s^23p^2$	•Si•
phosphorus	$[\text{Ne}]3s^23p^3$	•P•
sulfur	$[\text{Ne}]3s^23p^4$	•S•
chlorine	$[\text{Ne}]3s^23p^5$	•Cl•
argon	$[\text{Ne}]3s^23p^6$	•Ar•

Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.



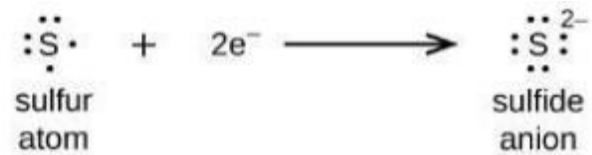
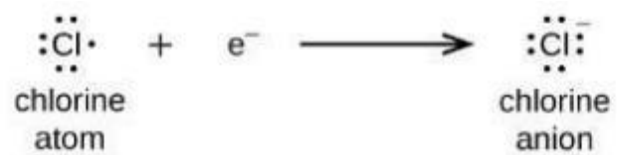


Figure 7.10

Metal		Nonmetal		Ionic Compound
$\text{Na} \cdot$ sodium atom	+	$:\ddot{\text{Cl}}\cdot$ chlorine atom	→	$\text{Na}^+ \left[:\ddot{\text{Cl}}: \right]^-$ sodium chloride (sodium ion and chloride ion)
$\cdot\text{Mg}\cdot$ magnesium atom	+	$:\ddot{\text{O}}\cdot$ oxygen atom	→	$\text{Mg}^{2+} \left[:\ddot{\text{O}}: \right]^{2-}$ magnesium oxide (magnesium ion and oxide ion)
$\cdot\text{Ca}\cdot$ calcium atom	+	$2 : \ddot{\text{F}} \cdot$ fluorine atoms	→	$\text{Ca}^{2+} \left[:\ddot{\text{F}}: \right]_2^-$ calcium fluoride (calcium ion and two fluoride ions)

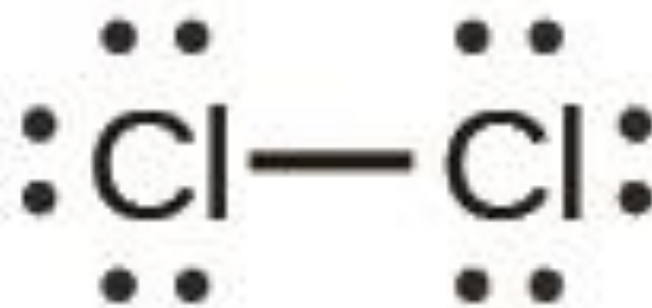
Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

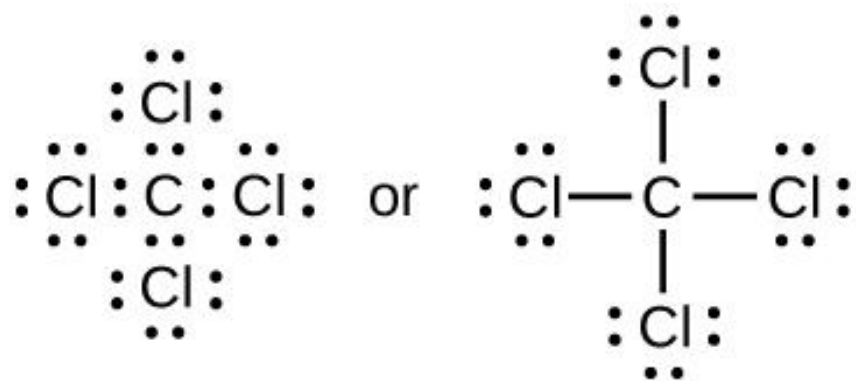


chlorine
atoms

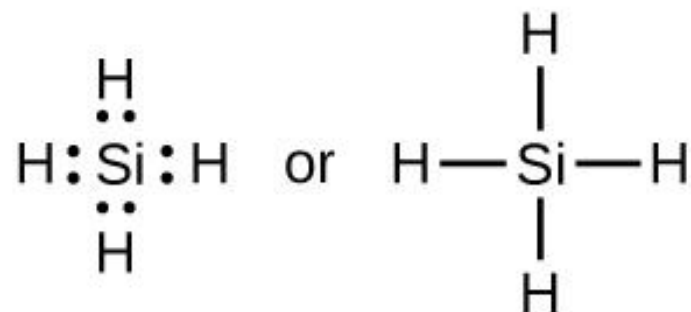


chlorine
molecule

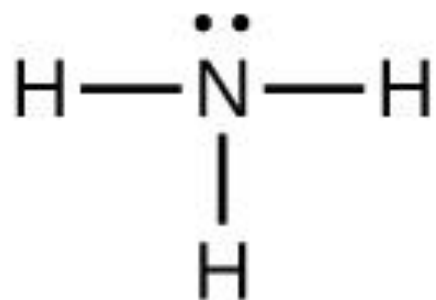




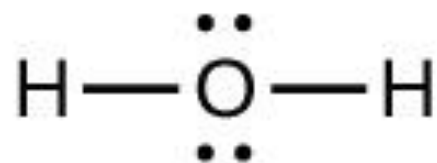
carbon tetrachloride



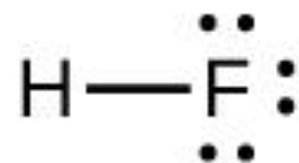
silane



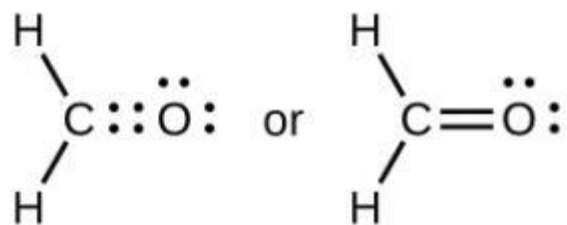
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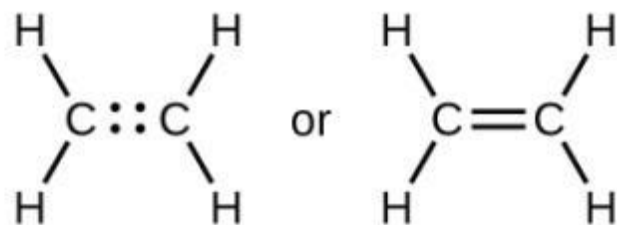
Water



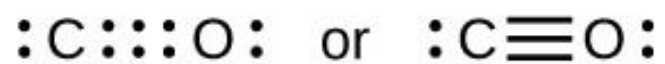
hydrogen
fluoride



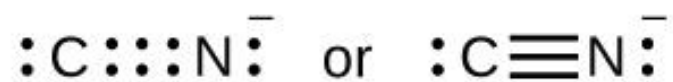
formaldehyde



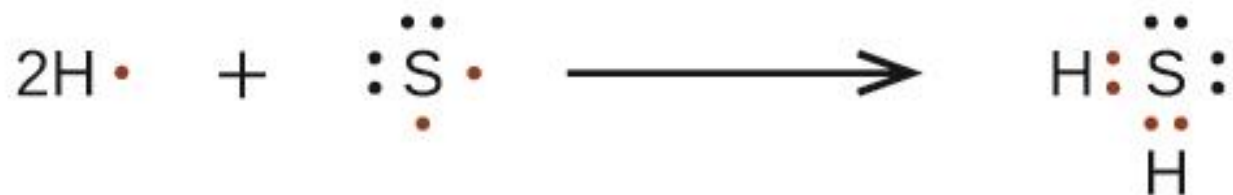
ethylene

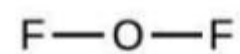
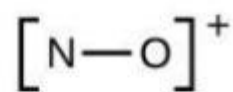
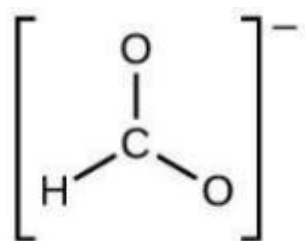
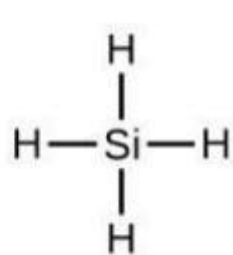


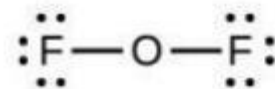
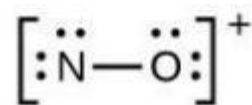
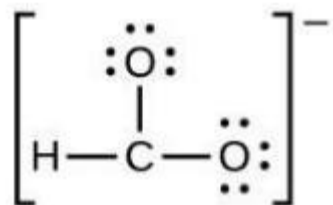
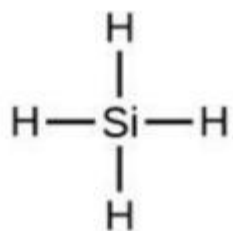
carbon monoxide



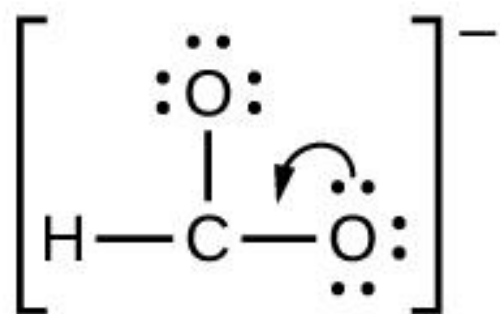
cyanide ion



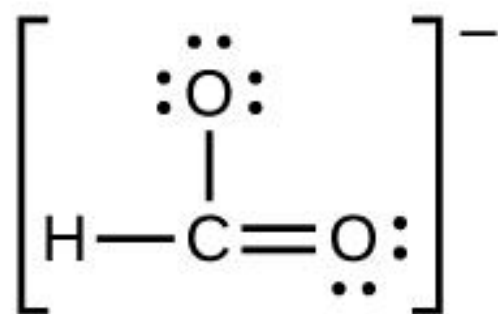


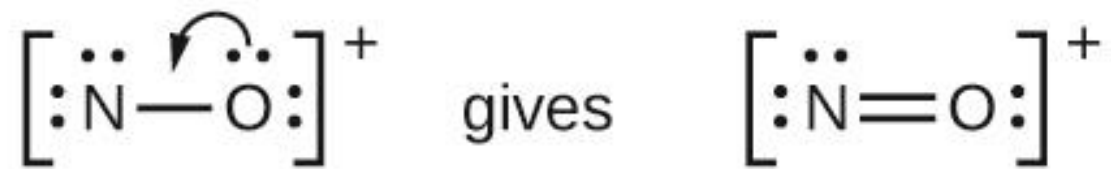


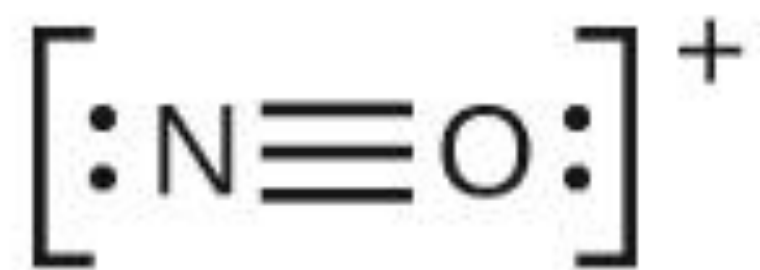




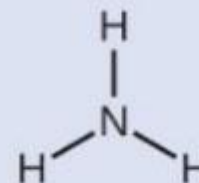
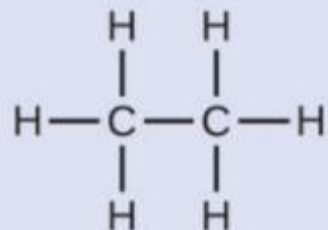
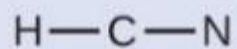
gives



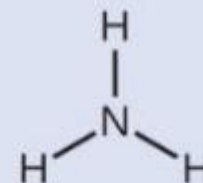
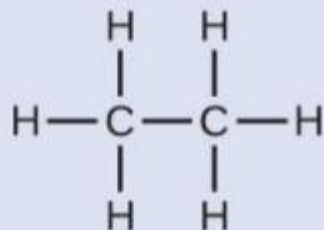
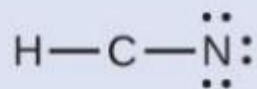




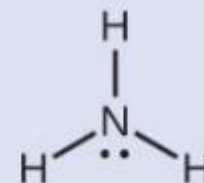
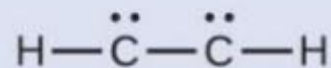
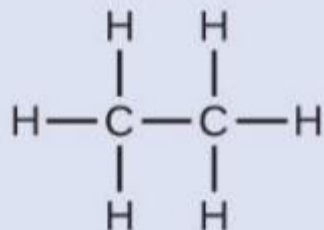
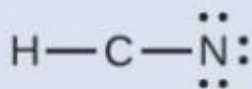
Example 7.4



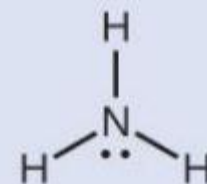
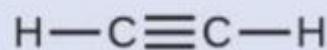
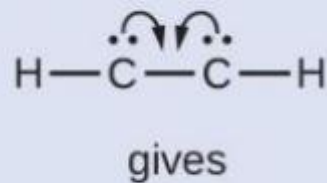
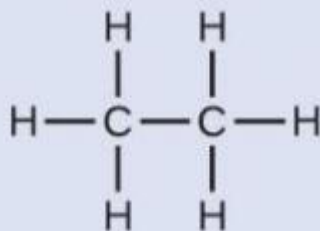
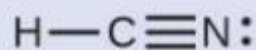
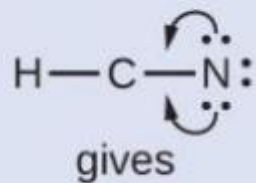
Example 7.4



Example 7.4



Example 7.4



Example 7.4

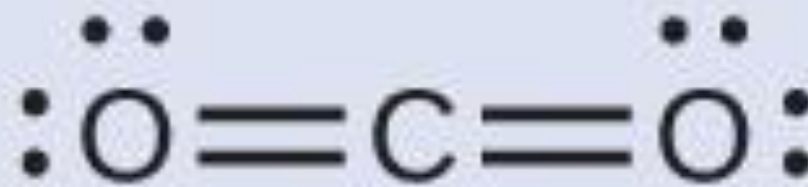
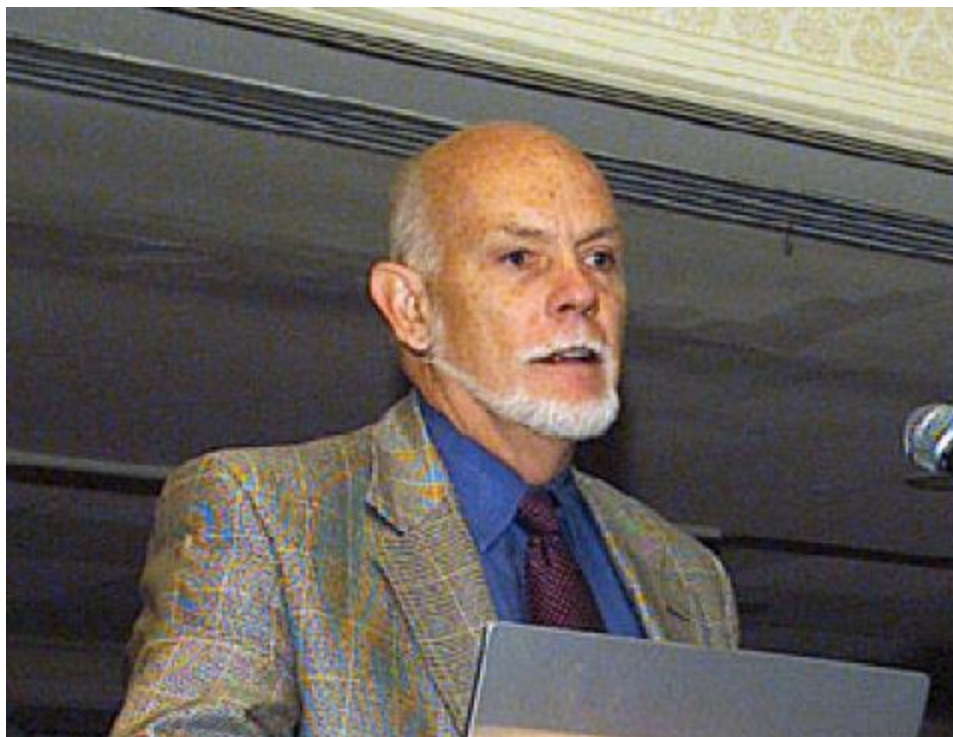
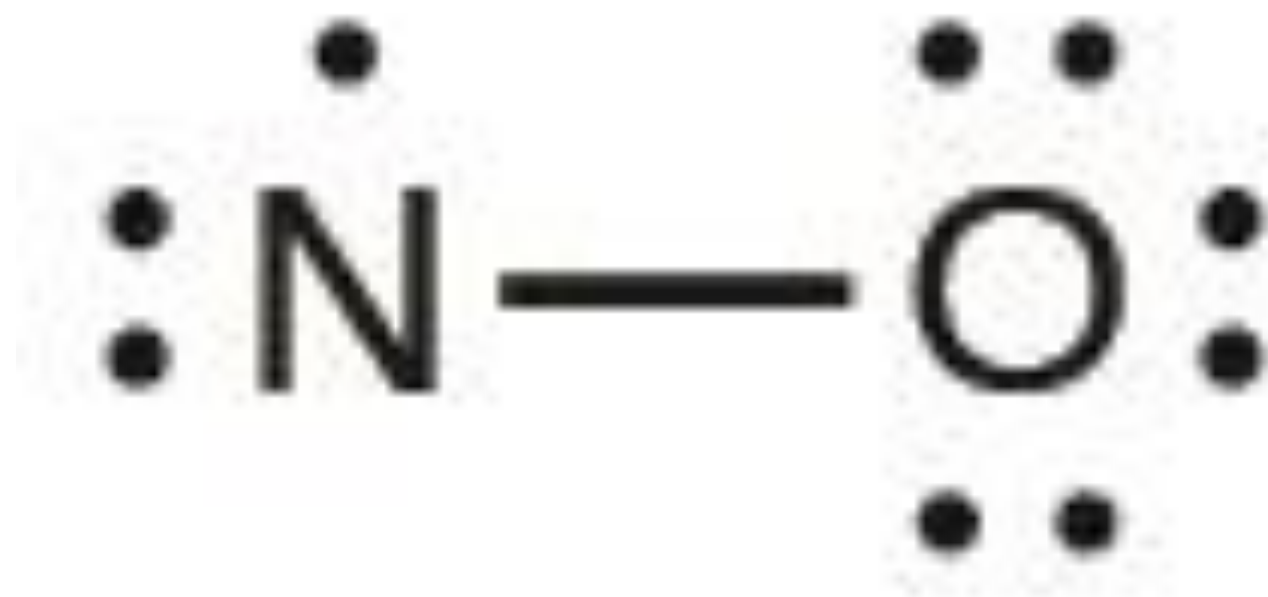


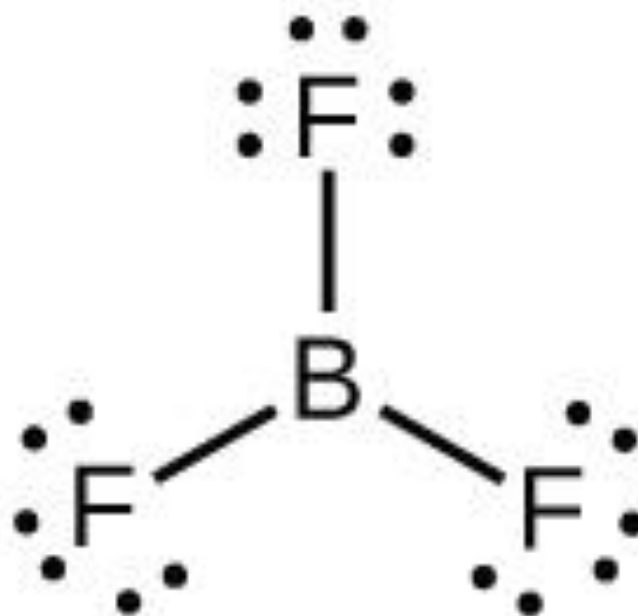
Figure 7.11



Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the “Father of Nanotechnology.” (credit: United States Department of Energy)







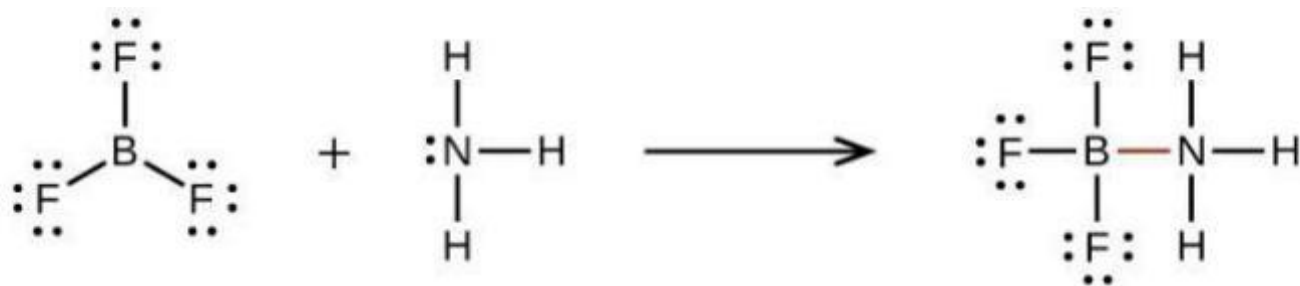
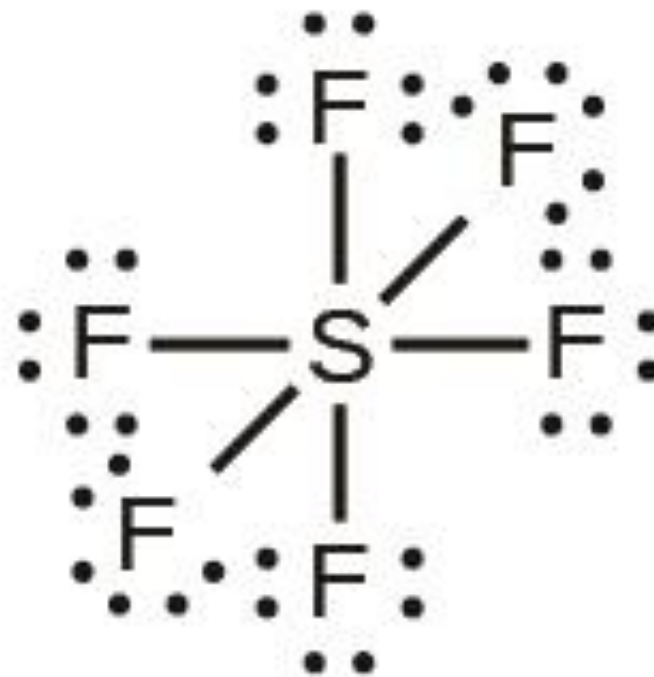
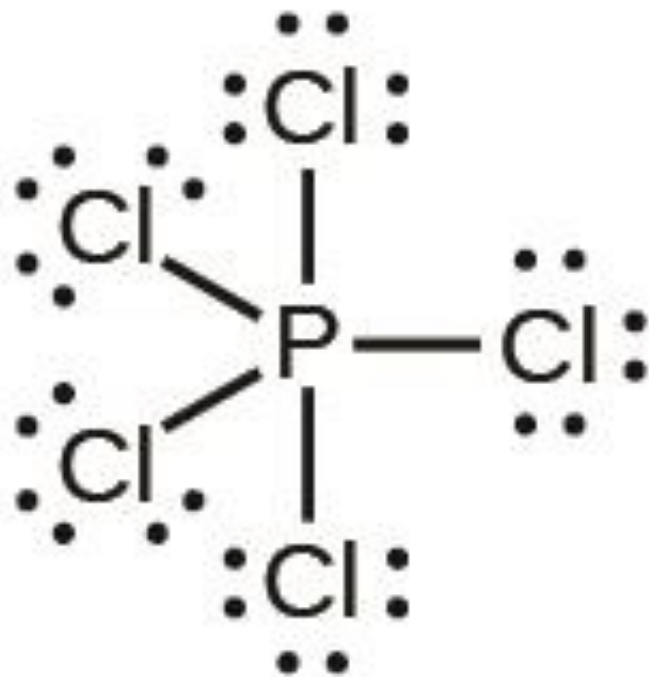
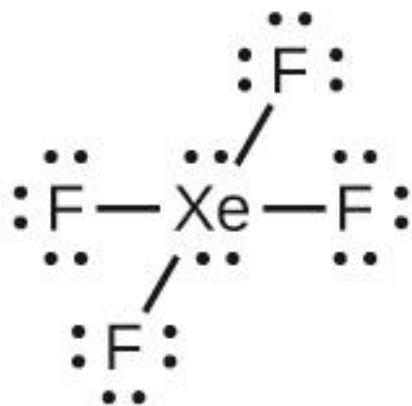
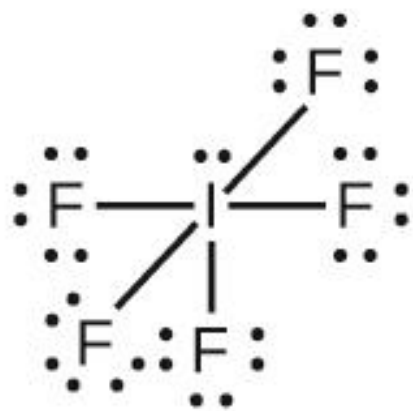


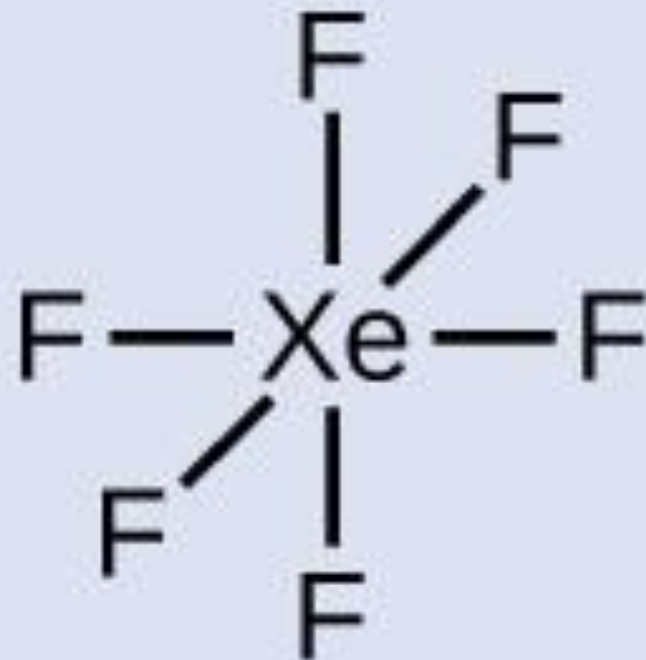
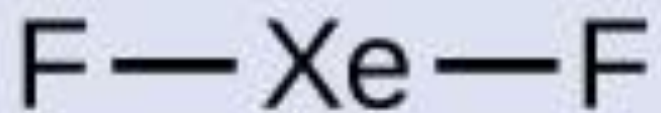
Figure 7.12



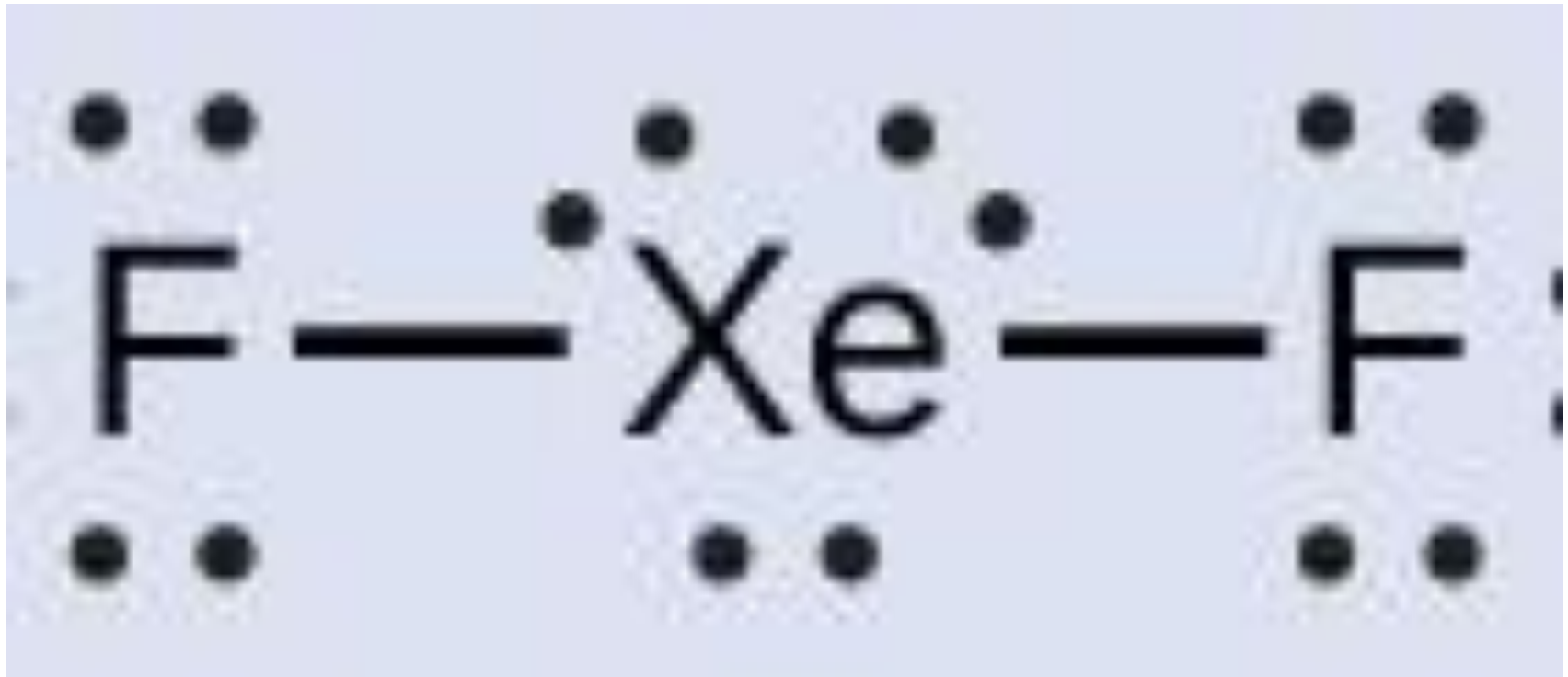
In PCl₅, the central atom phosphorus shares five pairs of electrons. In SF₆, sulfur shares six pairs of electrons.



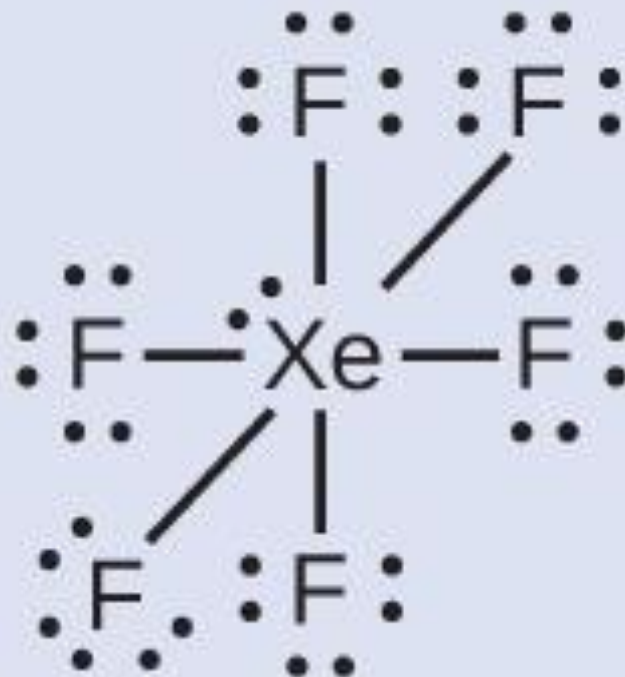
Example 7.5



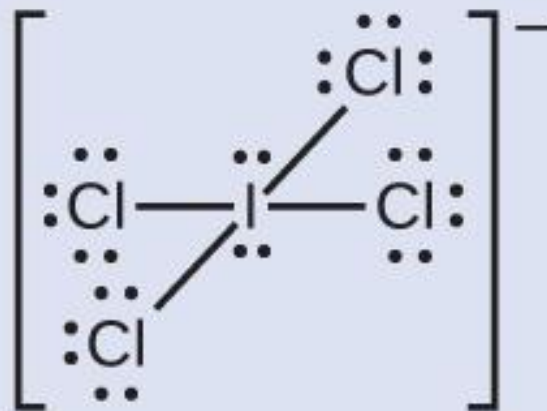
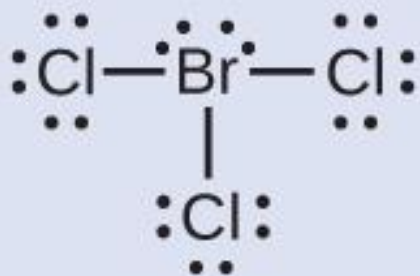
Example 7.5



Example 7.5



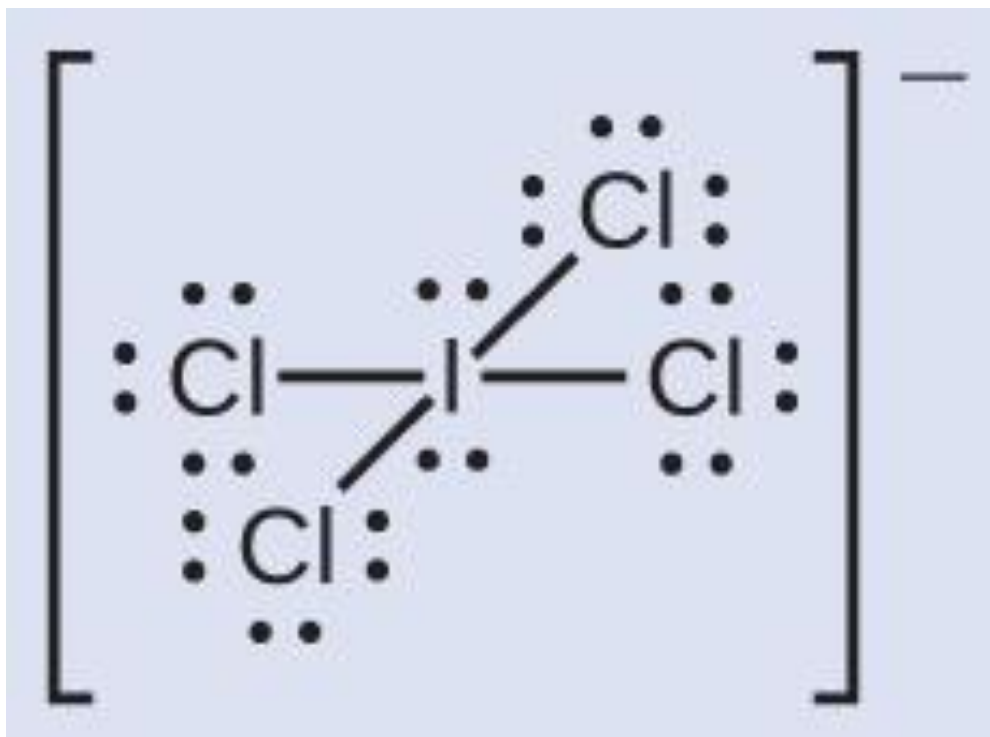
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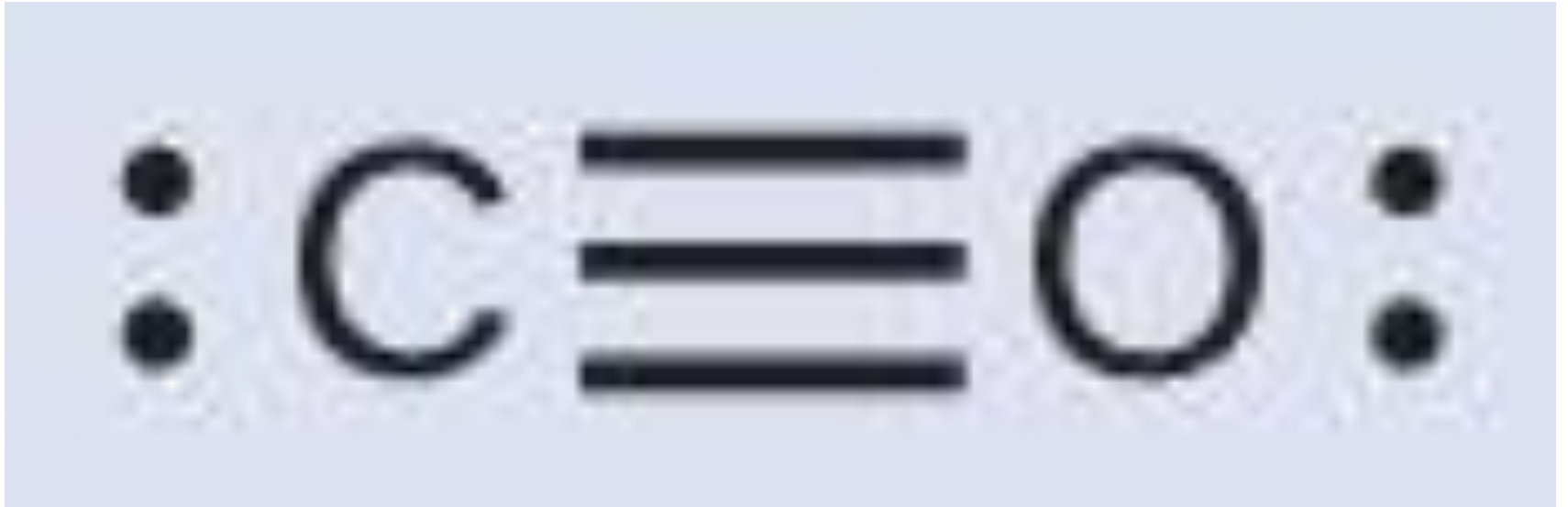
Learning Objectives

- 7.4 Formal Charges and Resonance
 - Compute formal charges for atoms in any Lewis structure
 - Use formal charges to identify the most reasonable Lewis structure for a given molecule
 - Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

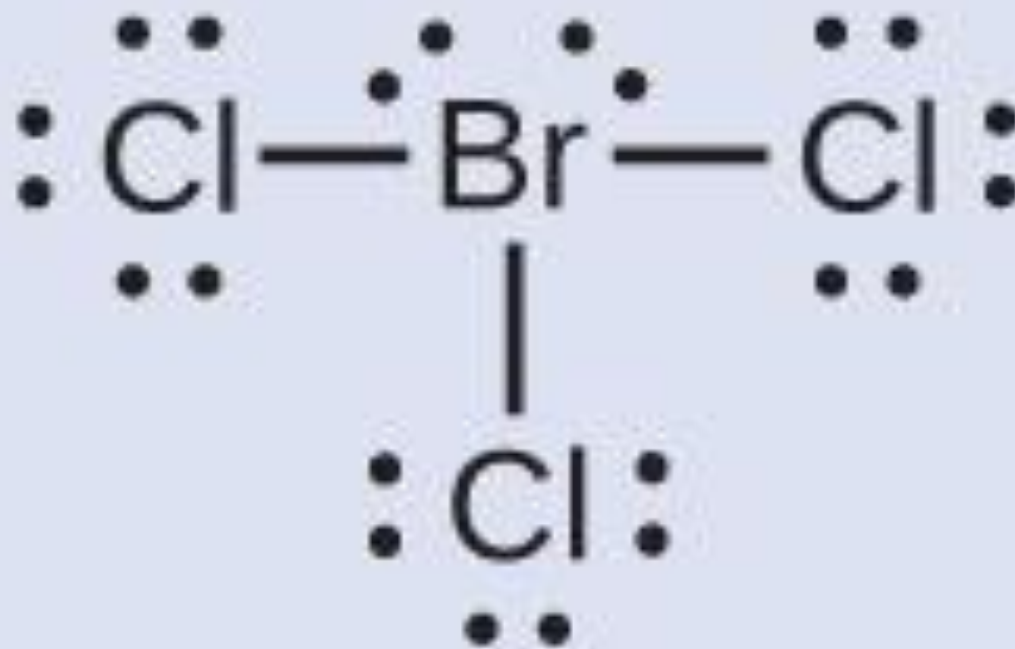
Example 7.6



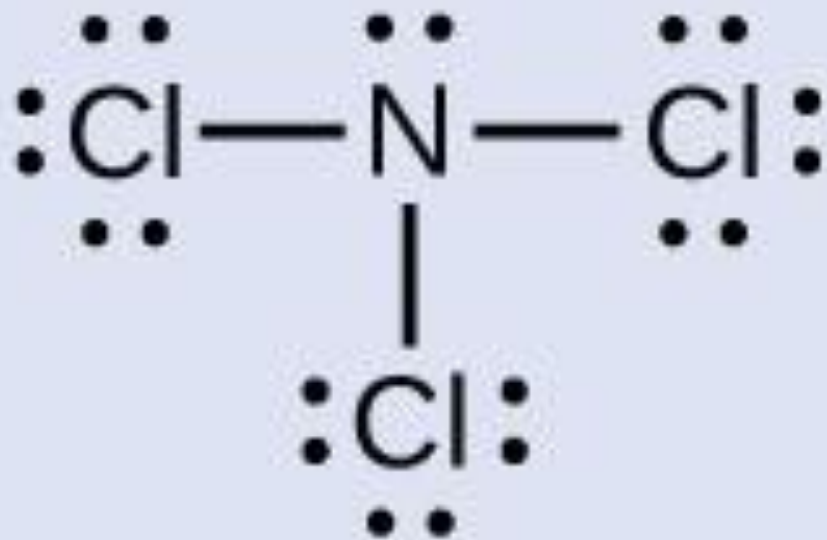
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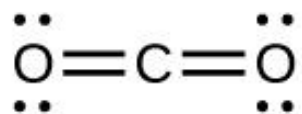


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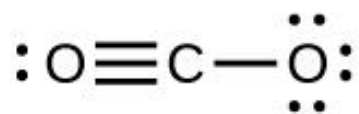


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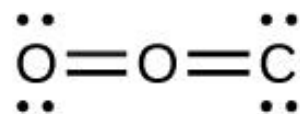




0 0 0



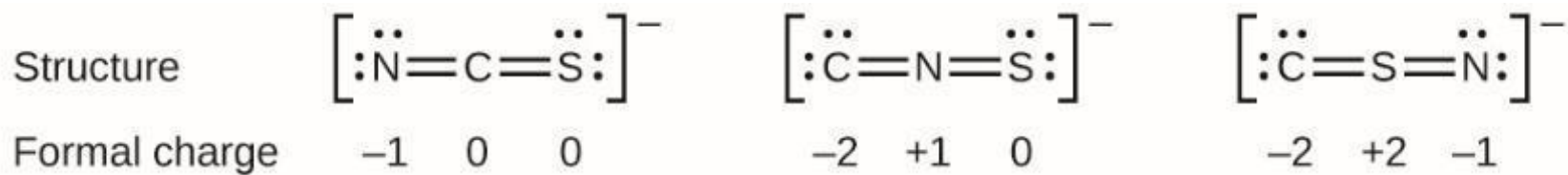
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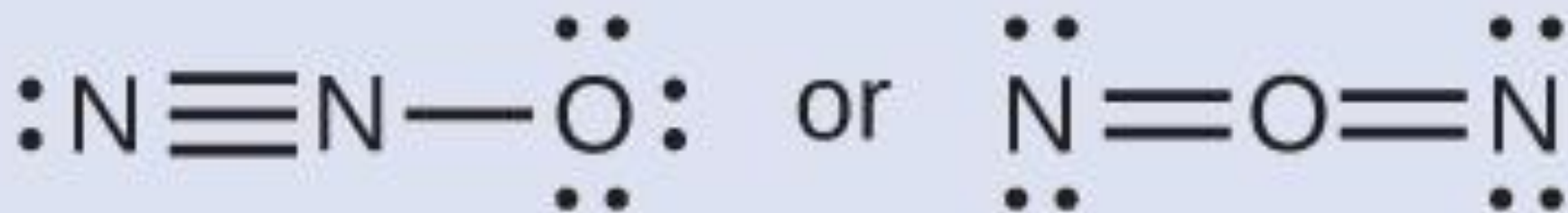
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Structure

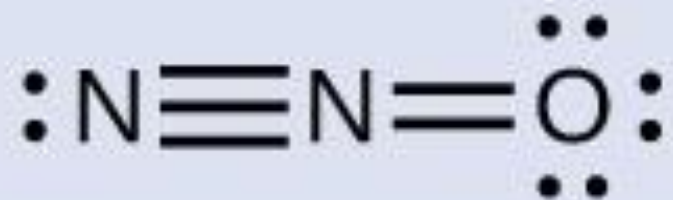
Formal charge



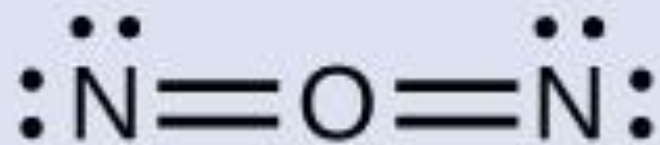
Example 7.8



Example 7.8

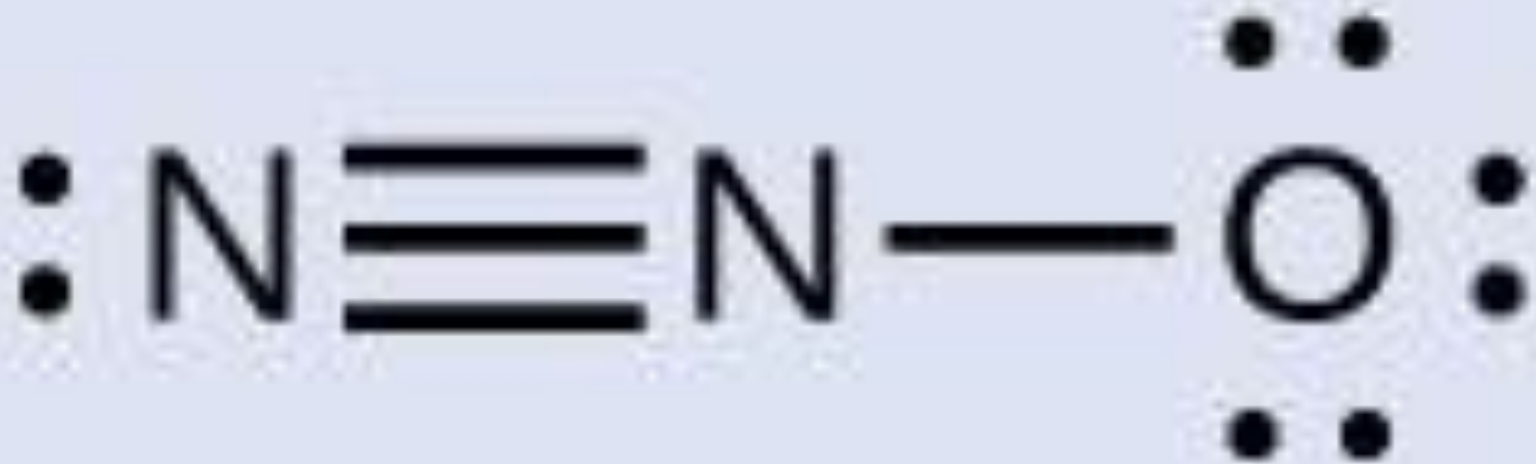


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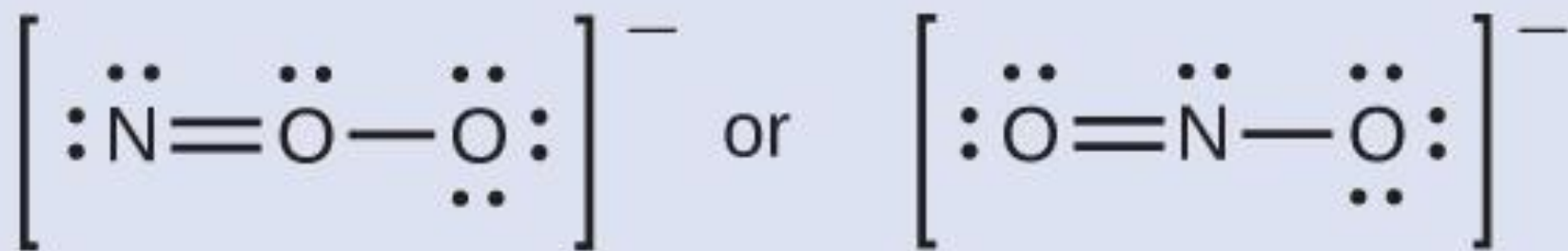


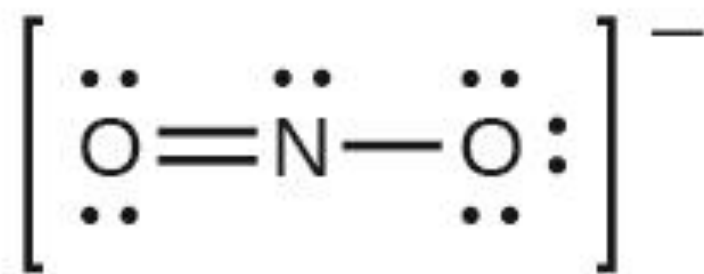
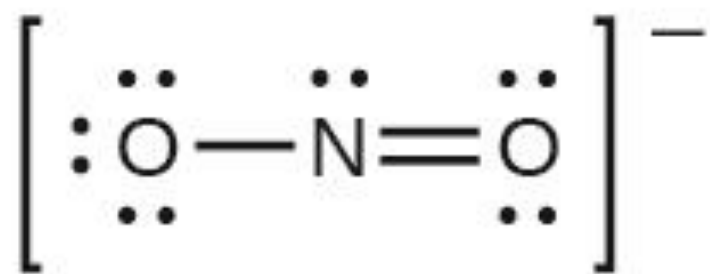
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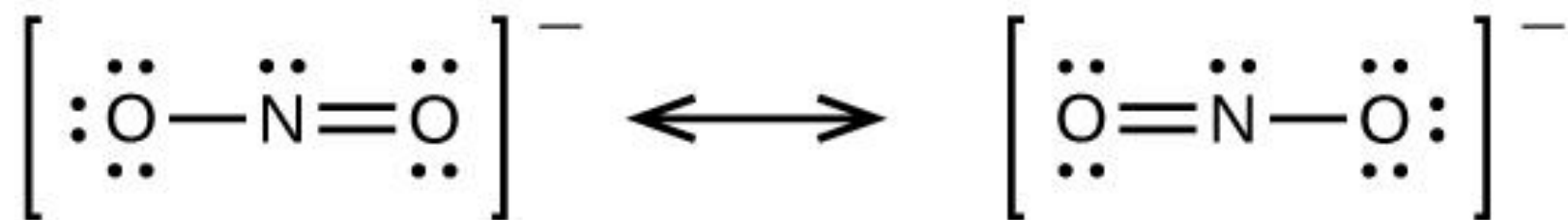
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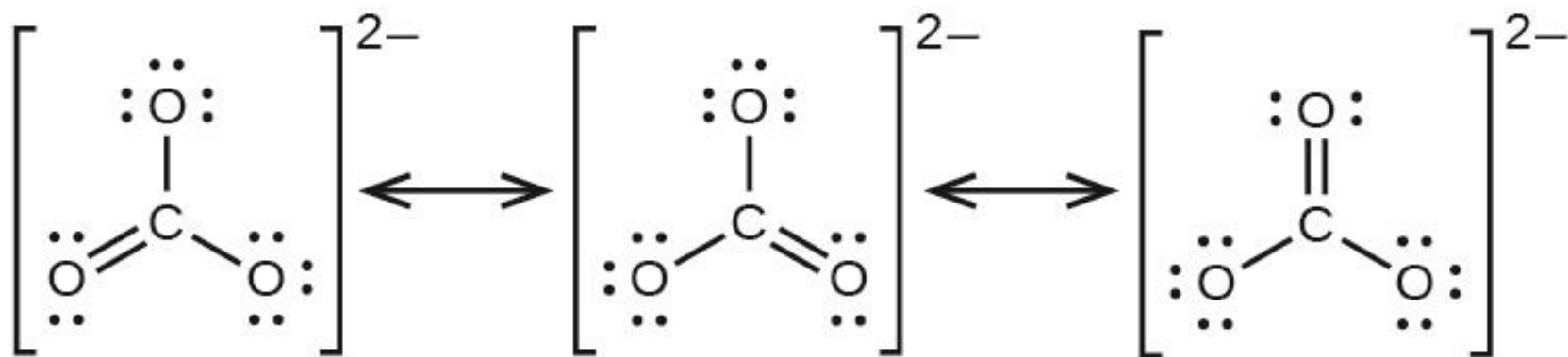


Example 7.8



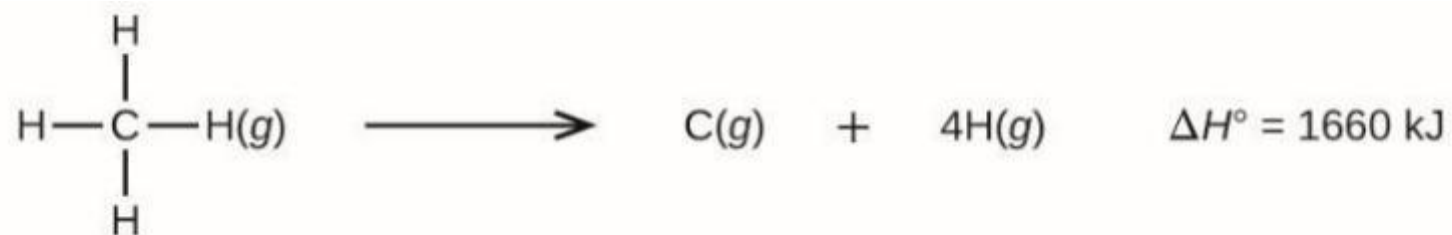




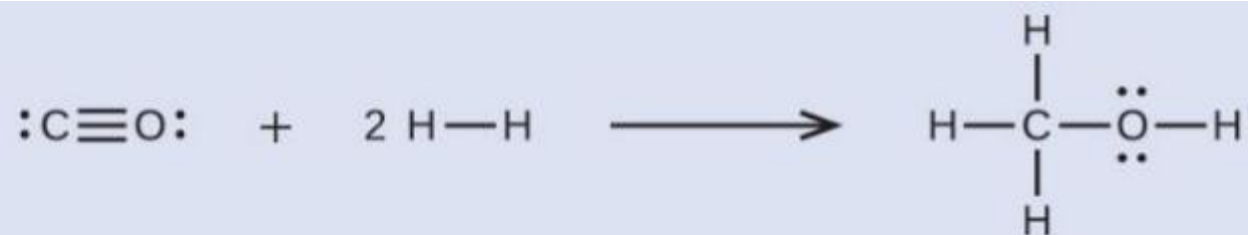


Learning Objectives

- 7.5 Strengths of Ionic and Covalent Bonds
 - Describe the energetics of covalent and ionic bond formation and breakage
 - Use the Born-Haber cycle to compute lattice energies for ionic compounds
 - Use average covalent bond energies to estimate enthalpies of reaction



Example 7.9



Example 7.9

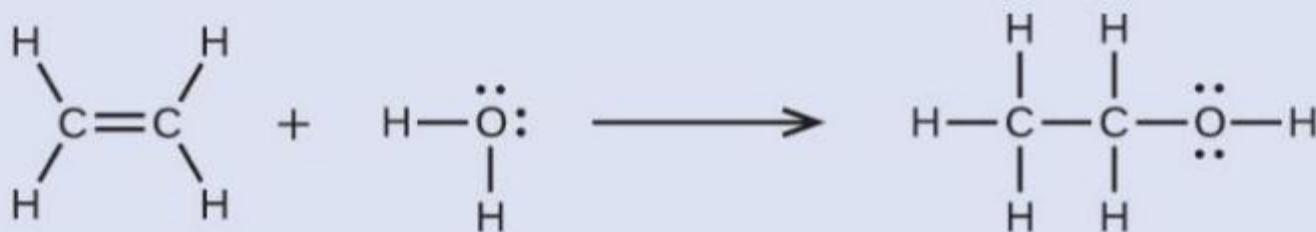
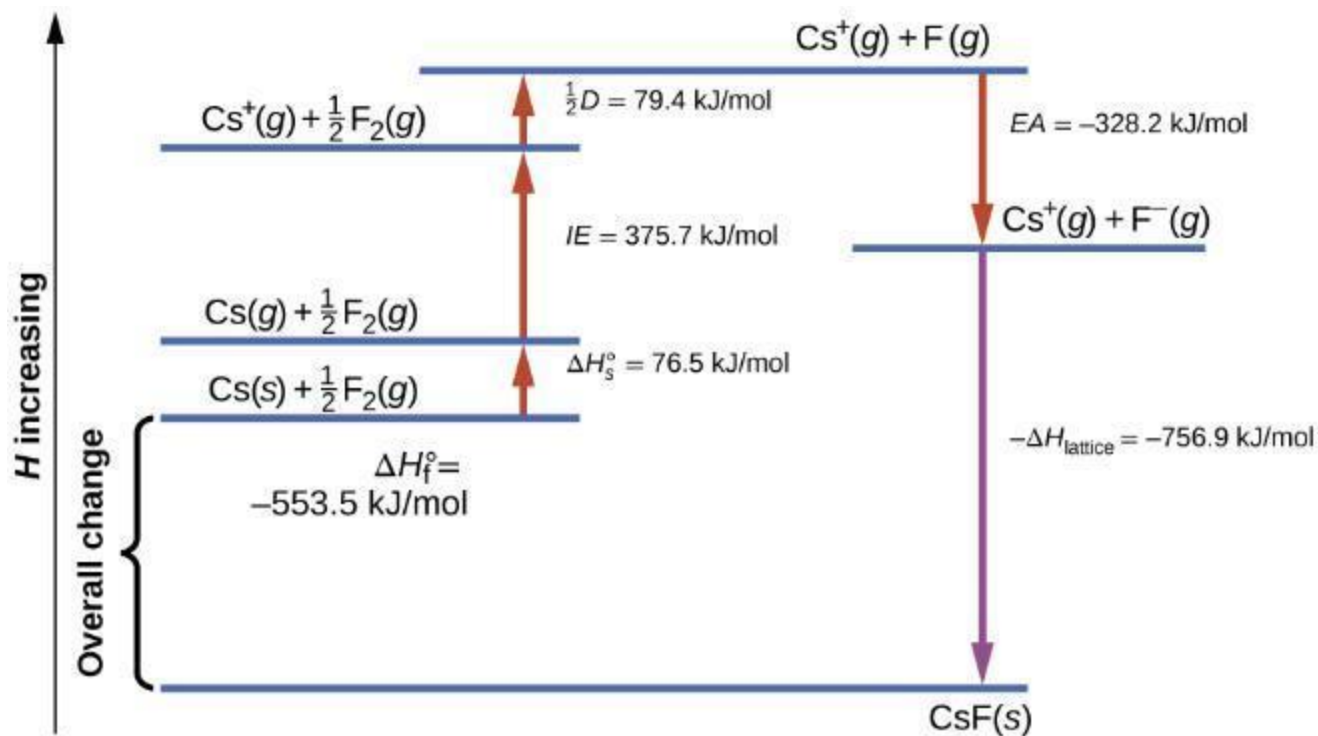


Figure 7.13

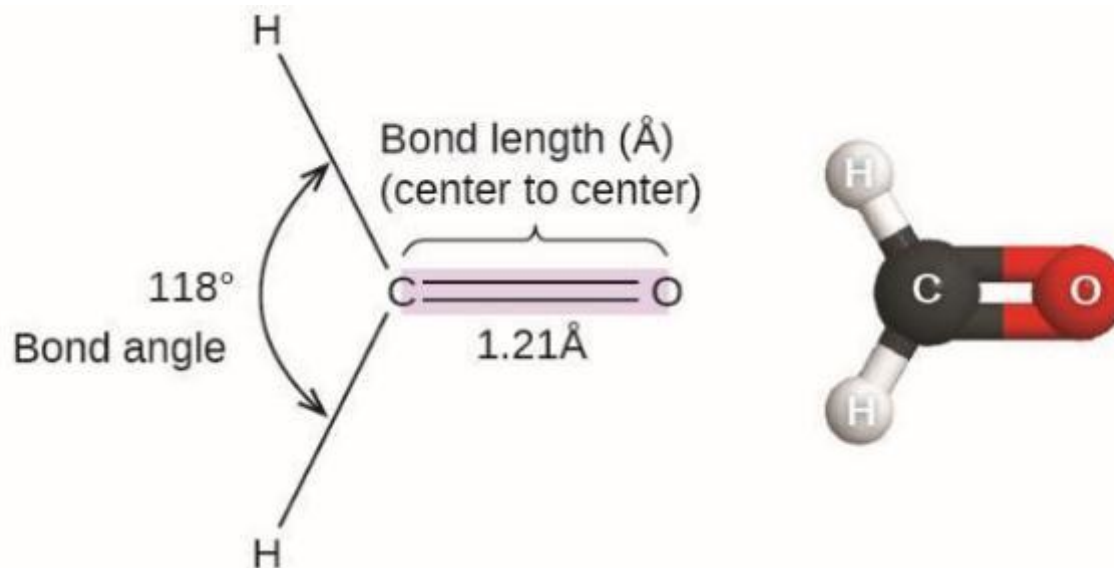


The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

Learning Objectives

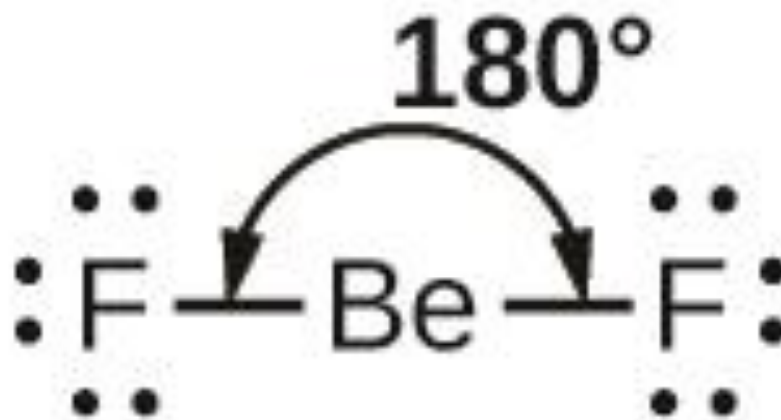
- 7.6 Molecular Structure and Polarity
 - Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
 - Explain the concepts of polar covalent bonds and molecular polarity
 - Assess the polarity of a molecule based on its bonding and structure

Figure 7.14



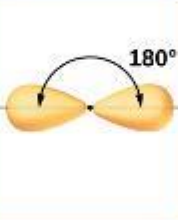
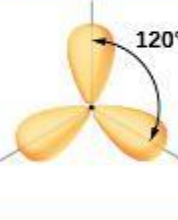

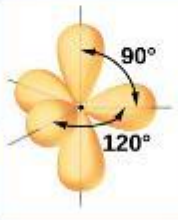
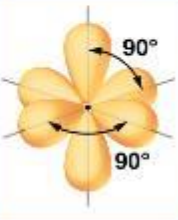
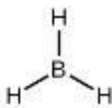
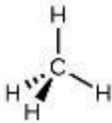


Bond distances (lengths) and angles are shown for the formaldehyde molecule, H₂CO.

Figure 7.15



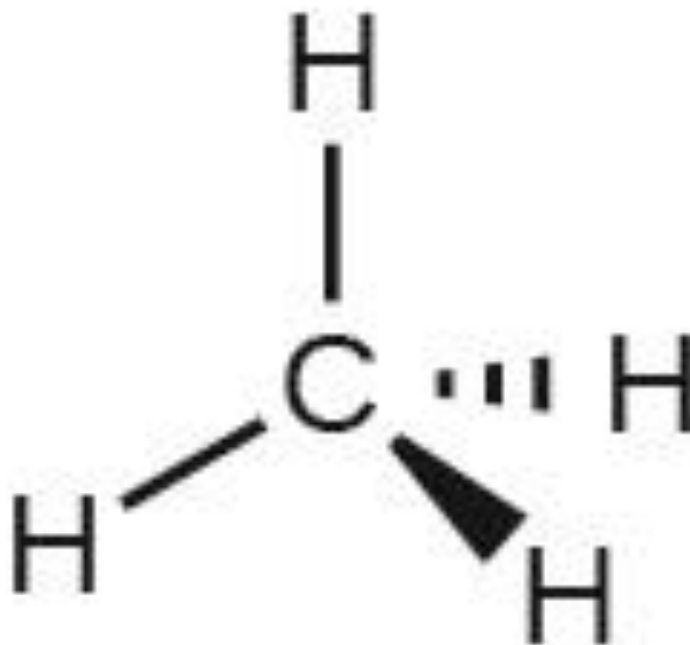
The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 7.16

Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	$\text{H}-\text{Be}-\text{H}$				
Electron region geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

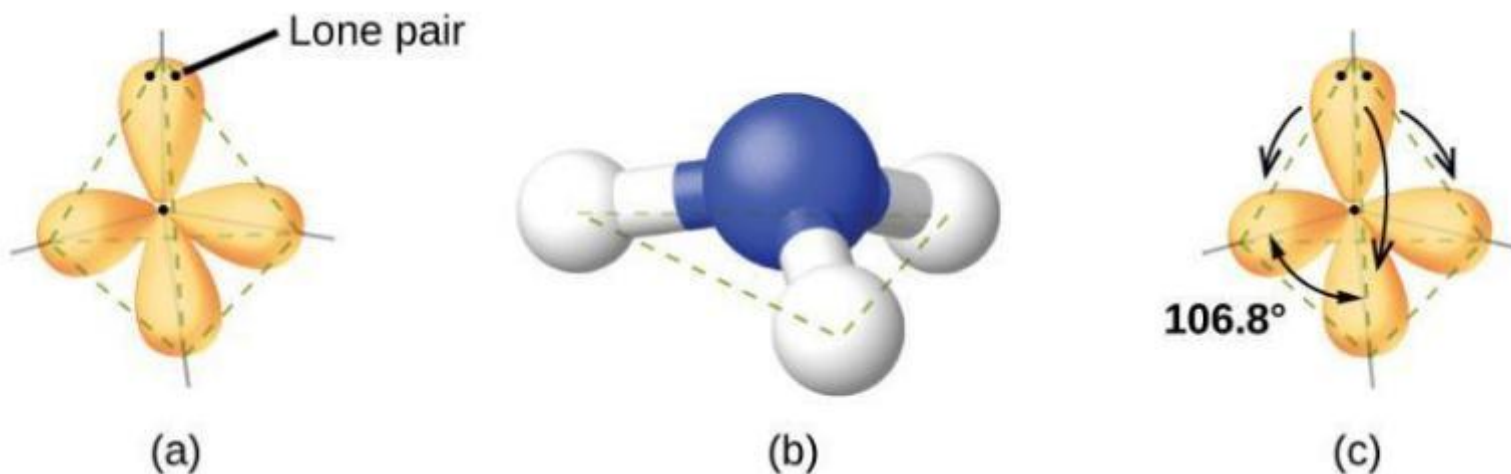
The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Figure 7.17



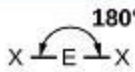
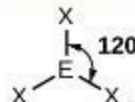

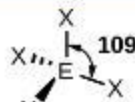


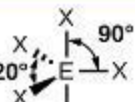
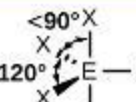
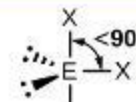
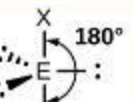





The molecular structure of the methane molecule, CH₄, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

Figure 7.18



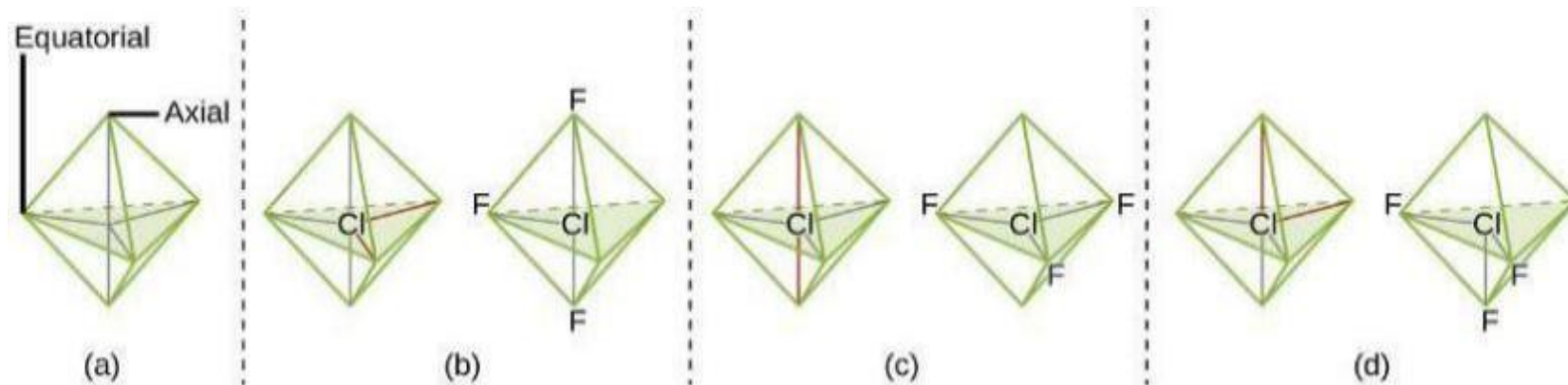
(a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

Figure 7.19

Number of electron regions	Electron region geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 <p>Linear</p>				
3	 <p>Trigonal planar</p>	 <p>Bent or angular</p>			
4	 <p>Tetrahedral</p>	 <p>Trigonal pyramid</p>	 <p>Bent or angular</p>		
5	 <p>Trigonal bipyramid</p>	 <p>Sawhorse or seesaw</p>	 <p>T-shape</p>	 <p>Linear</p>	
6	 <p>Octahedral</p>	 <p>Square pyramid</p>	 <p>Square planar</p>	 <p>T-shape</p>	 <p>Linear</p>

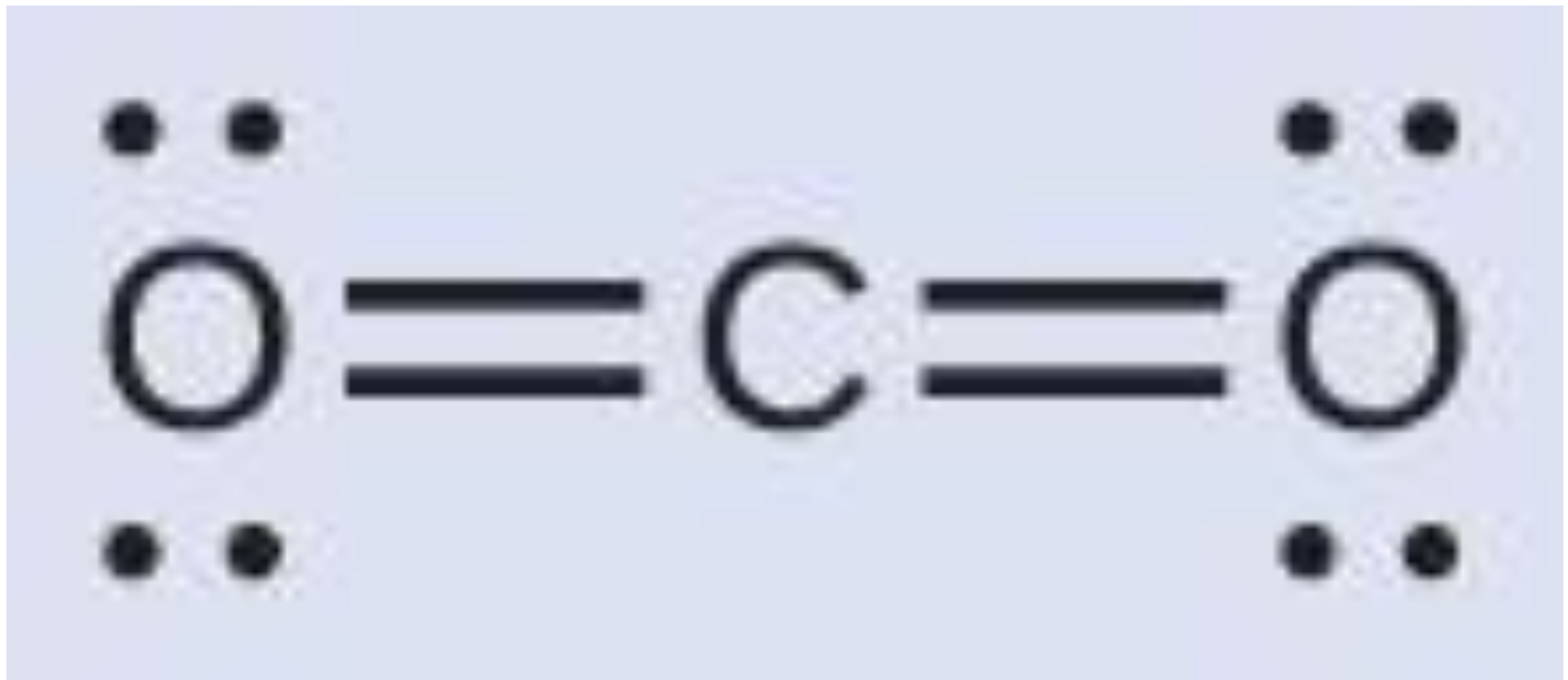
The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

Figure 7.20



(a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

Example 7.11



Example 7.11

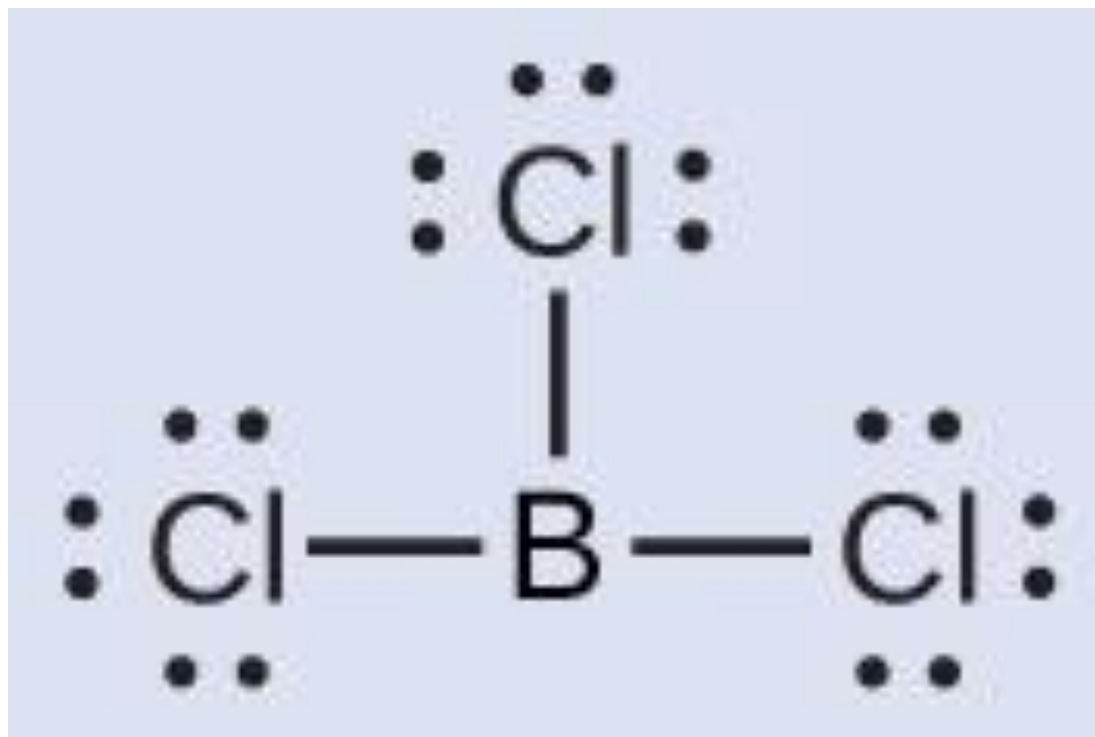
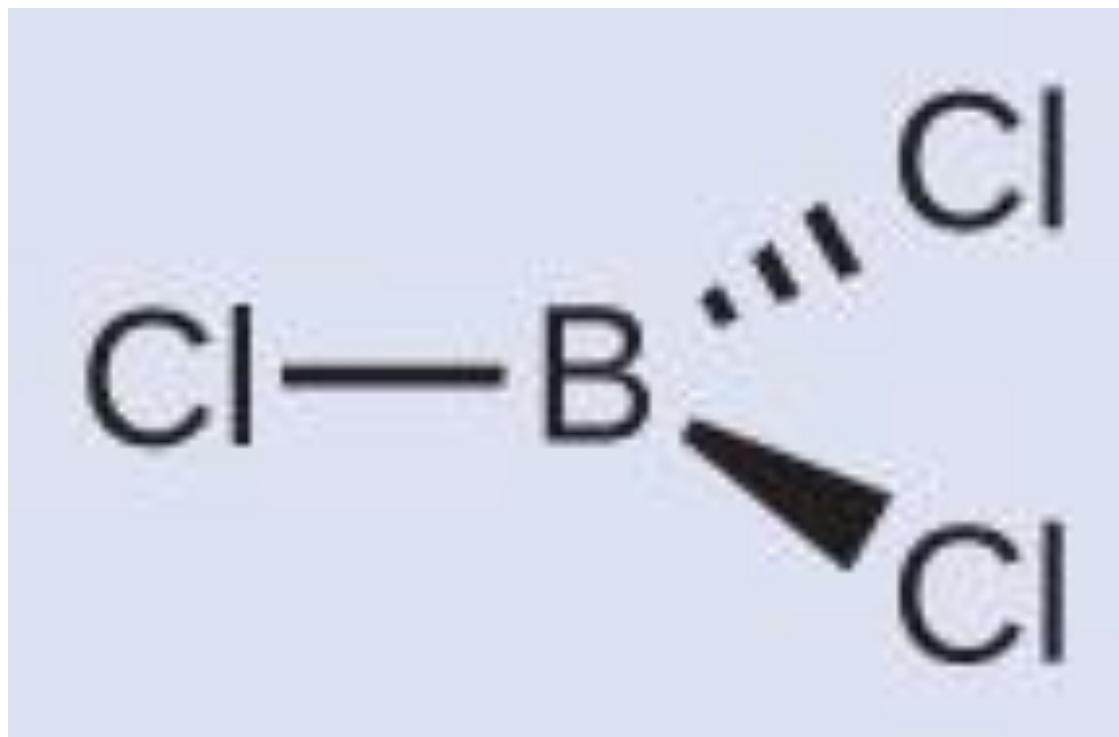


Figure 7.21



Example 7.12

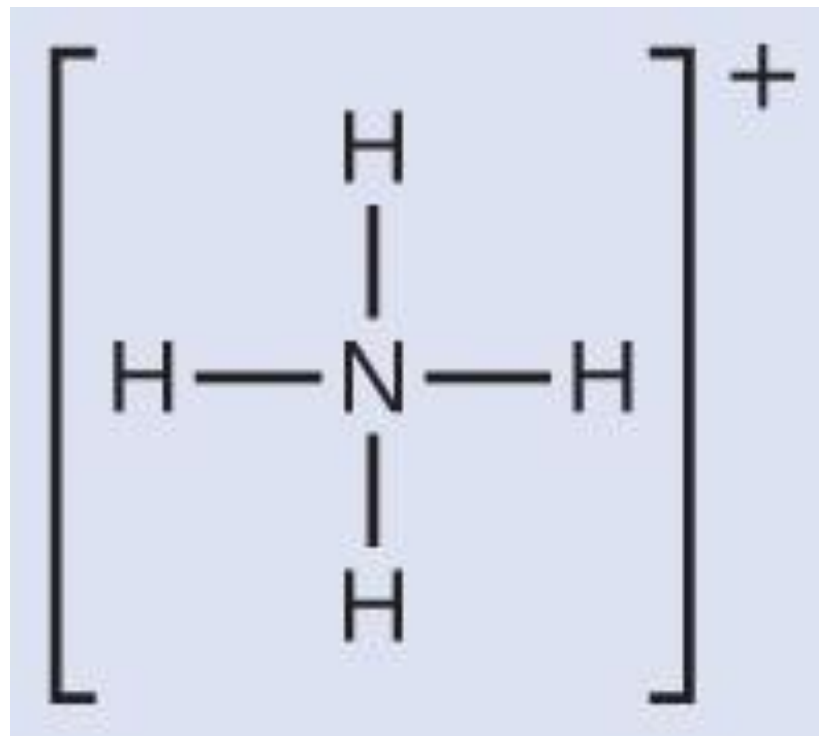
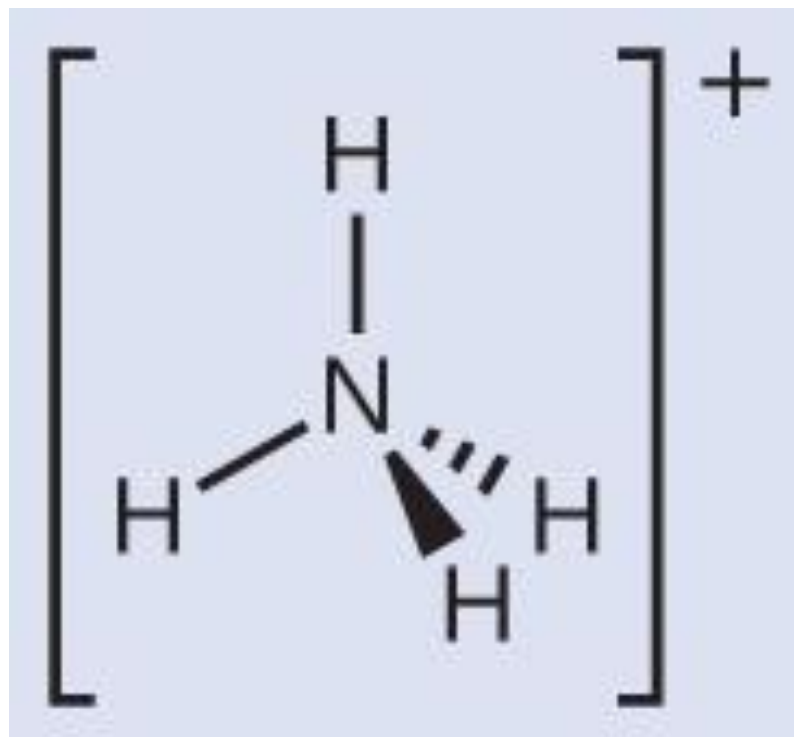


Figure 7.22



The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Example 7.13

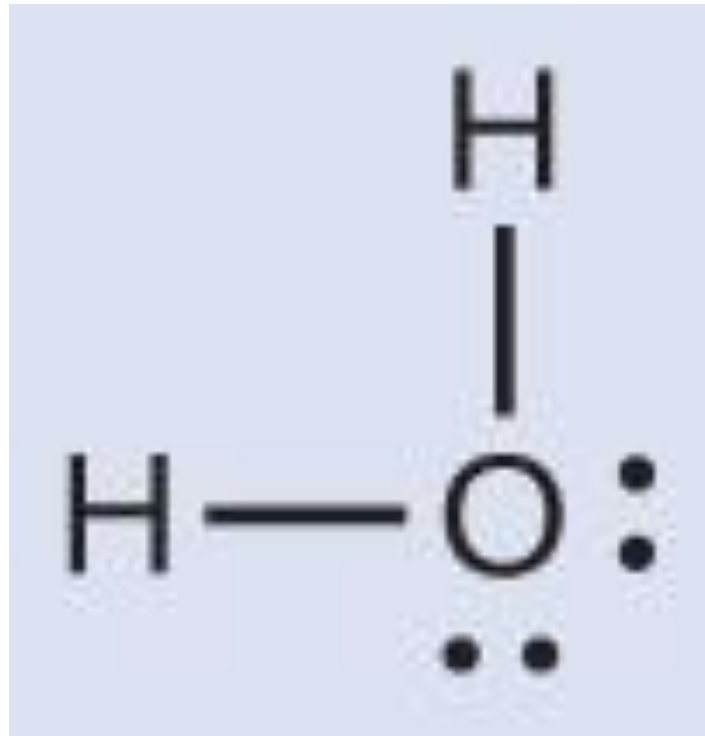
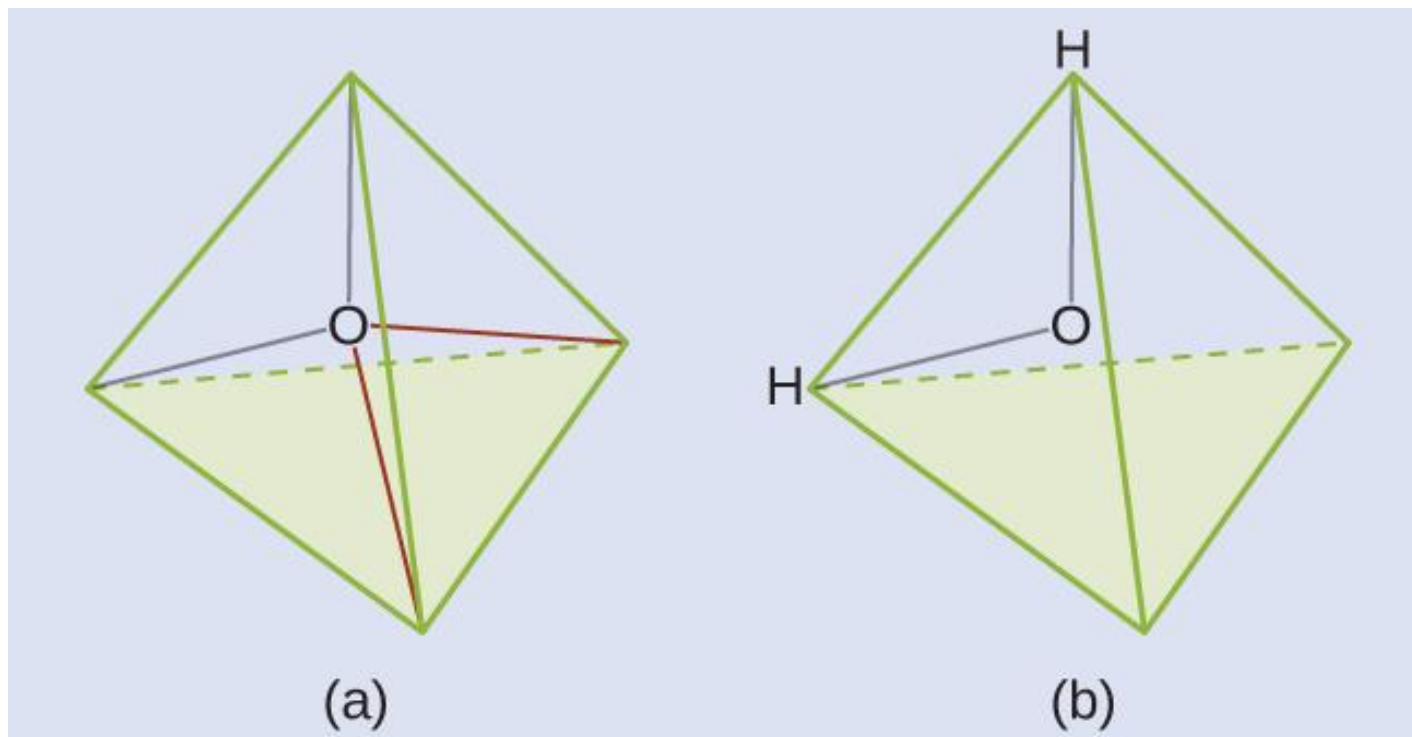


Figure 7.23



(a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Example 7.14

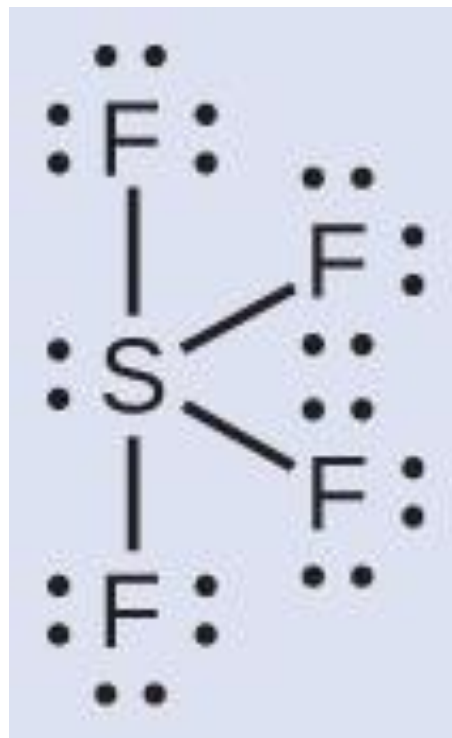
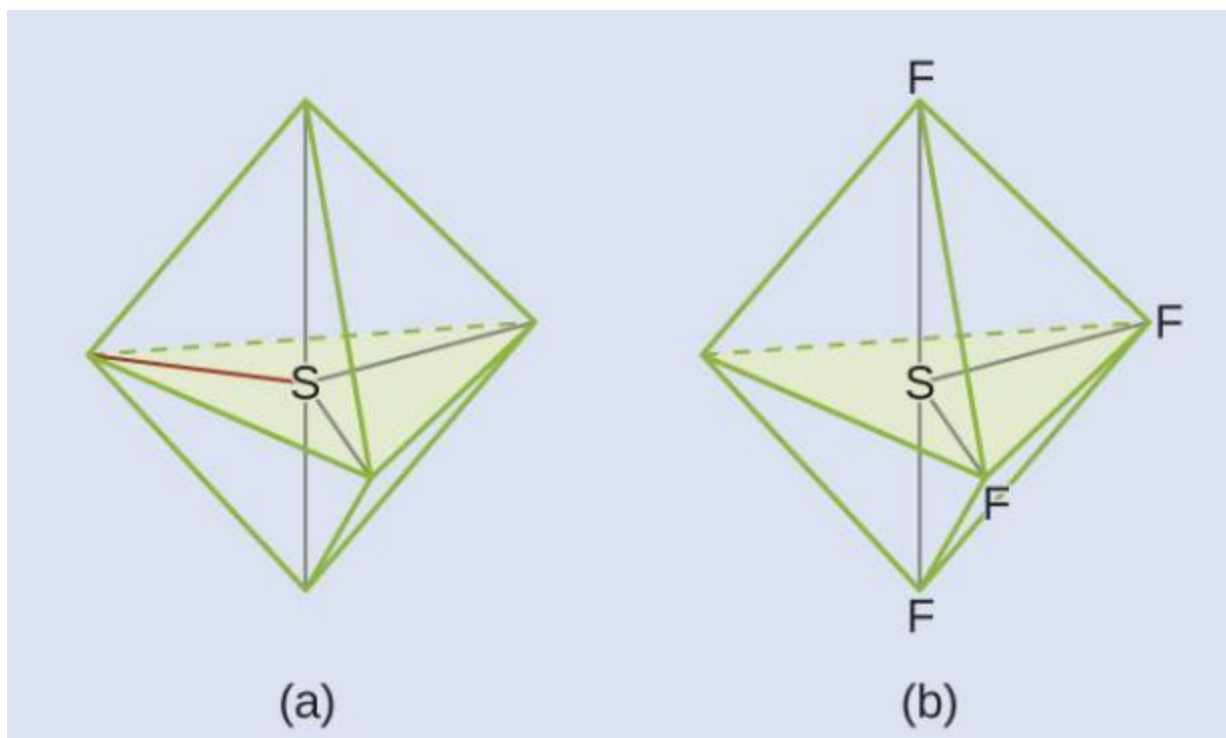


Figure 7.24



(a) SF₄ has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Example 7.15

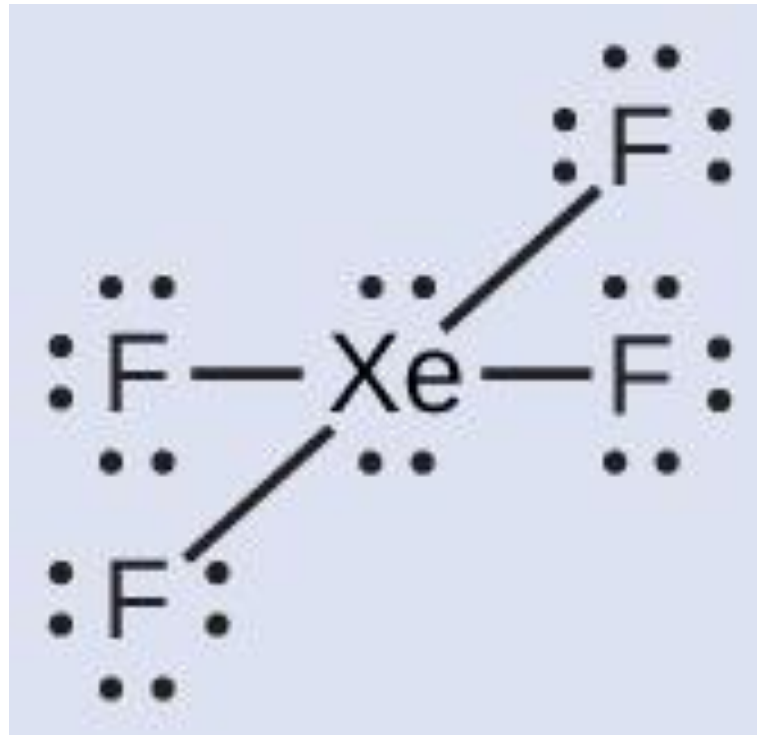
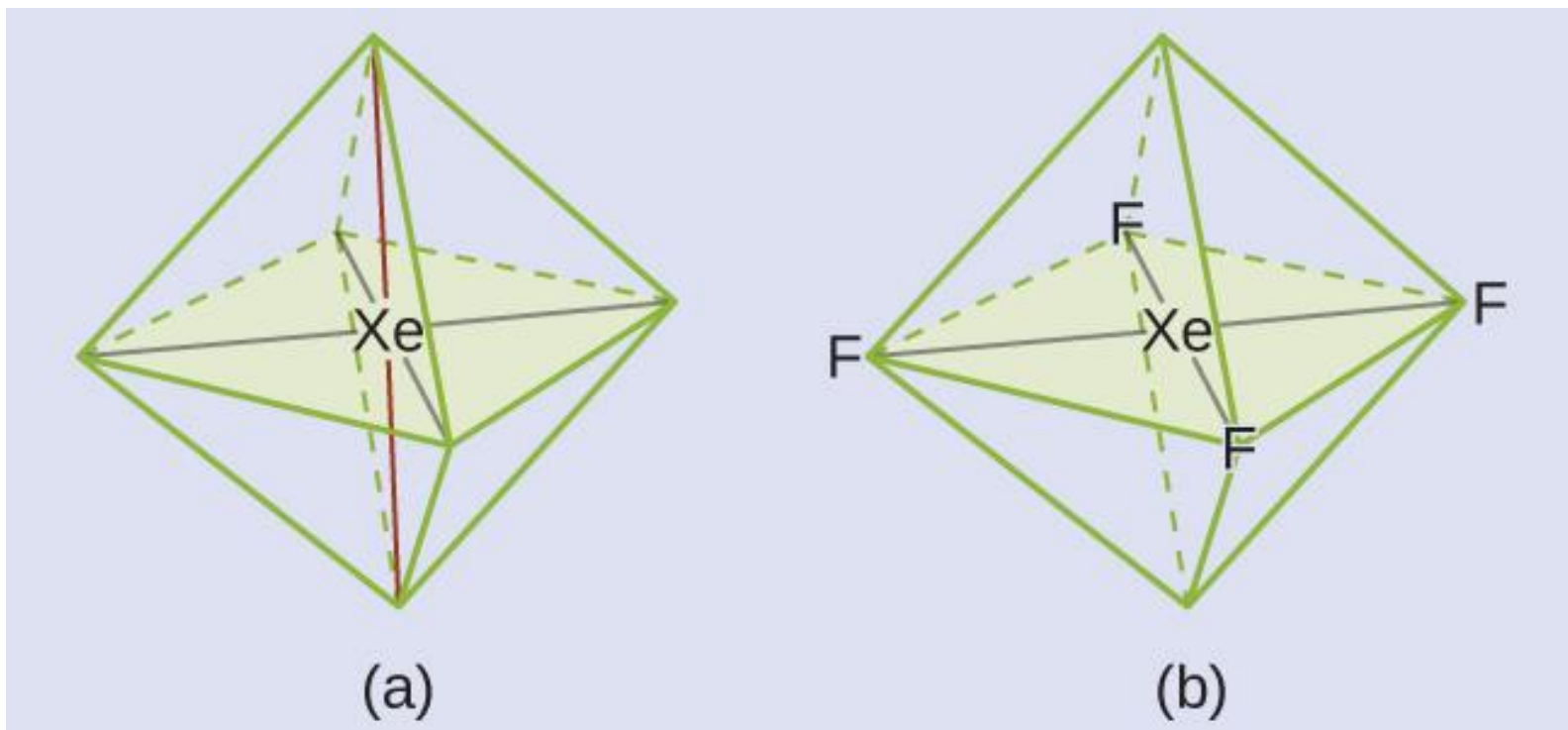
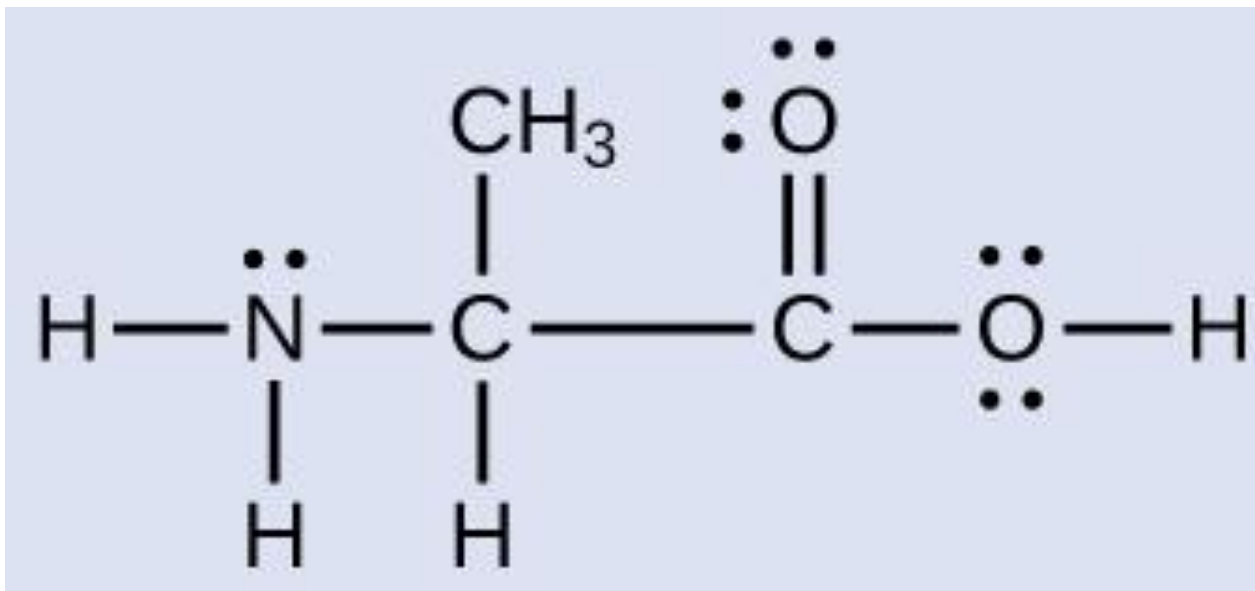


Figure 7.25

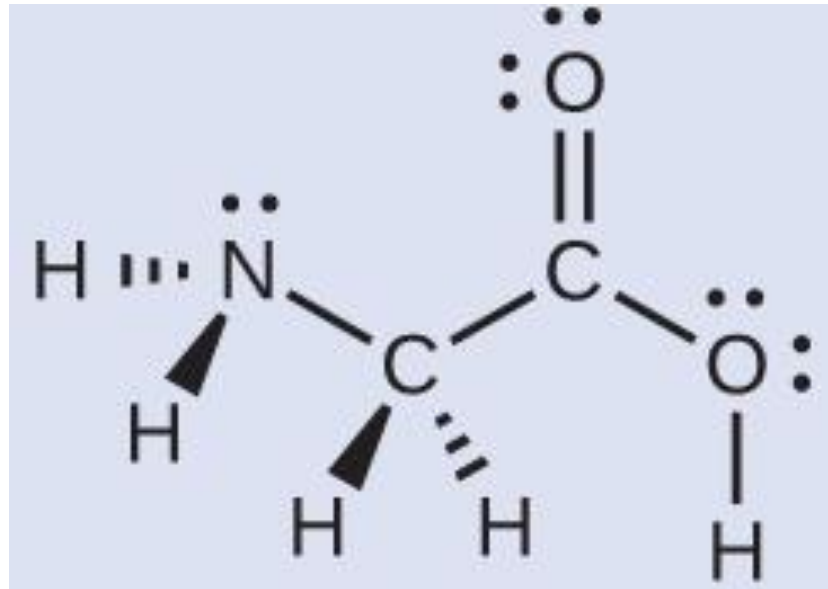


(a) XeF₄ adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Example 7.16



Example 7.16



Example 7.16

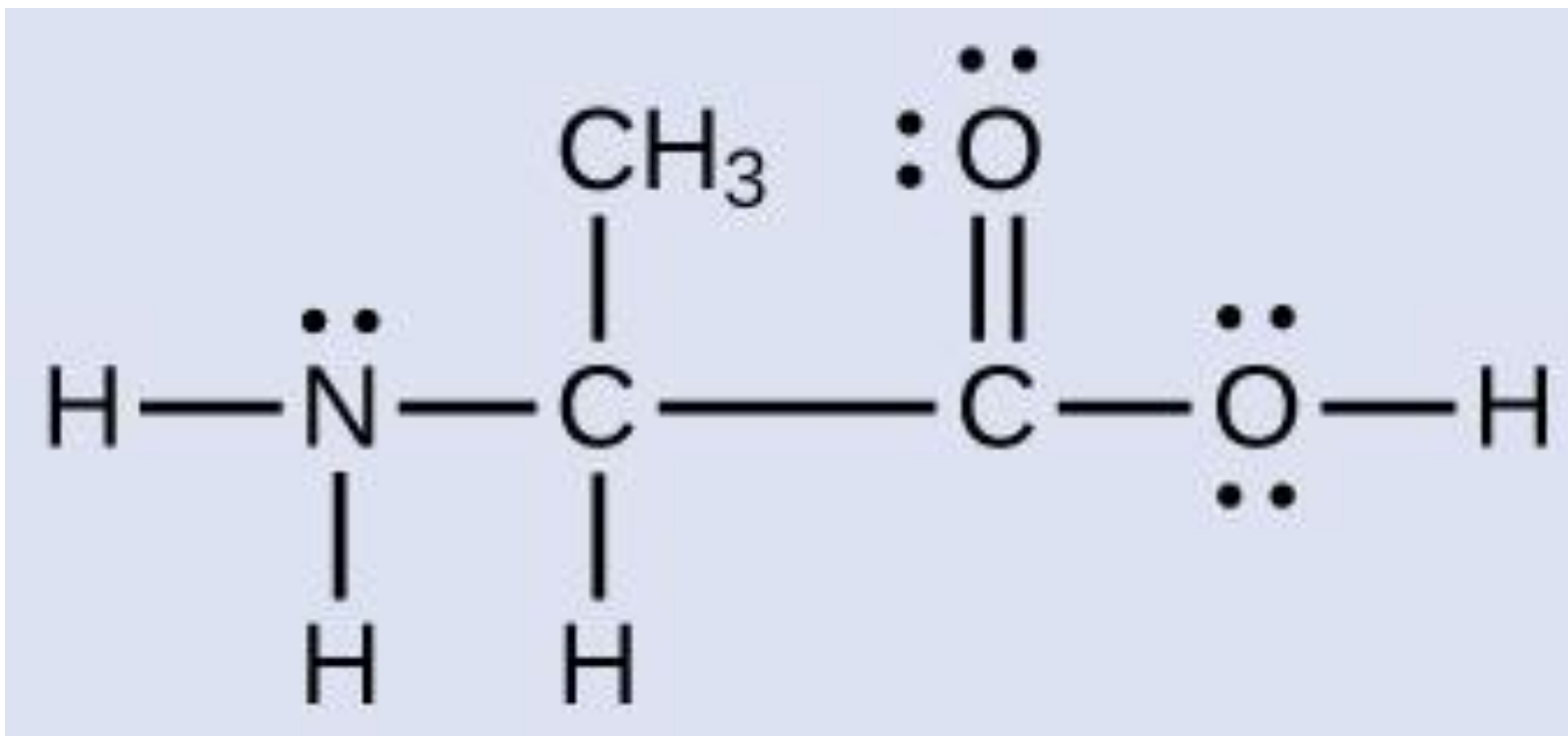
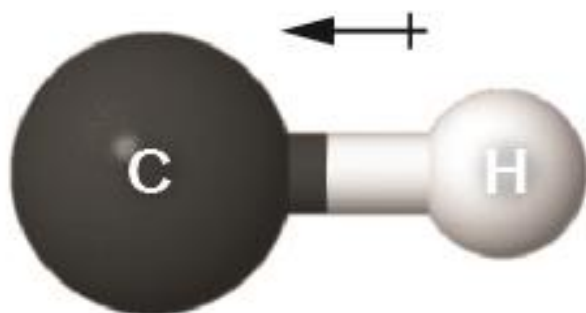
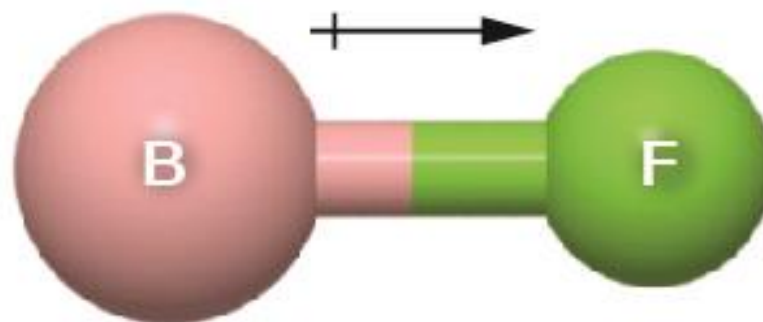


Figure 7.26



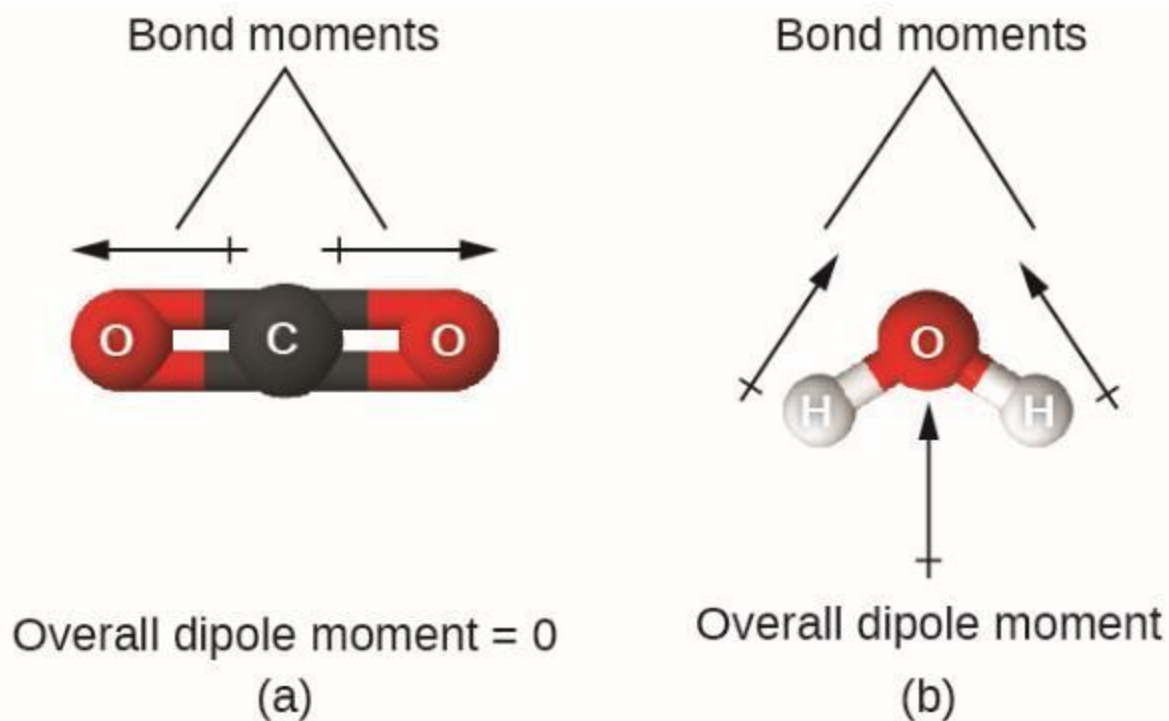
(a)



(b)

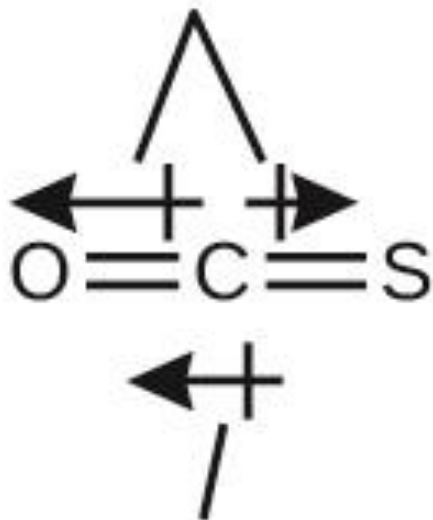
(a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

Figure 7.27

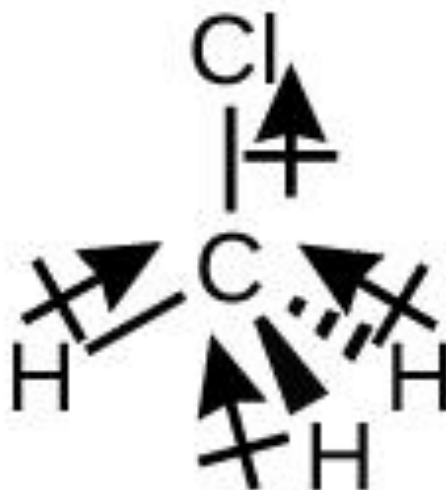


The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO₂ molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

Bond moments



Overall dipole moment



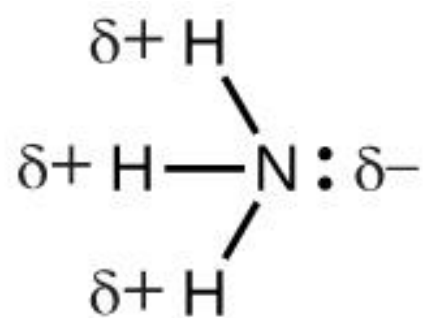
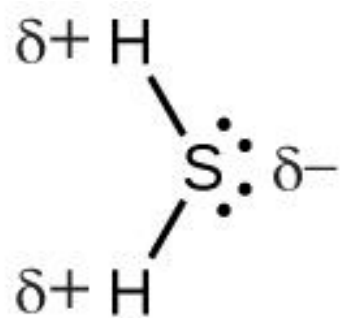
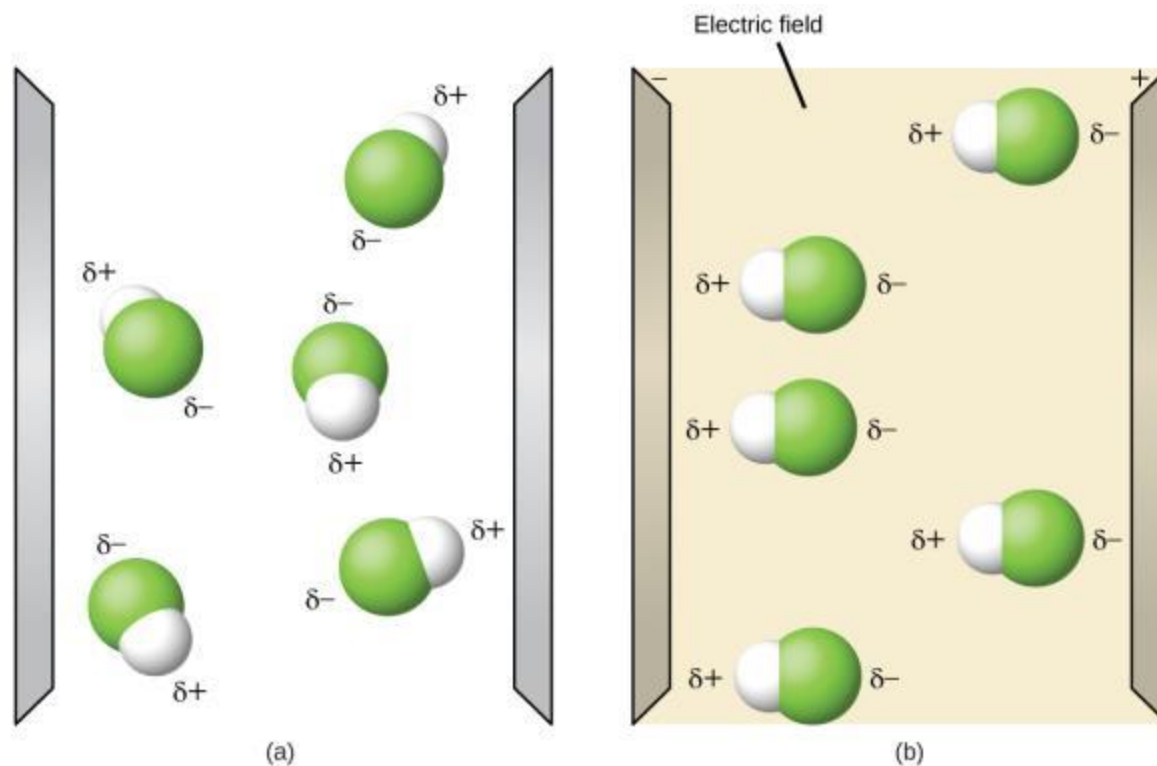
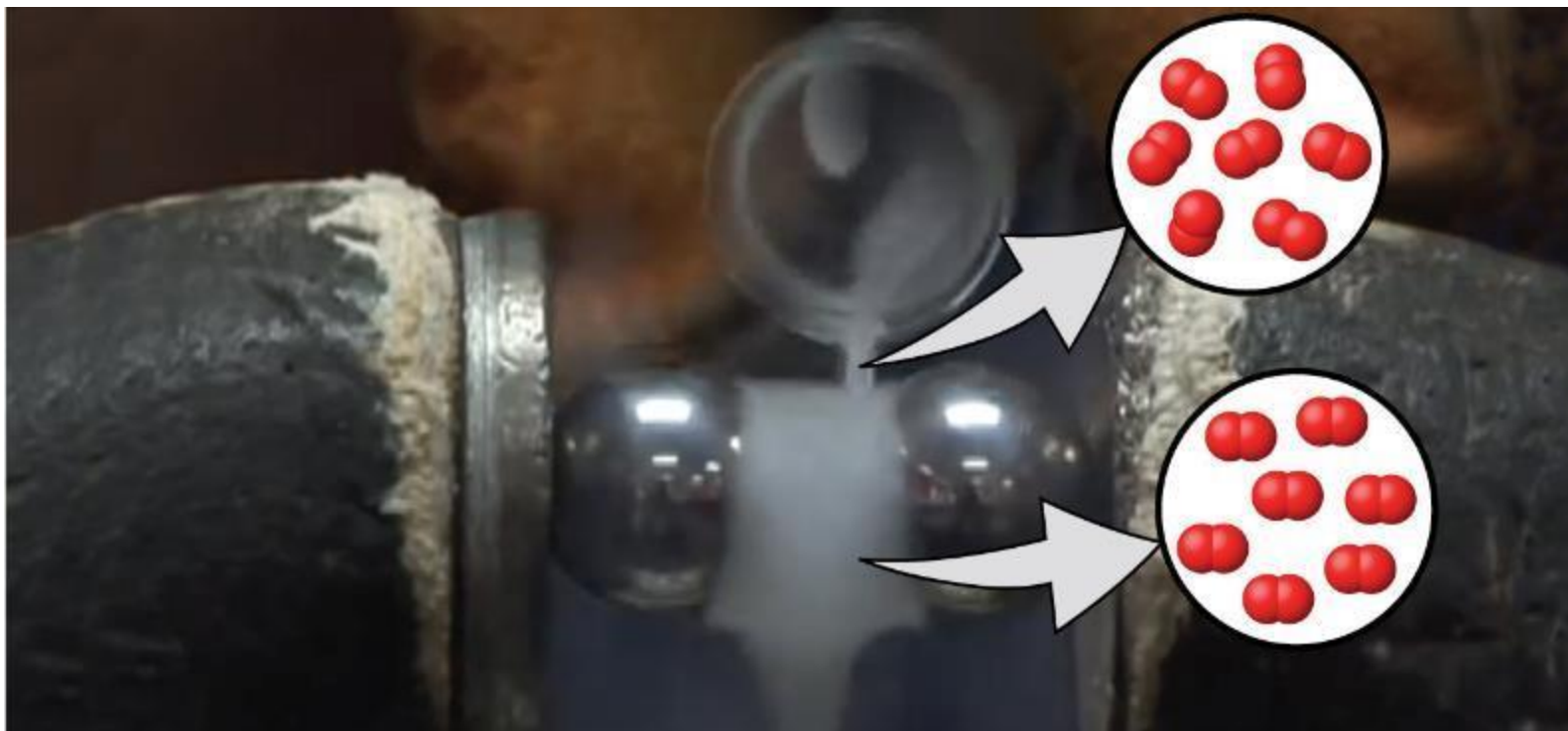


Figure 7.28



(a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Figure 8.1



Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field is strongest. Other diatomic molecules (like N_2) flow past the magnet. The detailed explanation of bonding described in this chapter allows us to understand this phenomenon. (credit: modification of work by Jefferson Lab)

Learning Objectives

- 8.1 Valance Bond Theory
 - Describe the formation of covalent bonds in terms of atomic orbital overlap
 - Define and give examples of σ and π bonds

Orbitals and Covalent Bonding

- Linus Pauling and others (1930s) developed the **valance bond theory** of covalent bonding.
- Electrons reside in orbitals.
- Covalent bonds form when electrons are shared by the overlapping of singly occupied orbitals.
- Electrons in these overlapping orbitals must have opposite spins.

Valance Bond Theory

- Consider the formation of the H₂ molecule.

Valance Bond Theory

- Consider the formation of the HF molecule.

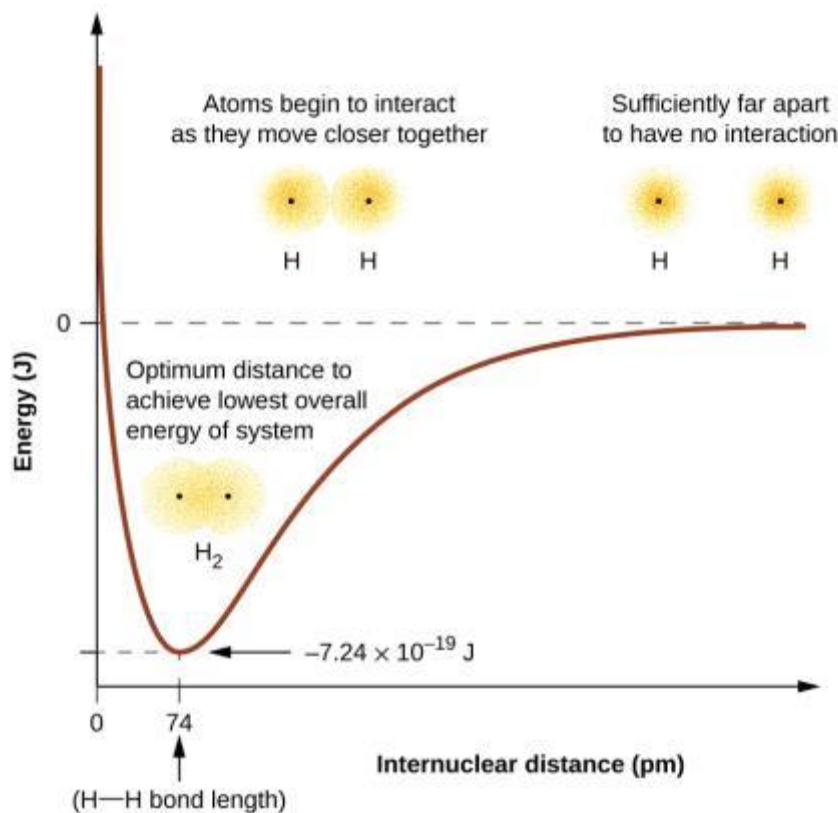
Valence Bond Theory

- To form a covalent bond, an atom must have an unpaired electron.
- Number of bonds formed by an atom is determined by the number of unpaired electrons.
- This theory works well for explaining the bonding in diatomic molecules with only single bonds.
- This theory also works well for explaining the lack of bonding experienced by the noble gases.

Limitations of the Valence Bond Model

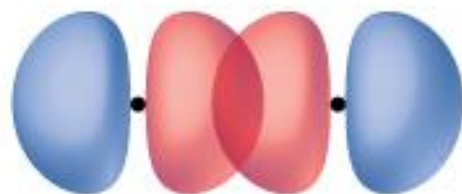
- Valence bond theory must be modified to explain the covalent bonds formed in other molecules.
- Consider BeF_2 , BF_3 , and CH_4

Figure 8.2

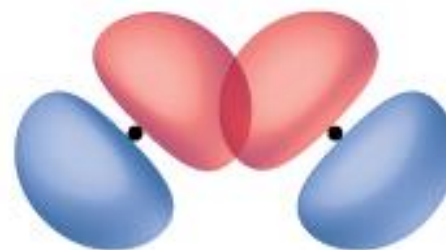


(a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

Figure 8.3



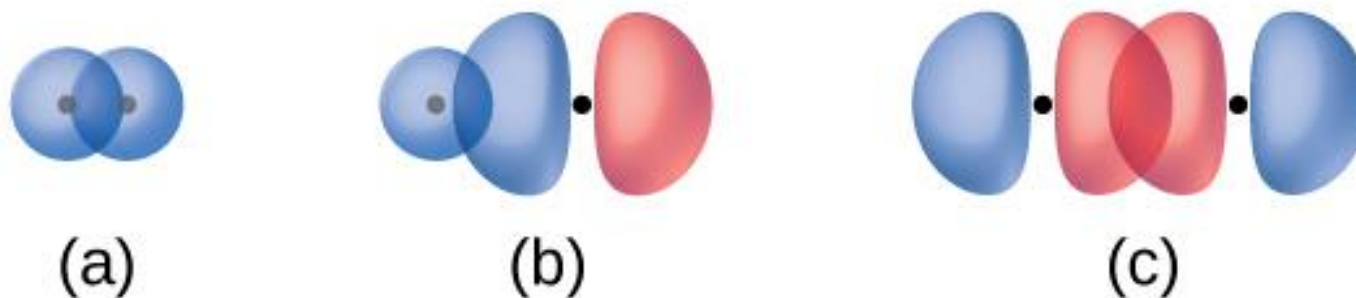
(a)



(b)

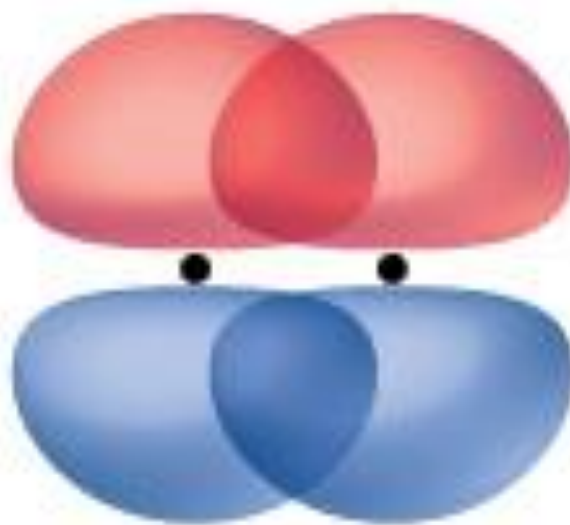
(a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The plus signs indicate the locations of the nuclei.

Figure 8.4

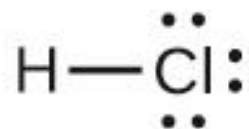


Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The plus signs indicate the locations of the nuclei.

Figure 8.5



Pi (π) bonds form from the side-by-side overlap of two p orbitals. The plus signs indicate the location of the nuclei.



One σ bond
No π bonds

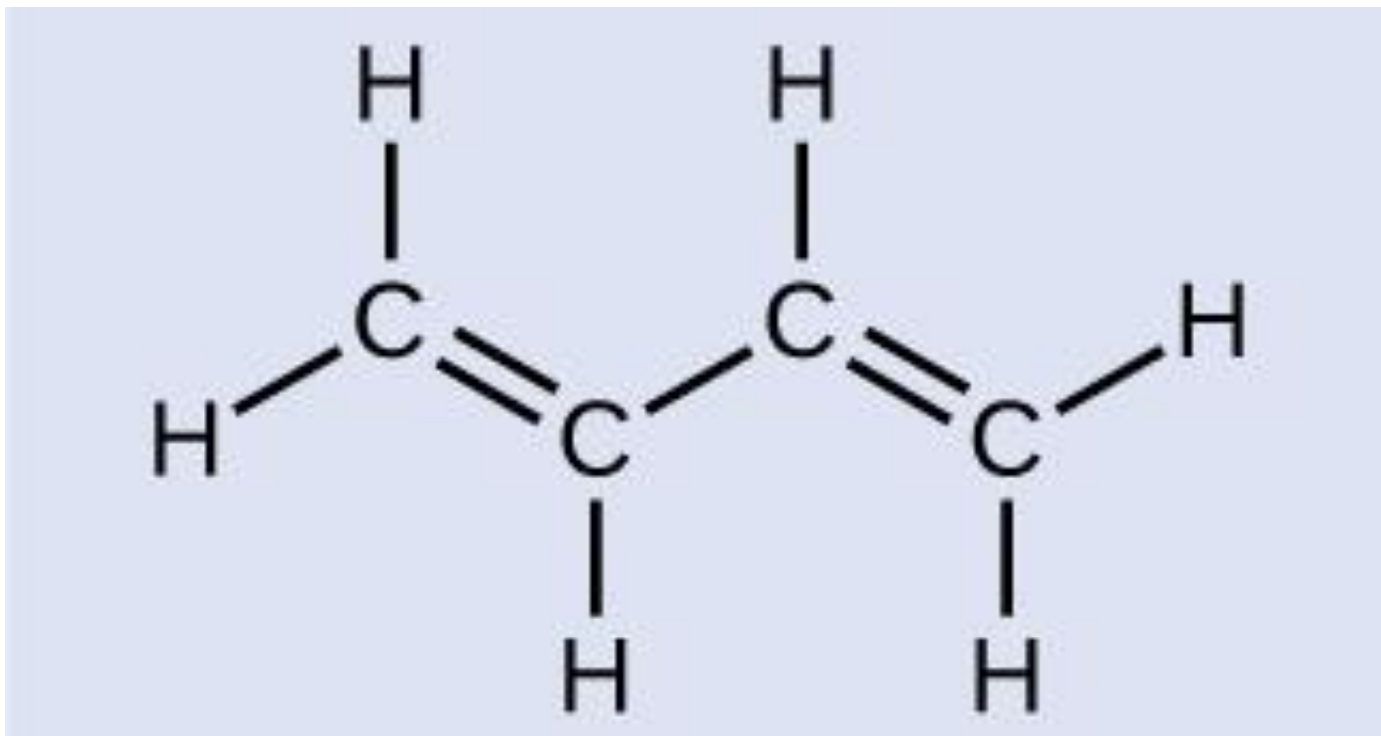


One σ bond
One π bond



One σ bond
Two π bonds

Example 8.1



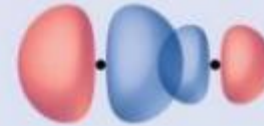
Example 8.1



(a)



(b)



(c)

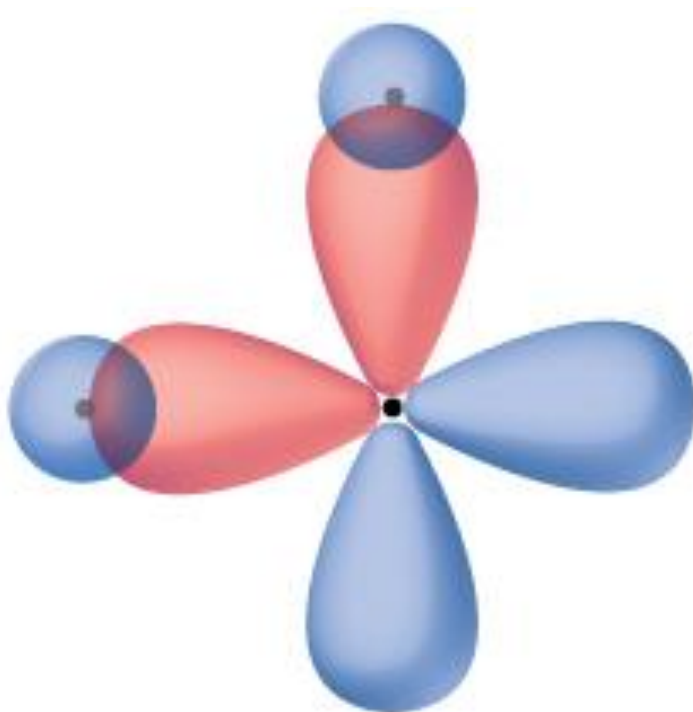
Learning Objectives

- 8.2 Hybrid Atomic Orbitals
 - Explain the concept of atomic orbital hybridization
 - Determine the hybrid orbitals associated with various molecular geometries

Hybrid Orbitals

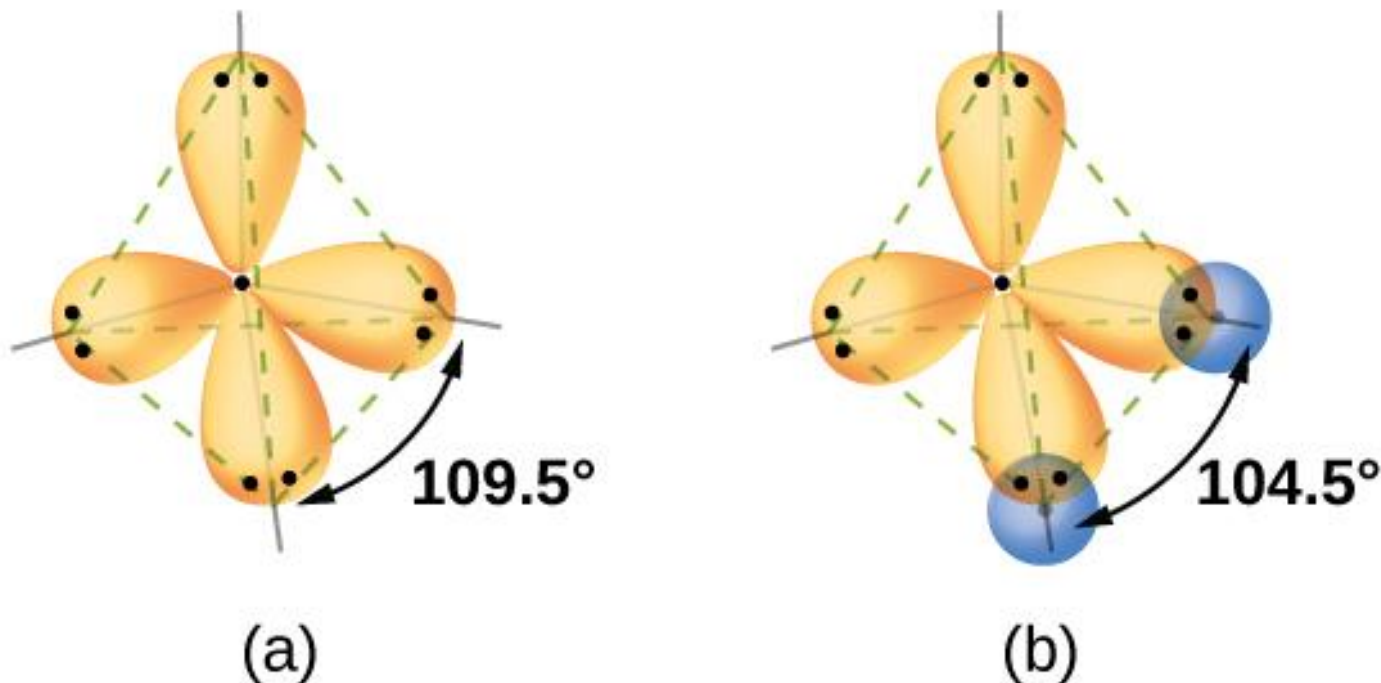
- Bonding in other molecules is best explained with hybrid orbitals.
- Keep in mind when working with hybrid orbitals.
 - The number of hybrid orbitals formed always equals the number of atomic orbitals that are combined.

Figure 8.6



The hypothetical overlap of two of the $2p$ orbitals on an oxygen atom (red) with the $1s$ orbitals of two hydrogen atoms (blue) would produce a bond angle of 90° . This is not consistent with experimental evidence. (Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.)

Figure 8.7



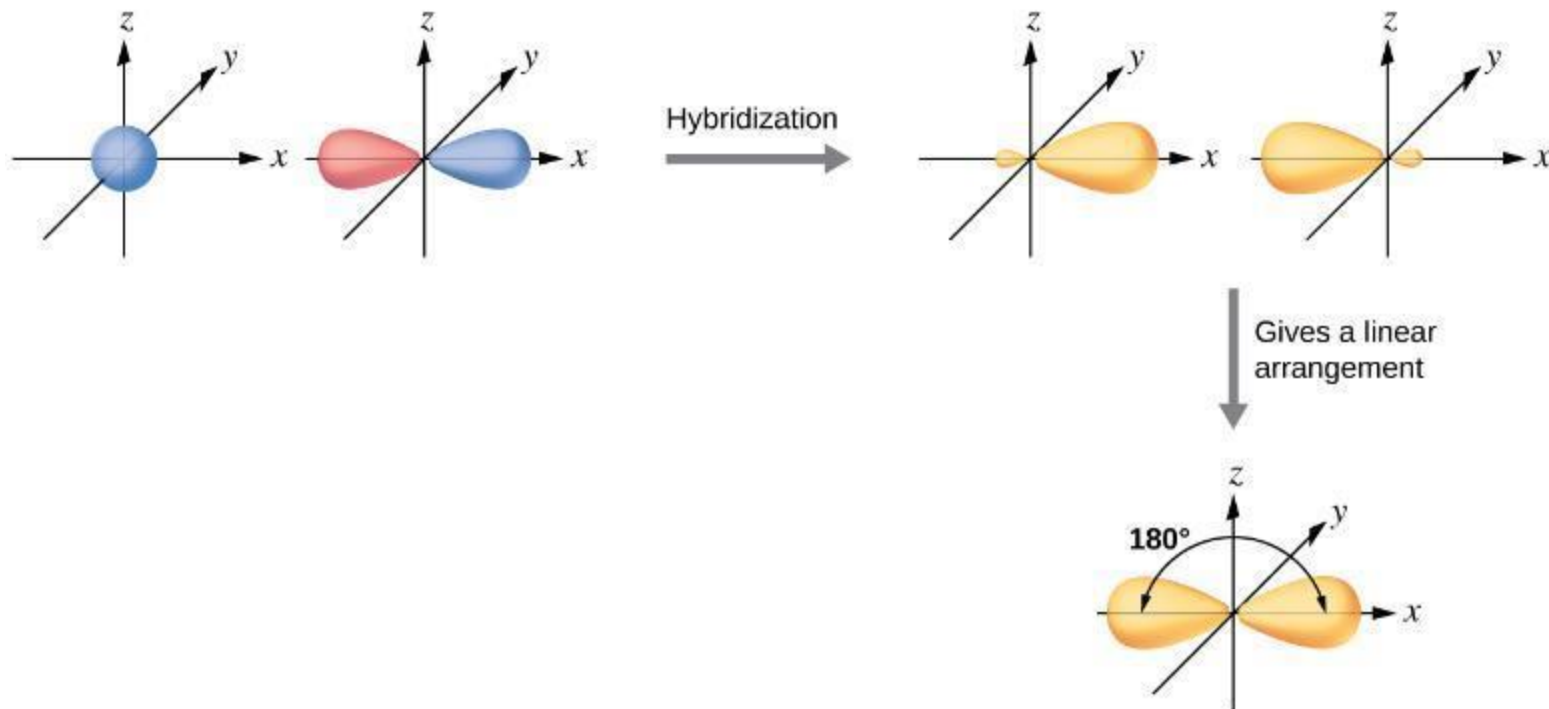
(a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H₂O. This description is more consistent with the experimental structure.

sp Hybrid Orbitals

- Two atomic orbitals can hybridize to produce two hybrid orbitals.

one *s* orbital + one *p* orbital → two *sp* hybrid orbitals

Figure 8.8

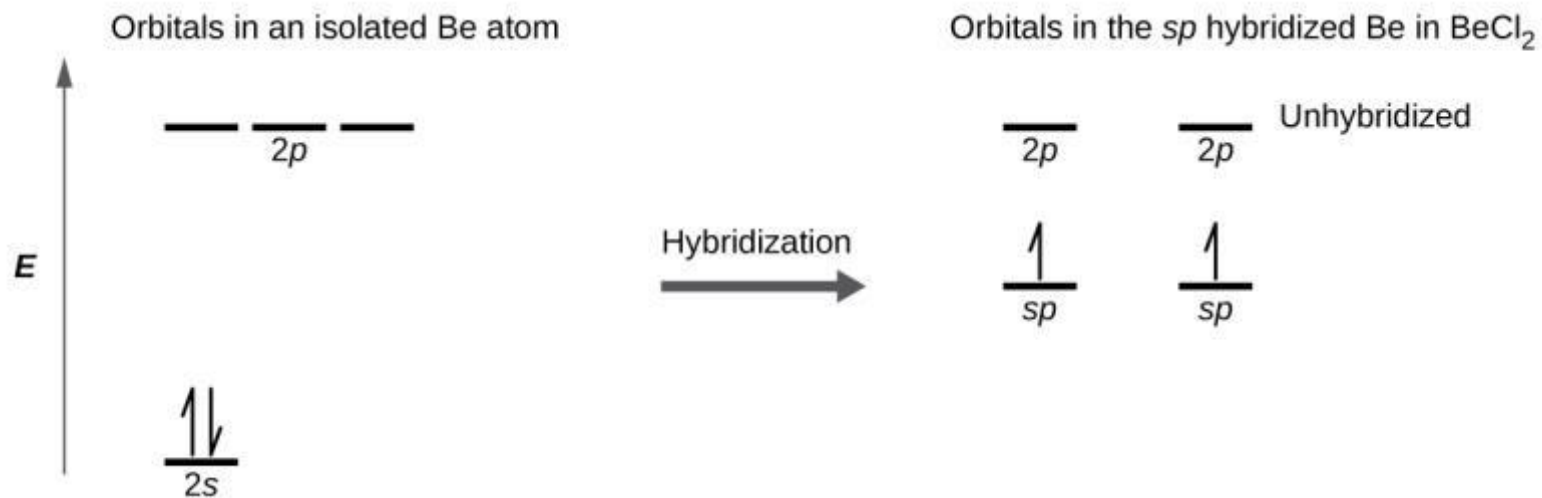


Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (purple). Each hybrid orbital is oriented primarily in just one direction. Note that each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180° , which is consistent with the geometry for two domains.

sp Hybrid Orbitals

- Occurs when a central atom is surrounded by **two** regions of electron density.

Figure 8.9

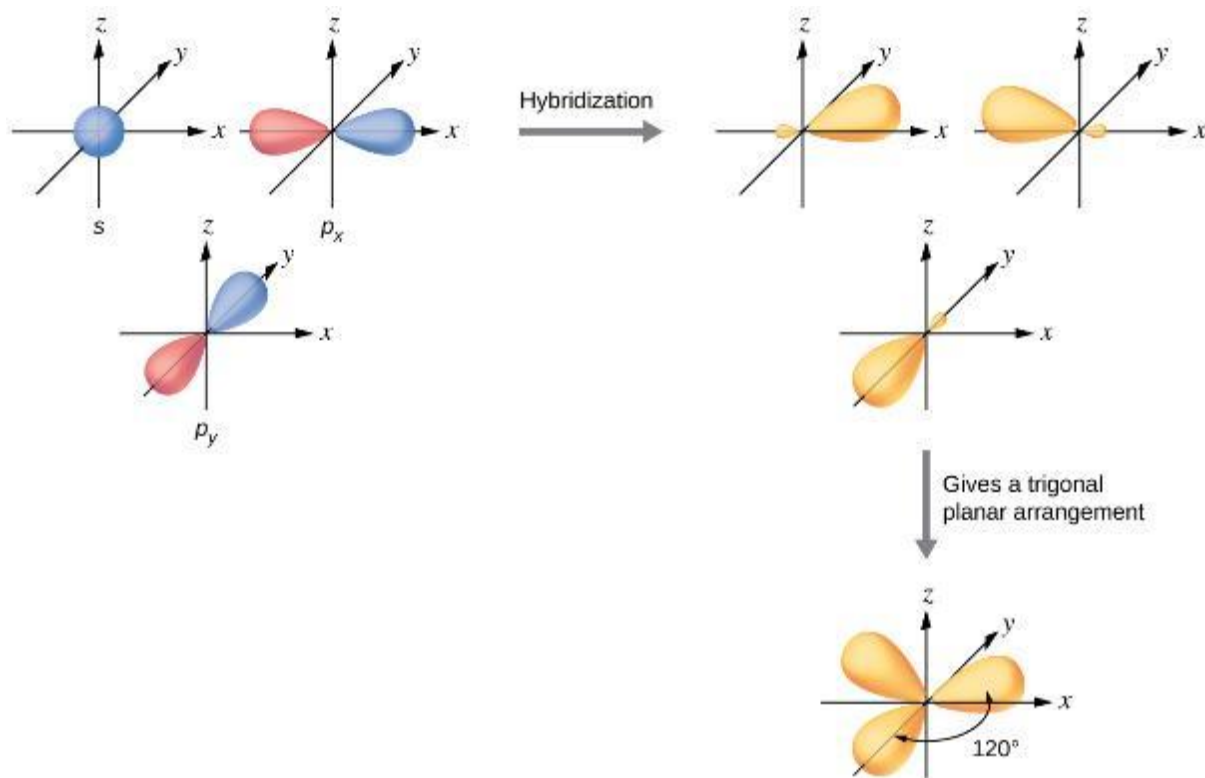


This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear BeCl_2 molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl $3p$ orbital.

sp^2 Hybrid Orbitals

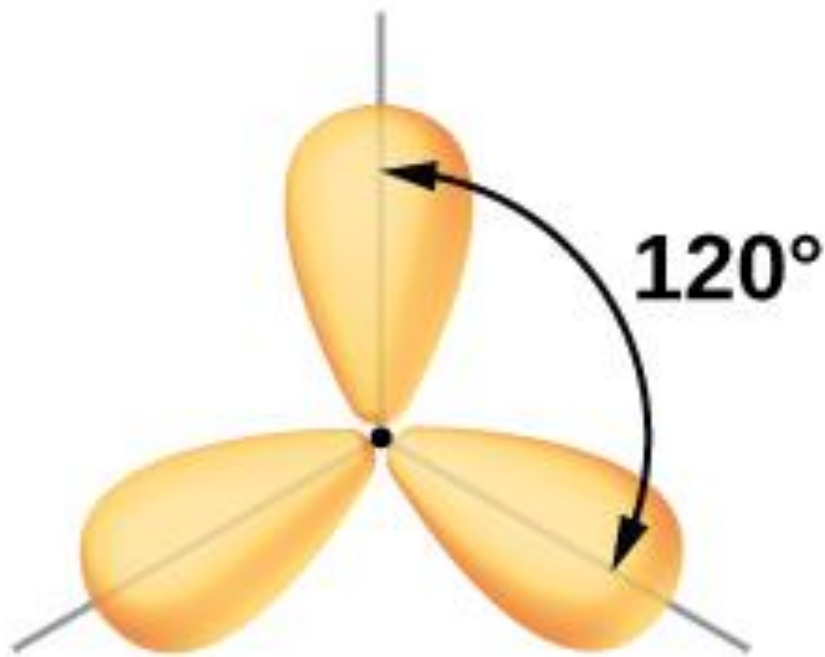
- Three atomic orbitals can hybridize to produce three hybrid orbitals.
one s orbital + two p orbitals \rightarrow three sp^2 hybrid orbitals
- Occurs when a central atom is surrounded by *three* regions of electron density.

Figure 8.10



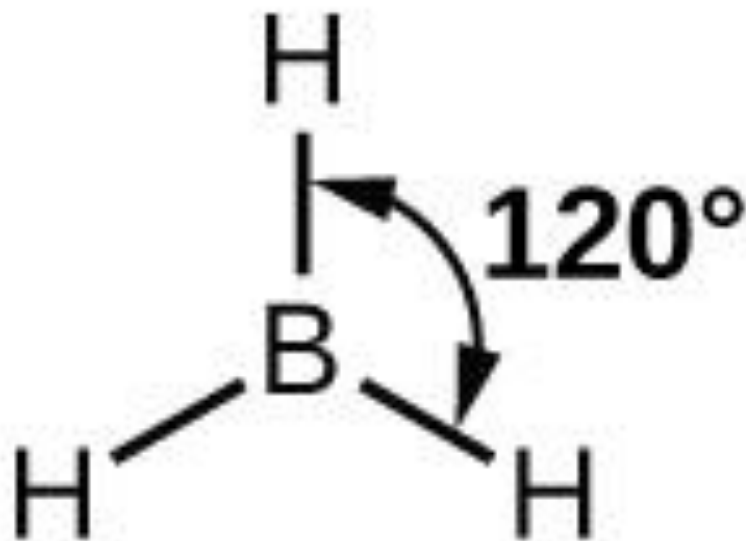
The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (purple) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.

Figure 8.11



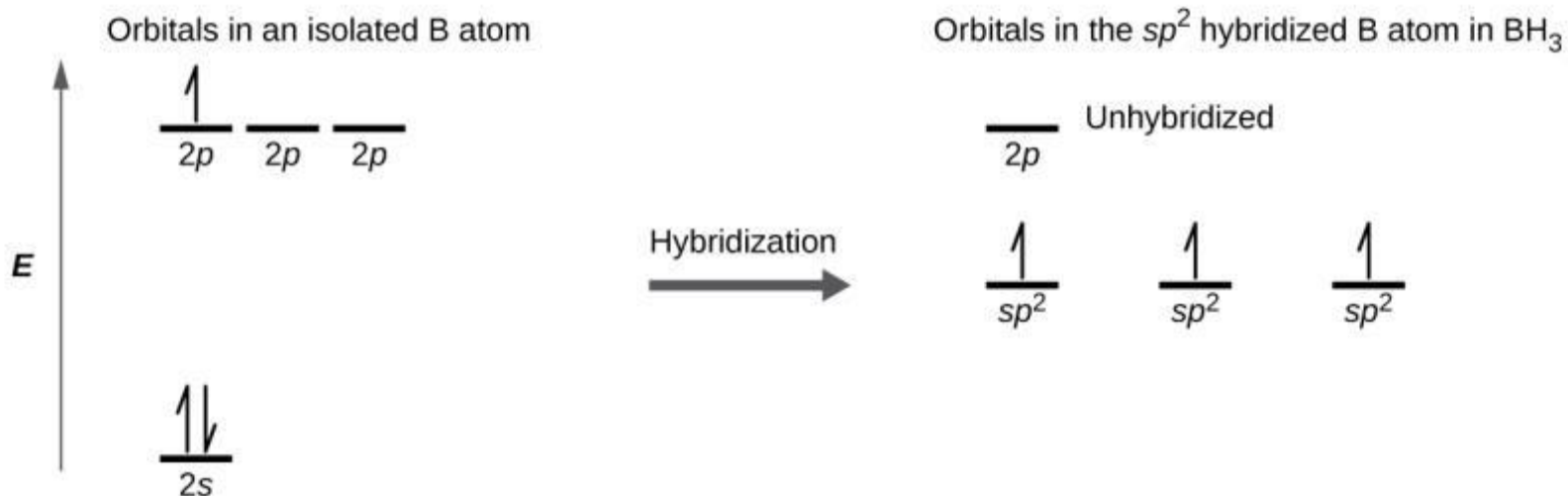
This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

Figure 8.12



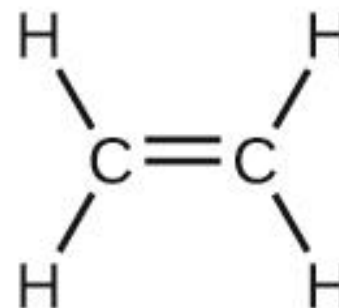
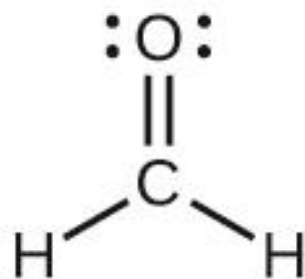
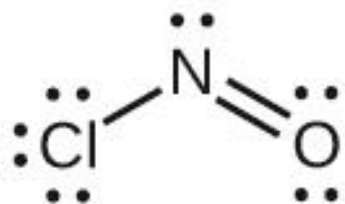
BH₃ is an electron-deficient molecule with a trigonal planar structure.

Figure 8.13



In an isolated B atom, there are one $2s$ and three $2p$ valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized $2p$ orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3 .

Figure 8.14

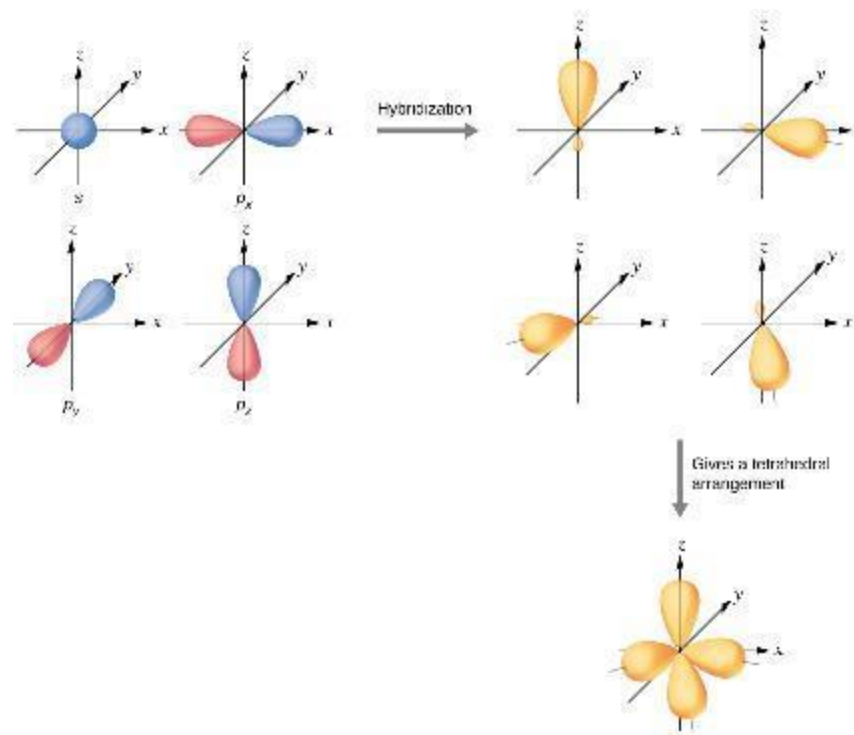


The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

sp^3 Hybrid Orbitals

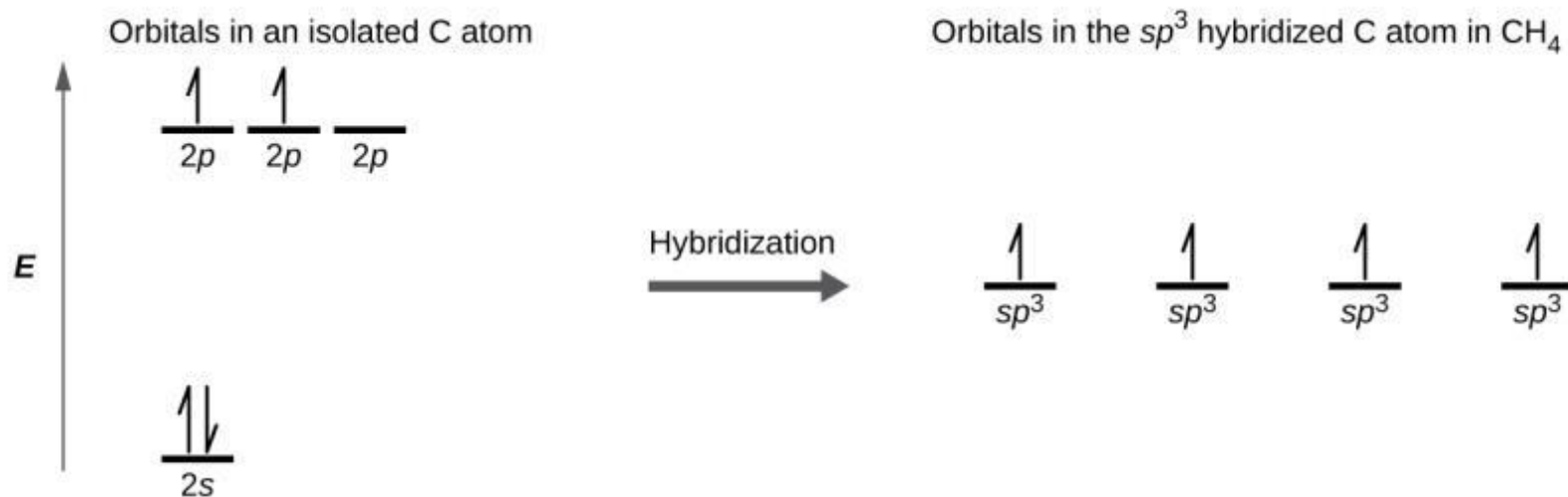
- Four atomic orbitals can hybridize to produce four hybrid orbitals.
one s orbital + three p orbitals → **four sp^3 hybrid orbitals**
- Occurs when a central atom is surrounded by *four* regions of electron density.

Figure 8.15



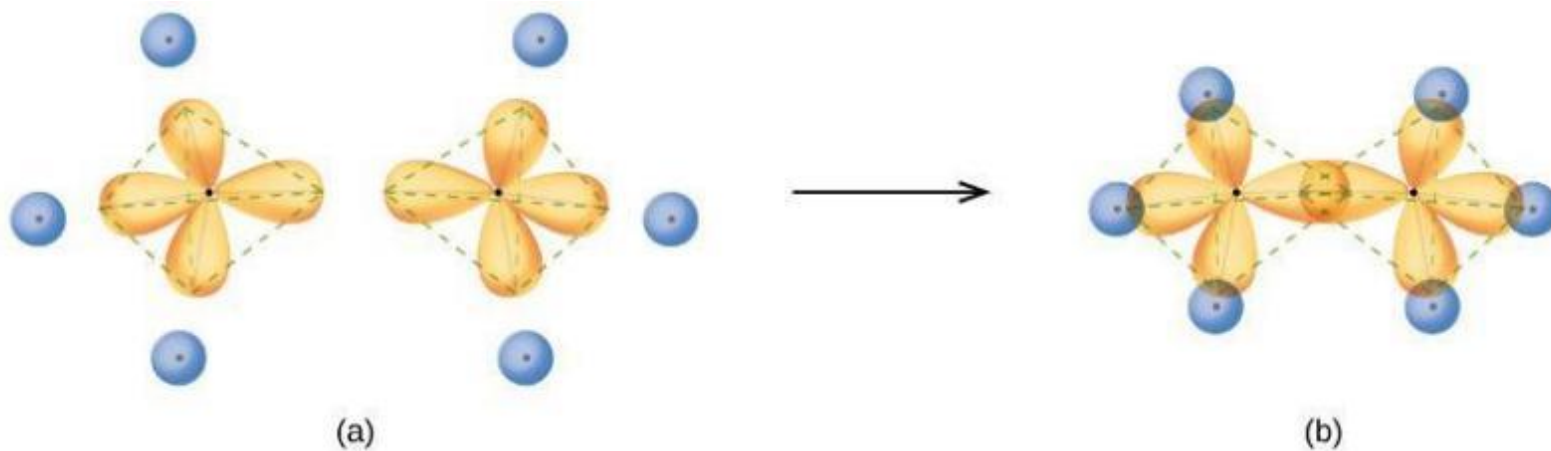
The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (purple) oriented at 109.5° with respect to each other.

Figure 8.16



The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

Figure 8.17



(a) In the ethane molecule, C_2H_6 , each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

sp^3d Hybrid Orbitals

- Five atomic orbitals can hybridize to produce five hybrid orbitals.

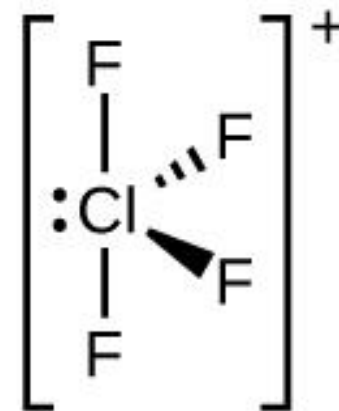
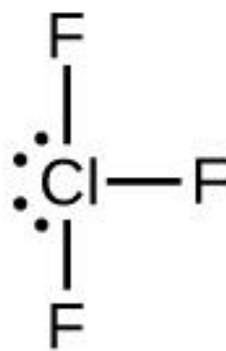
one s orbital + three p orbitals + one d orbital → **five sp^3d hybrid orbitals**

- Occurs when a central atom is surrounded by *five* regions of electron density.

sp^3d^2 Hybrid Orbitals

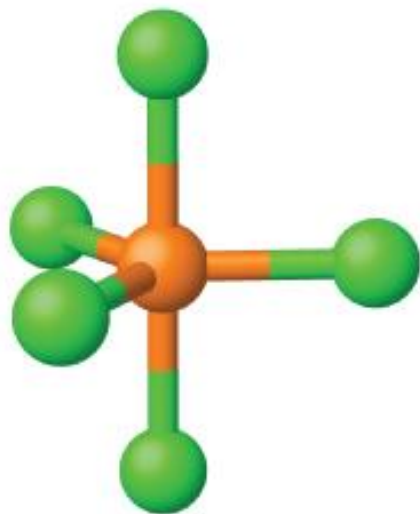
- Six atomic orbitals can hybridize to produce six hybrid orbitals.
one s orbital + three p orbitals + two d orbitals \rightarrow six sp^3d^2 hybrid orbitals
- Occurs when a central atom is surrounded by *six* regions of electron density.

Figure 8.18

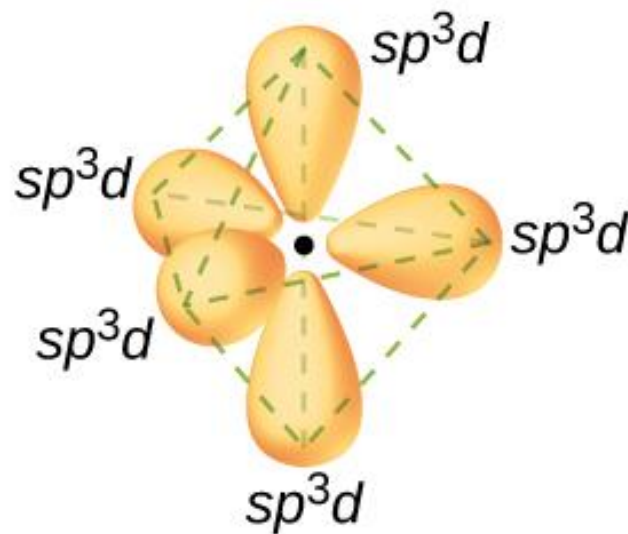


The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and ClF_4^+ have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

Figure 8.19



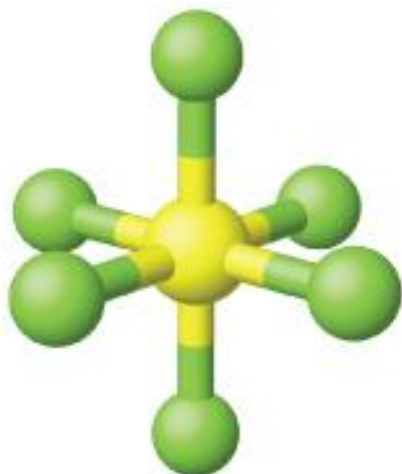
(a)



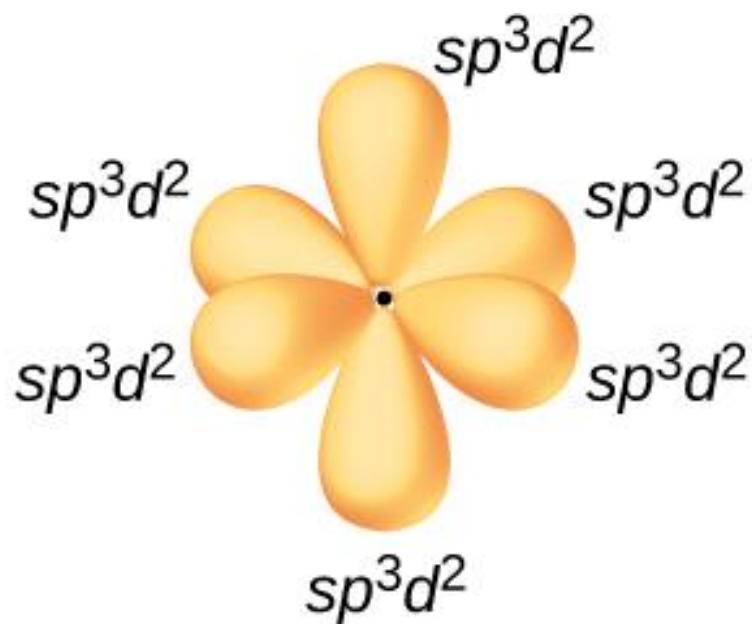
(b)

(a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

Figure 8.20








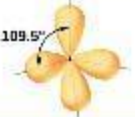

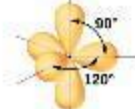

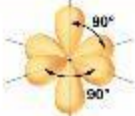
(a)



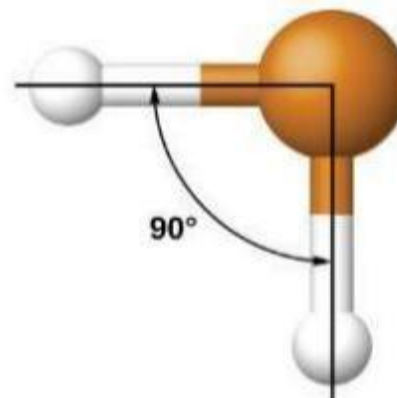
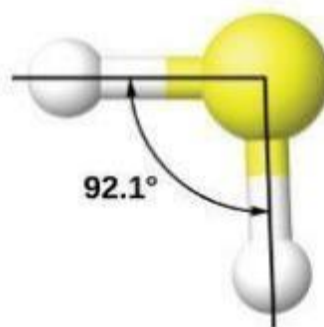
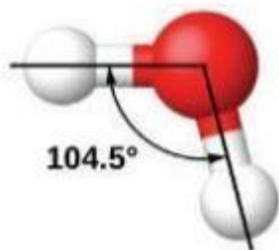
(b)

(a) Sulfur hexafluoride, SF₆, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

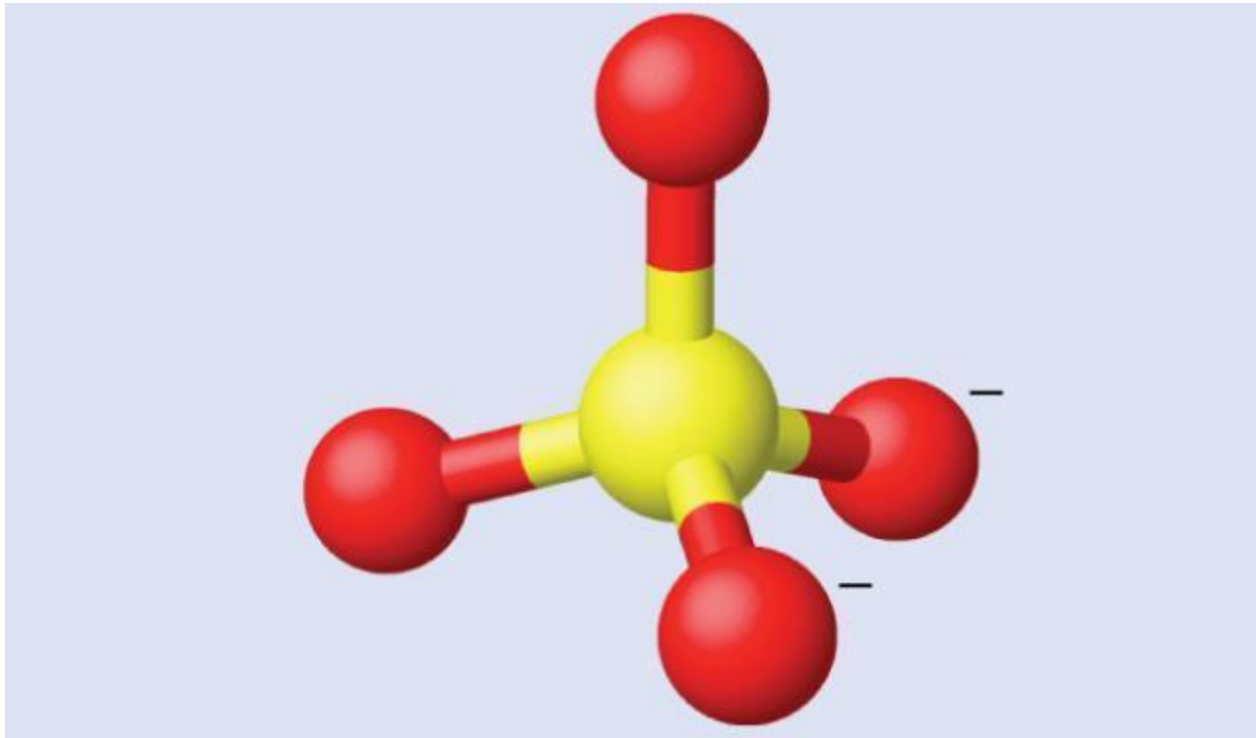
Figure 8.21

Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

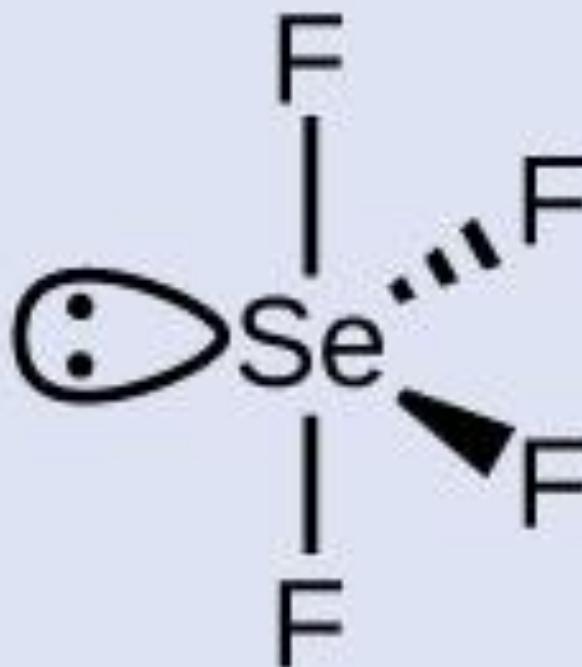
The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.



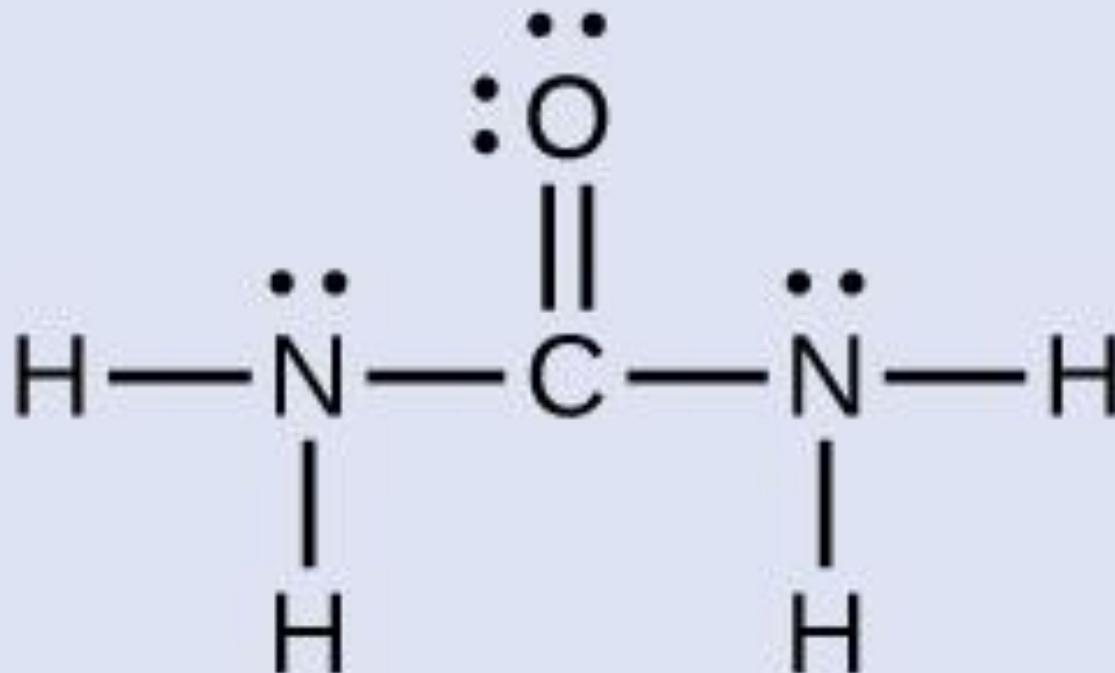
Example 8.2



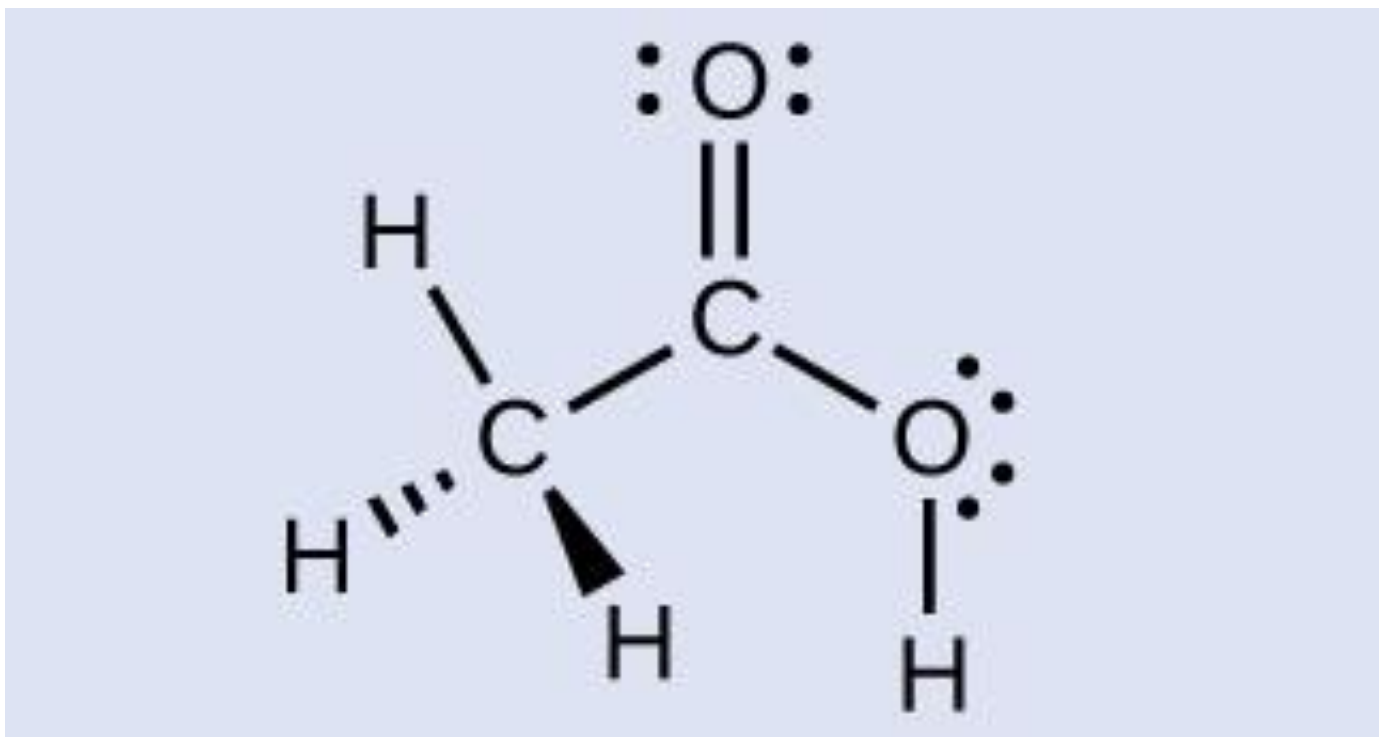
Example 8.2



Example 8.3



Example 8.3



Learning Objectives

- 8.3 Multiple Bonds
 - Describe multiple covalent bonding in terms of atomic orbital overlap
 - Relate the concept of resonance to π -bonding and electron delocalization

Single, Double, and Triple Bonds

- Single bonds are formed by the direct overlap of two hybrid orbitals, p orbitals, or s orbitals.
 - These are called sigma (σ) bonds.
- The additional electrons shared in a multi bond are not a result of directly overlapping hybrid orbitals, but are a *result of side-by-side overlap of two regular “ p ” atomic orbitals*.
 - These are called pi (π) bonds.
- **Single bond = 1 sigma bond**
- **Double bond = 1 sigma bond, 1 pi bond**
- **Triple bond = 1 sigma bond, 2 pi bonds**

Double and Triple Bonds

- To determine the hybridization in molecules with multi bonds, recall that a double or triple bond is each one region of electron density.

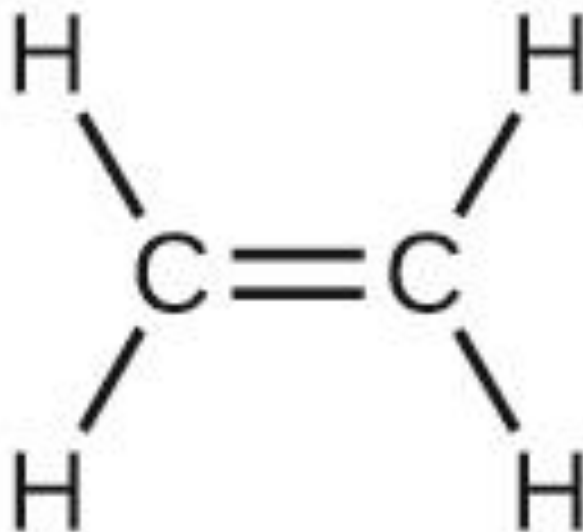
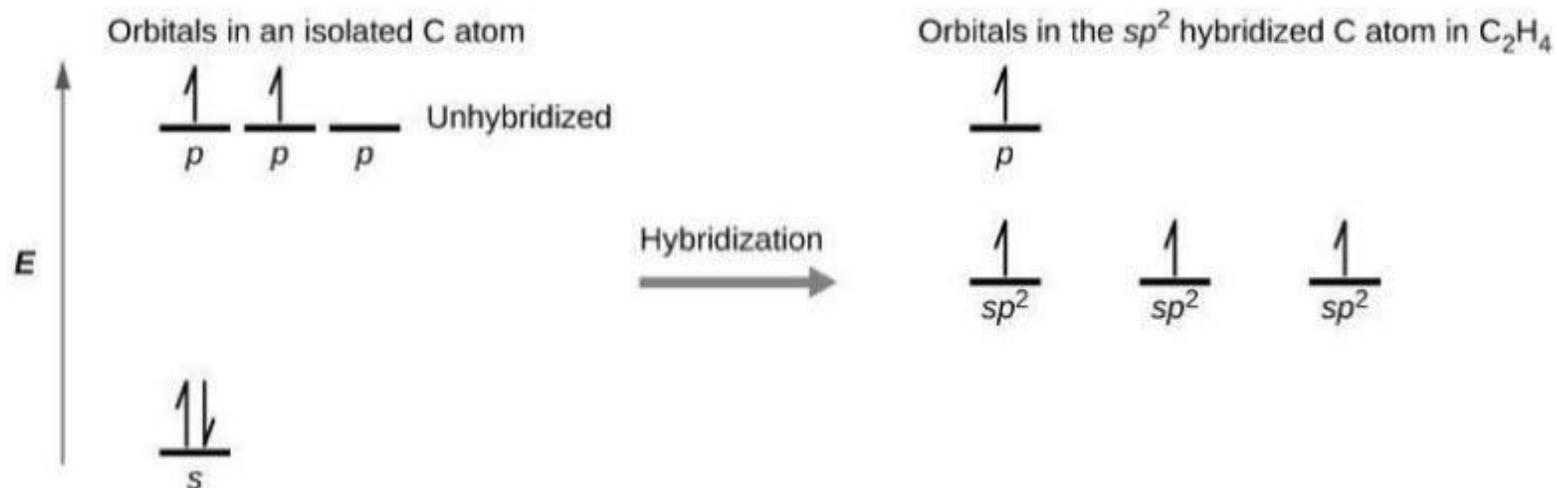
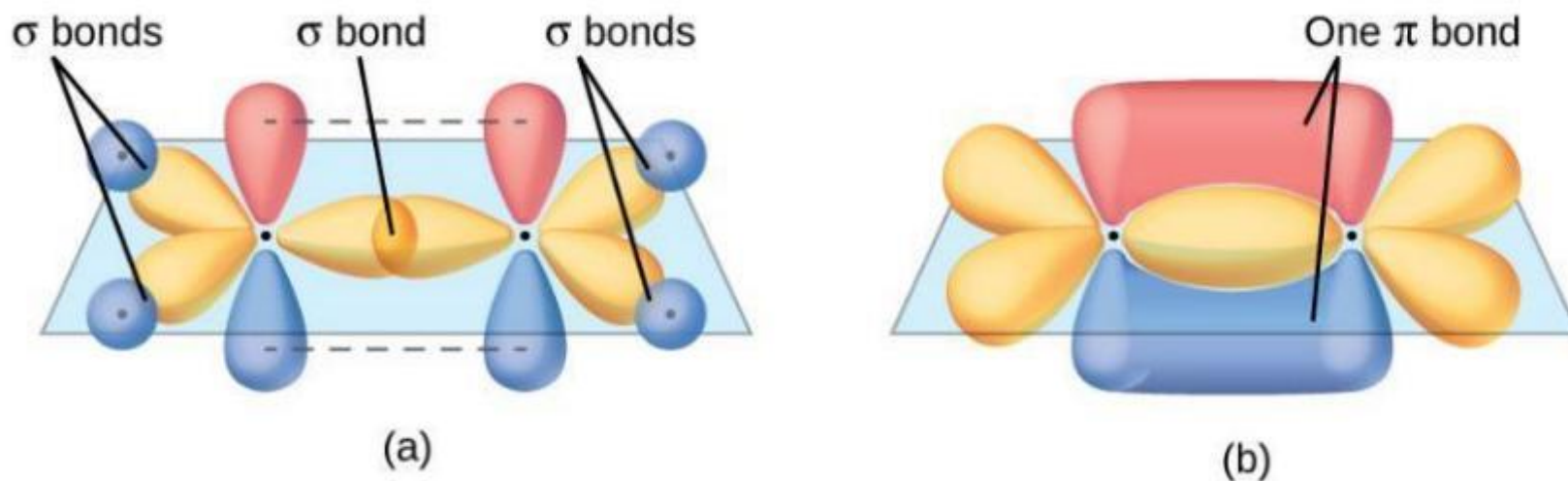


Figure 8.22



In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the p orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the p orbitals on each carbon atom overlap to form a π bond.

Figure 8.23



In the ethene molecule, C_2H_4 , there are (a) five σ bonds shown in purple. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms, which are shown in red. The two lobes of the π bond are above and below the plane of the σ system.

Double Bonds

- The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms, which are shown in red in Figure 8.23. The two lobes of the π bond are above and below the plane of the σ system.

Figure 8.24

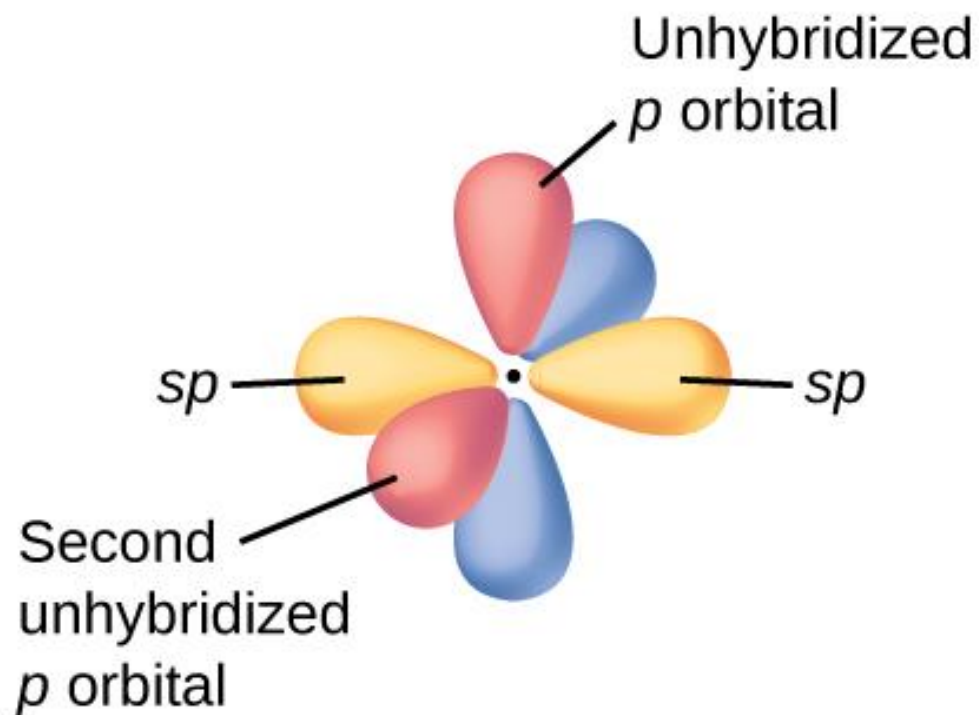
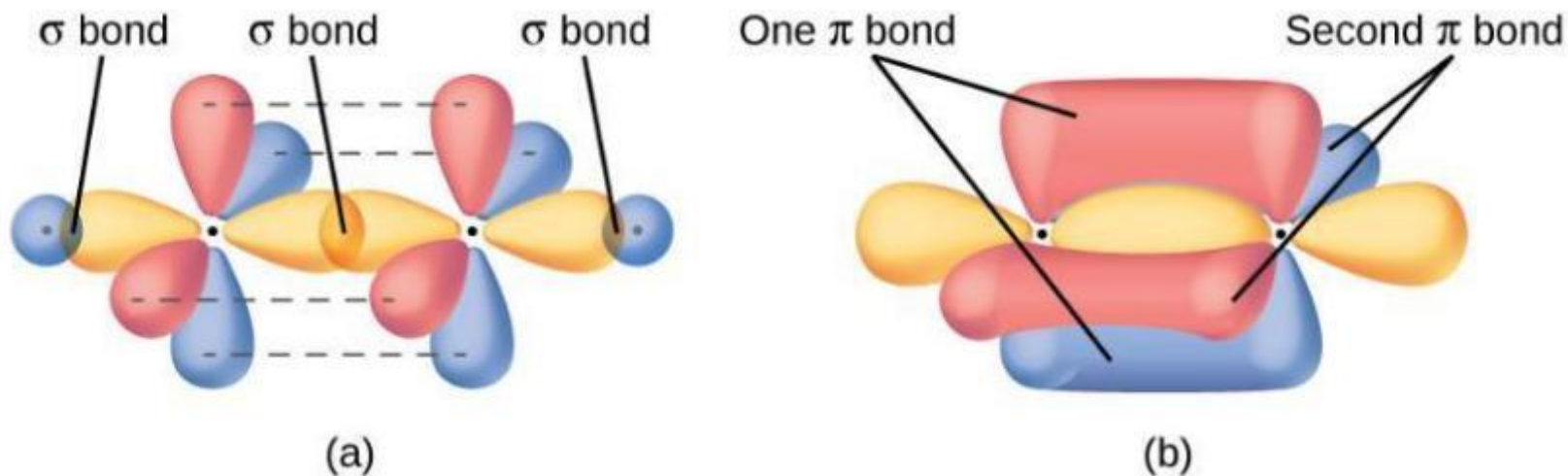


Diagram of the two linear sp hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized p orbitals at perpendicular angles.

Figure 8.25

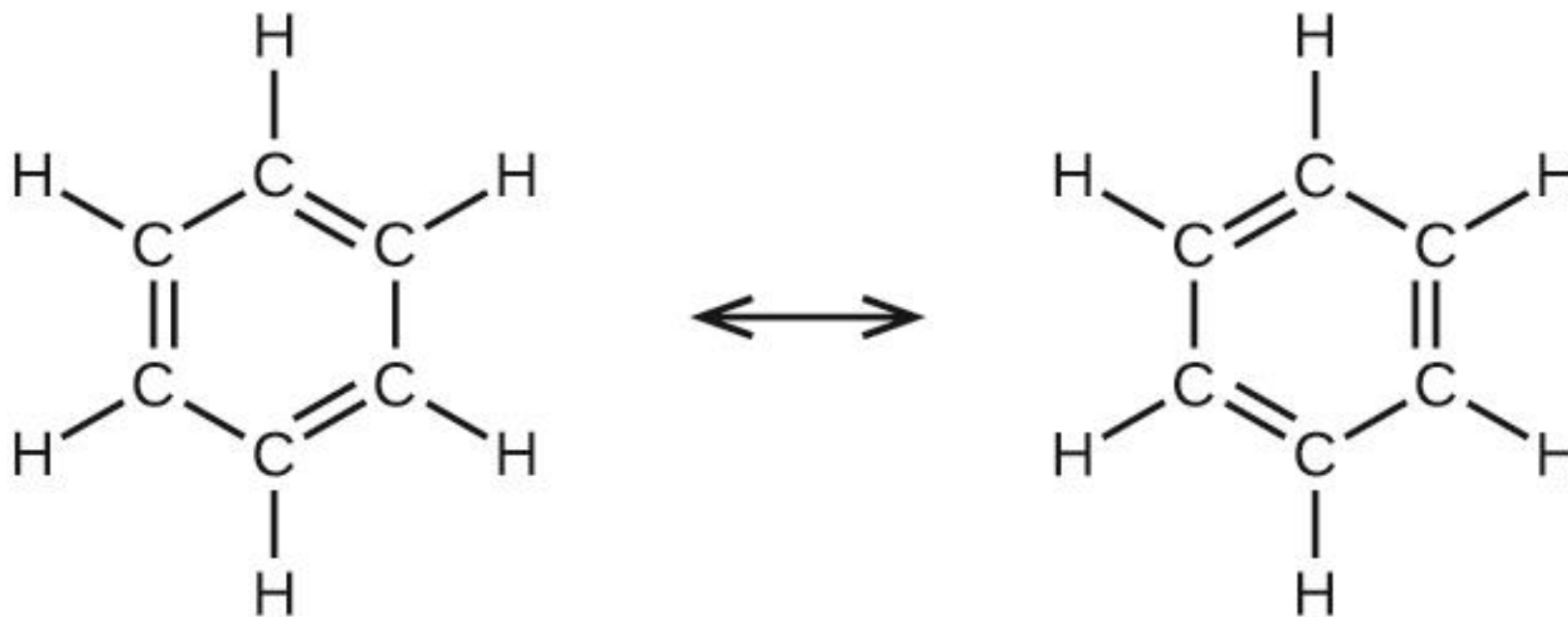


(a) In the acetylene molecule, C_2H_2 , there are two $C-H$ σ bonds and a $C \equiv C$ triple bond involving one $C-C$ σ bond and two $C-C$ π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized p orbitals. (b) This shows the overall outline of the bonds in C_2H_2 . The two lobes of each of the π bonds are positioned across from each other around the line of the $C-C$ σ bond.

Triple Bonds

- Figure 8.25 shows the overall outline of the bonds in C_2H_2 . The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Figure 8.26



Each carbon atom in benzene, C₆H₆, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of p orbitals or the other, but rather delocalized throughout the molecule.

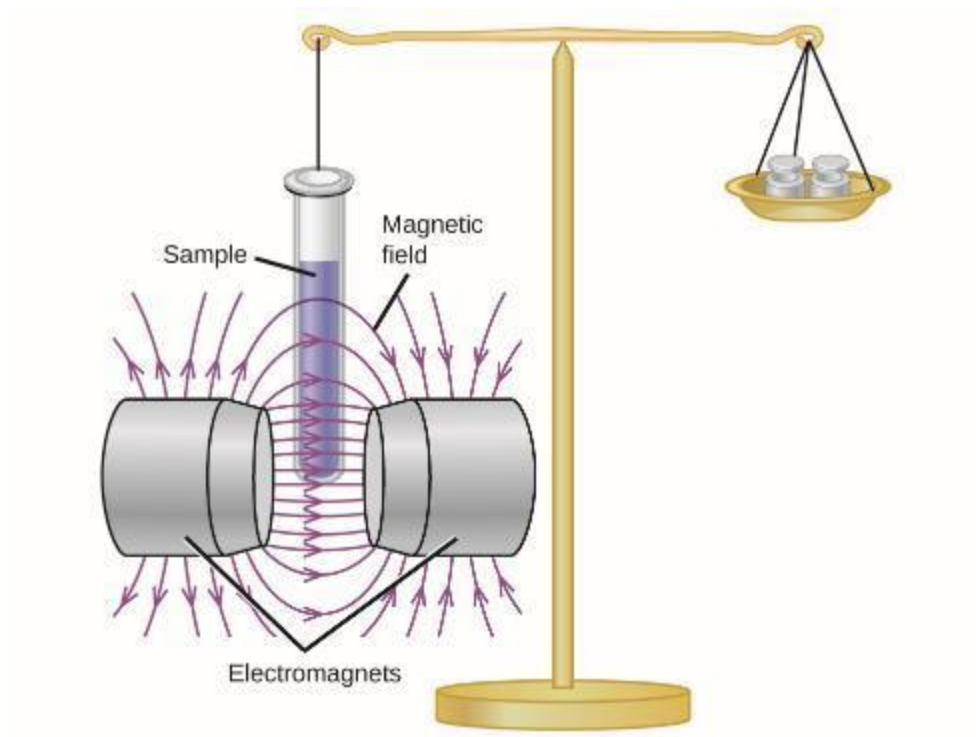
Example 8.4



Learning Objectives

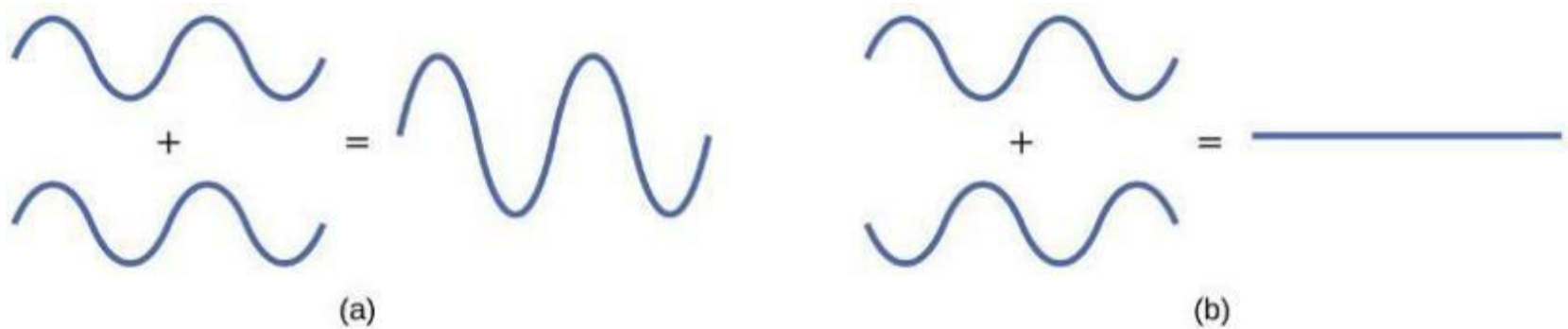
- 8.4 Molecular Orbital Theory
 - Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
 - Describe traits of bonding and antibonding molecular orbitals
 - Calculate bond orders based on molecular electron configurations
 - Write molecular electron configurations for first- and second-row diatomic molecules
 - Relate these electron configurations to the molecules' stabilities and magnetic properties

Figure 8.27



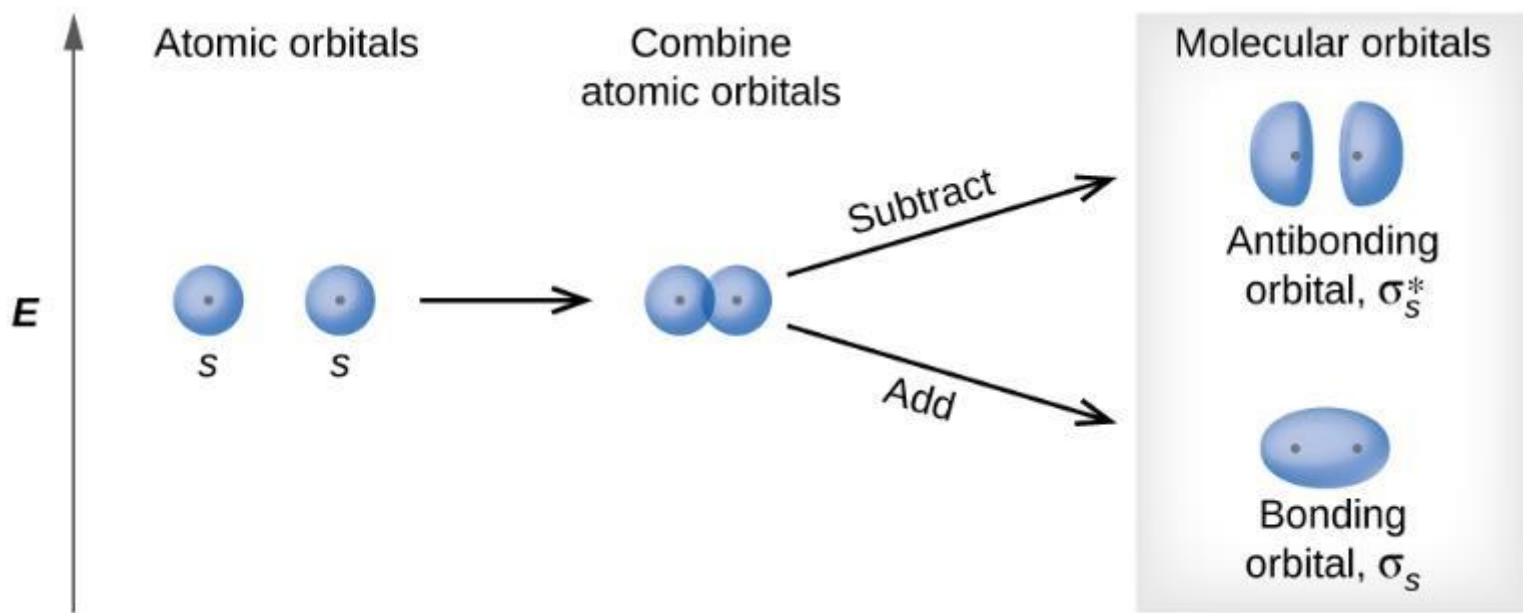
A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Figure 8.28



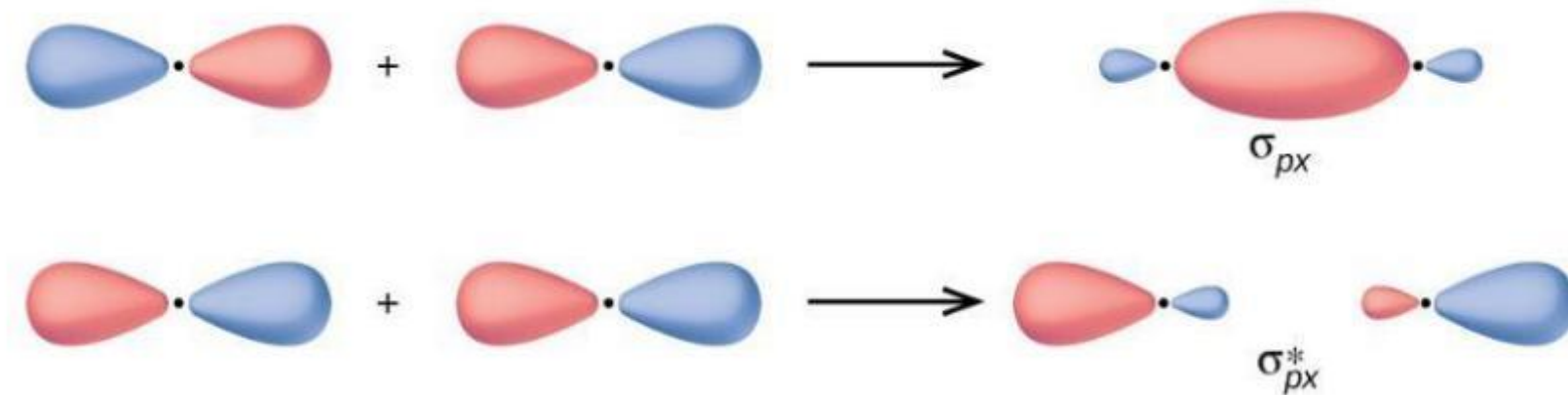
(a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

Figure 8.29



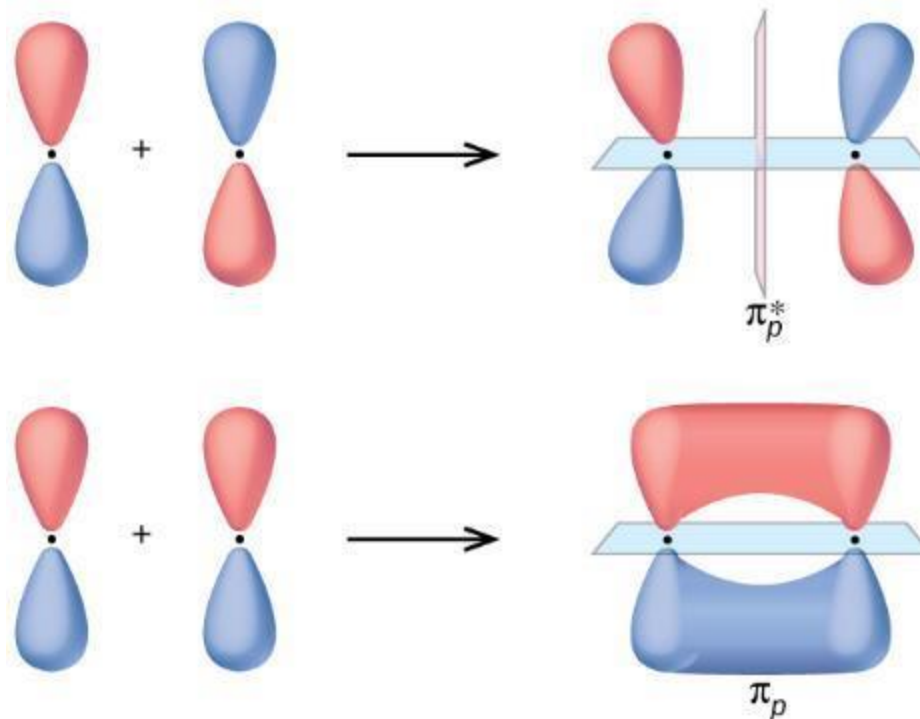
Sigma (σ) and sigma-star (σ^*) molecular orbitals are formed by the combination of two s atomic orbitals. The dots (•) indicate the locations of nuclei.

Figure 8.30



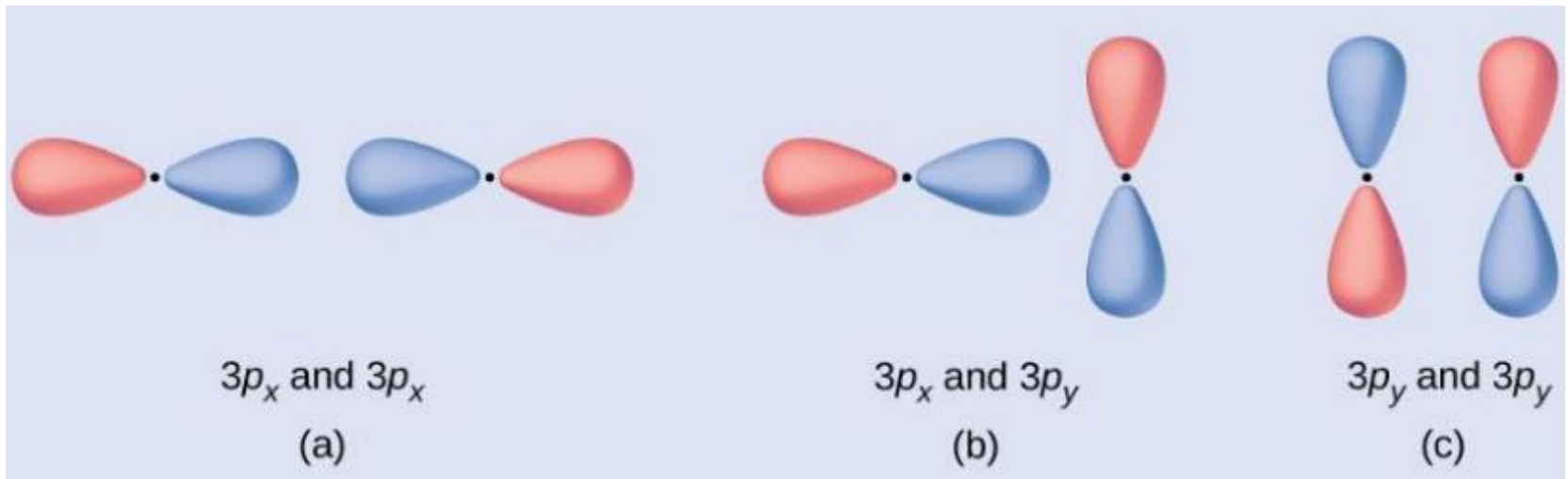
Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ_p^* .

Figure 8.31



Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the axis, and one contains the perpendicular. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue line) directly along the internuclear axis, but the orbital is located between the nuclei (red dots) above and below this node.

Example 8.5



Example 8.5



Example 8.5

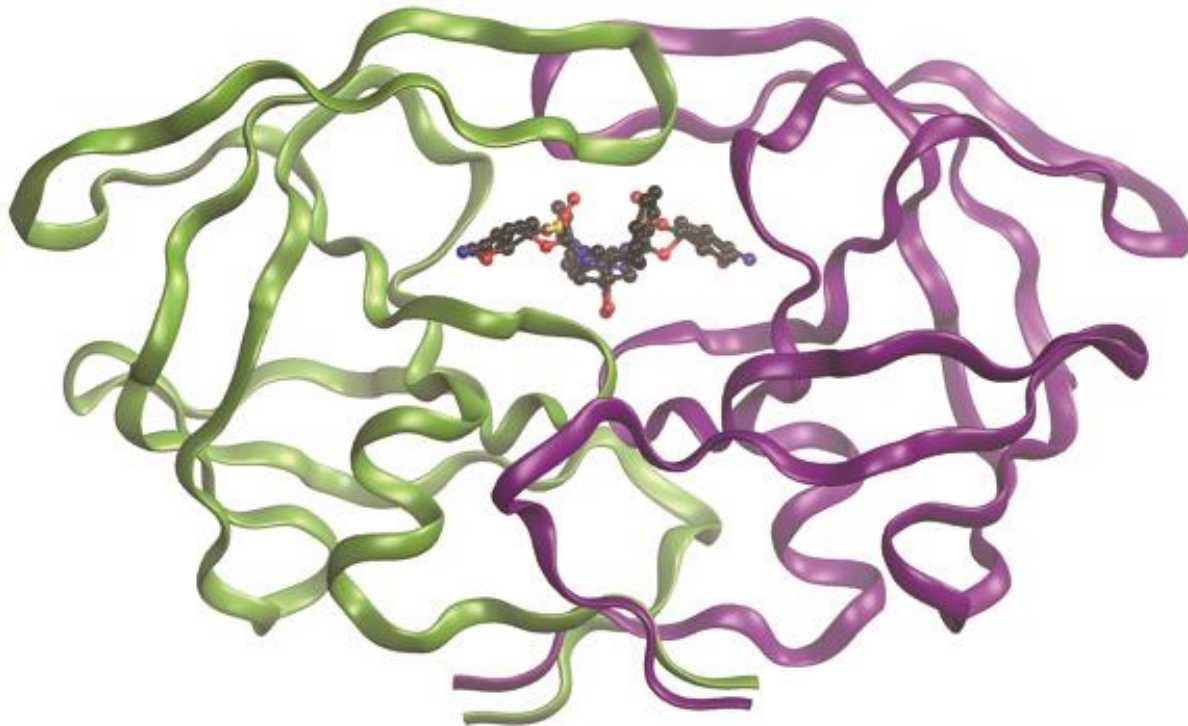


Figure 8.32



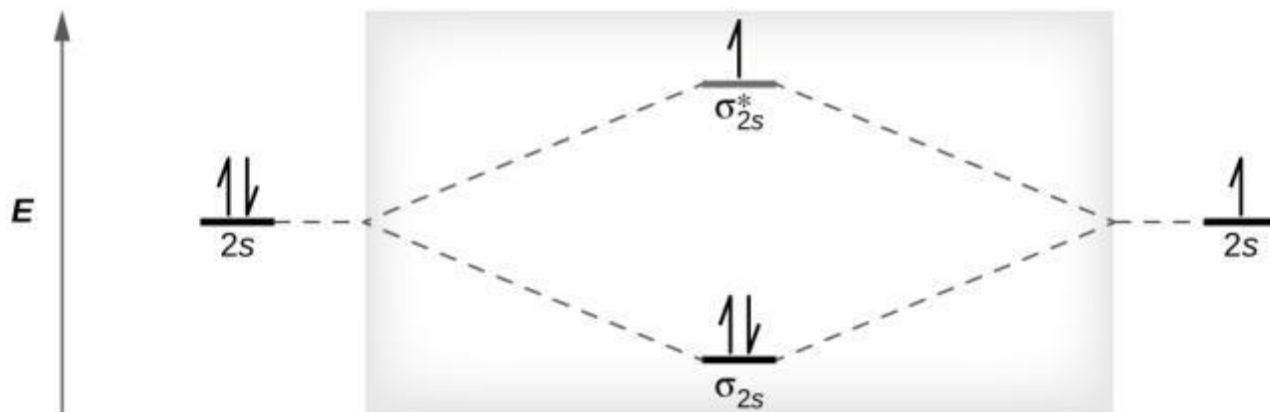
Walter Kohn developed methods to describe molecular orbitals. (credit: image courtesy of Walter Kohn)

Figure 8.33



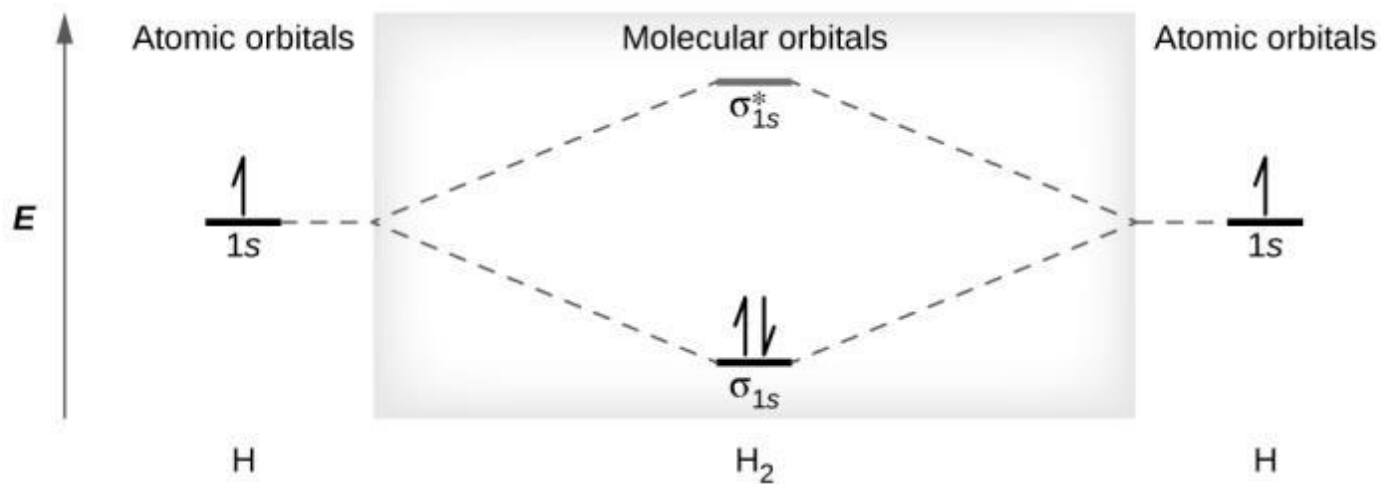
The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

Figure 8.34



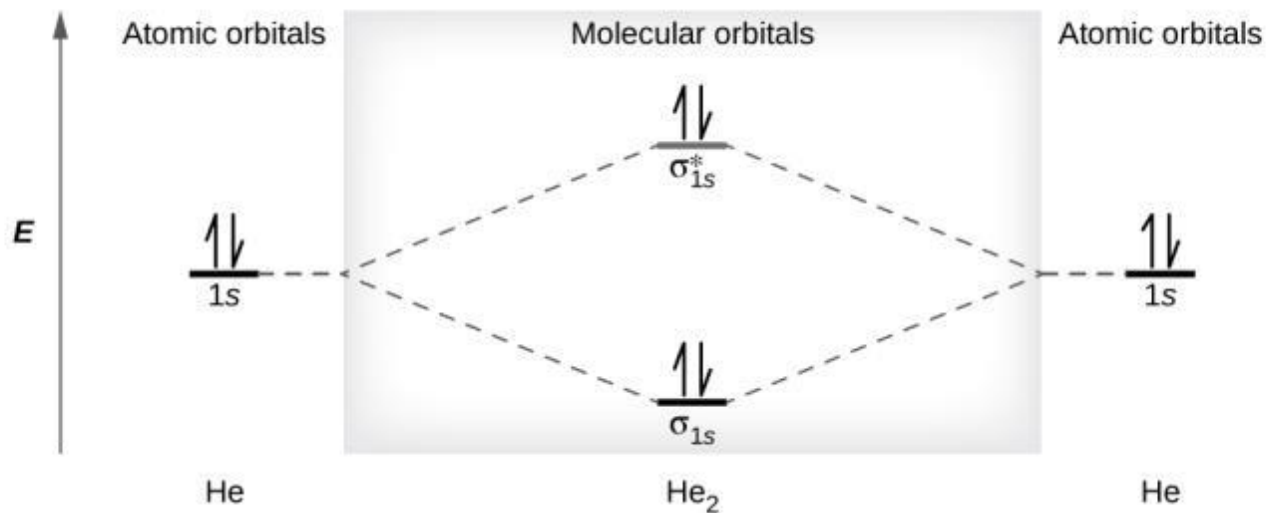
This is the molecular orbital diagram for the homonuclear diatomic Be_2^+ , showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Figure 8.35



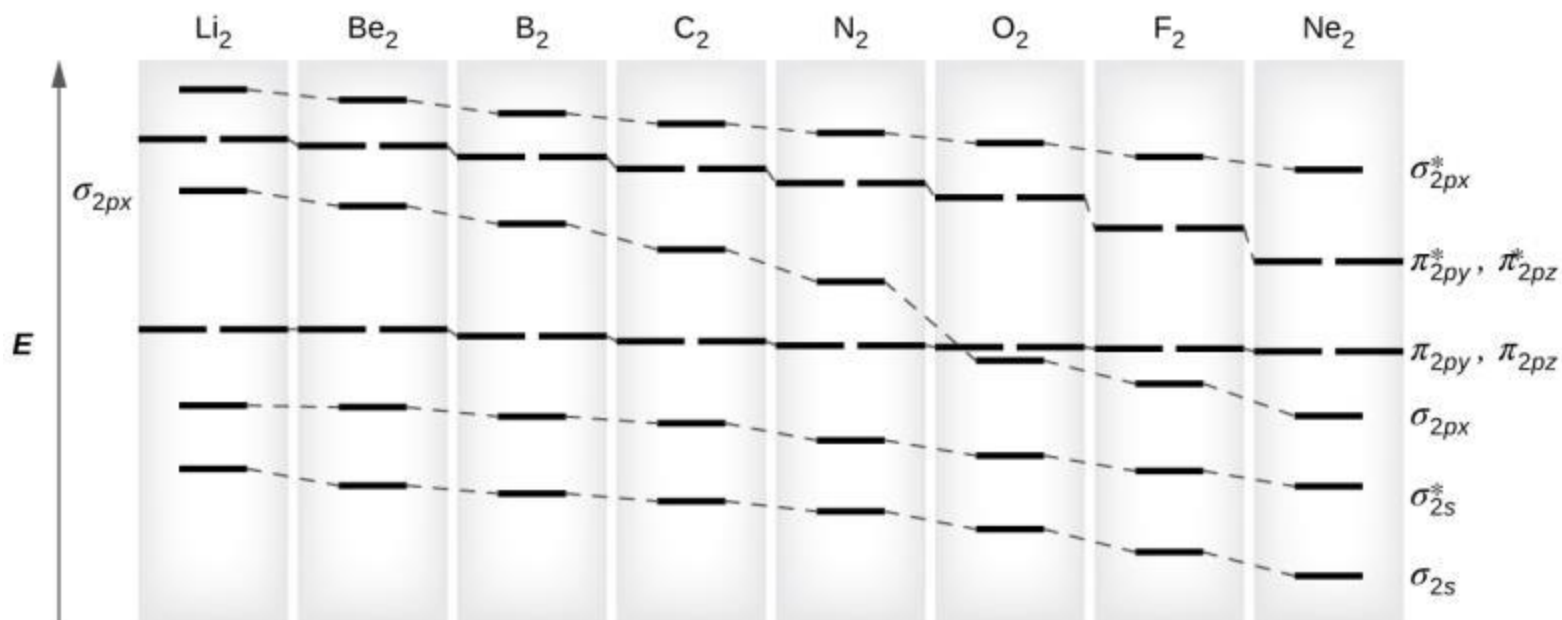
The molecular orbital energy diagram predicts that H₂ will be a stable molecule with lower energy than the separated atoms.

Figure 8.36



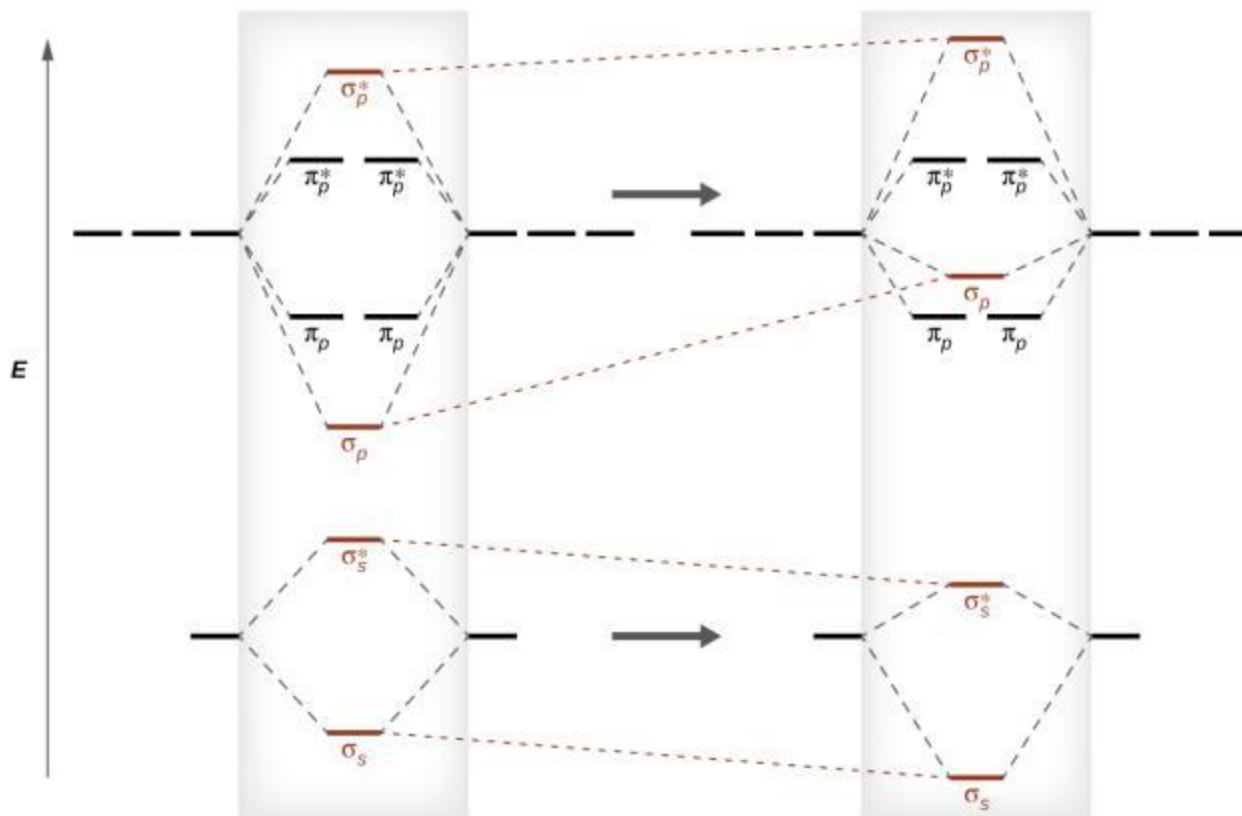
The molecular orbital energy diagram predicts that He₂ will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

Figure 8.37



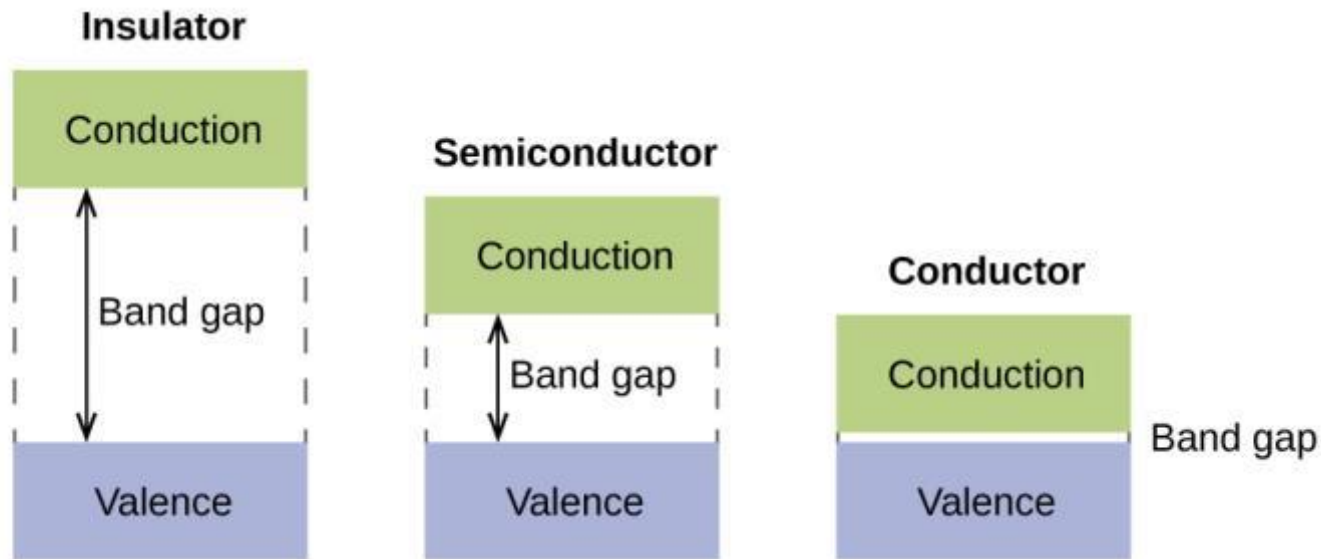
This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2 , the order of the orbitals changes.

Figure 8.38



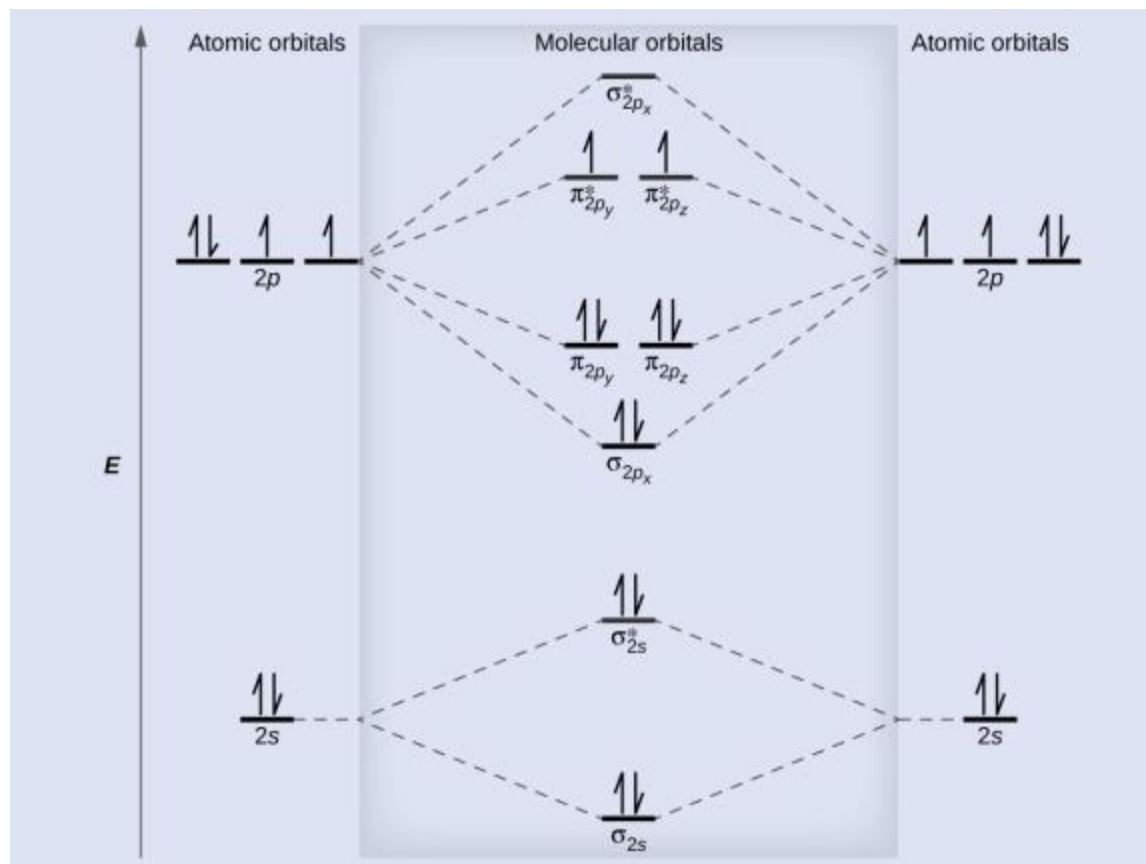
Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the π_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

Figure 8.39



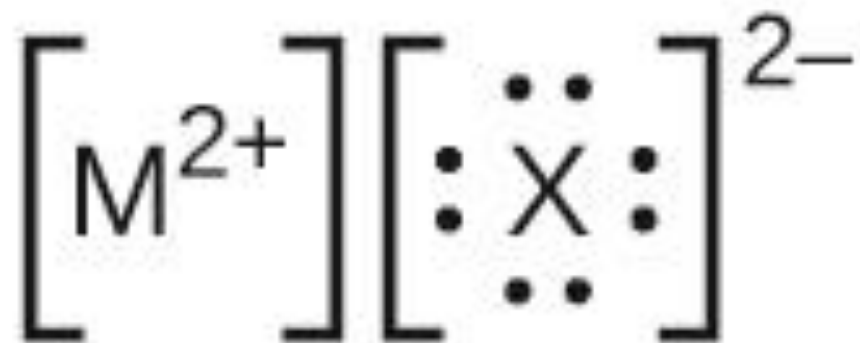
Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the “band gap” between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

Figure 8.40

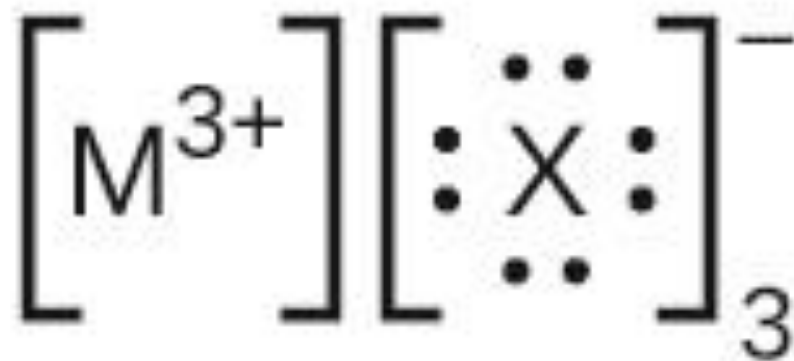


The molecular orbital energy diagram for O₂ predicts two unpaired electrons.

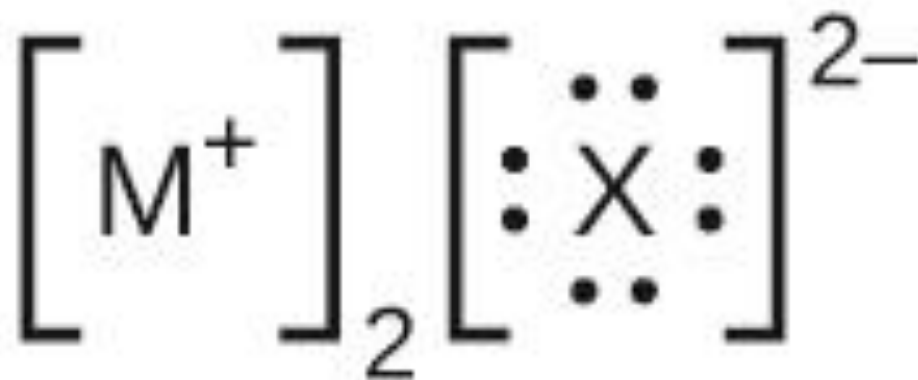
Exercise 26a



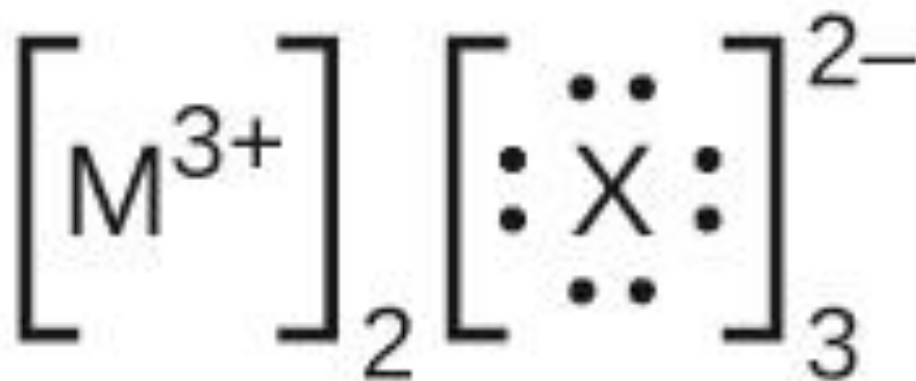
Exercise 26b



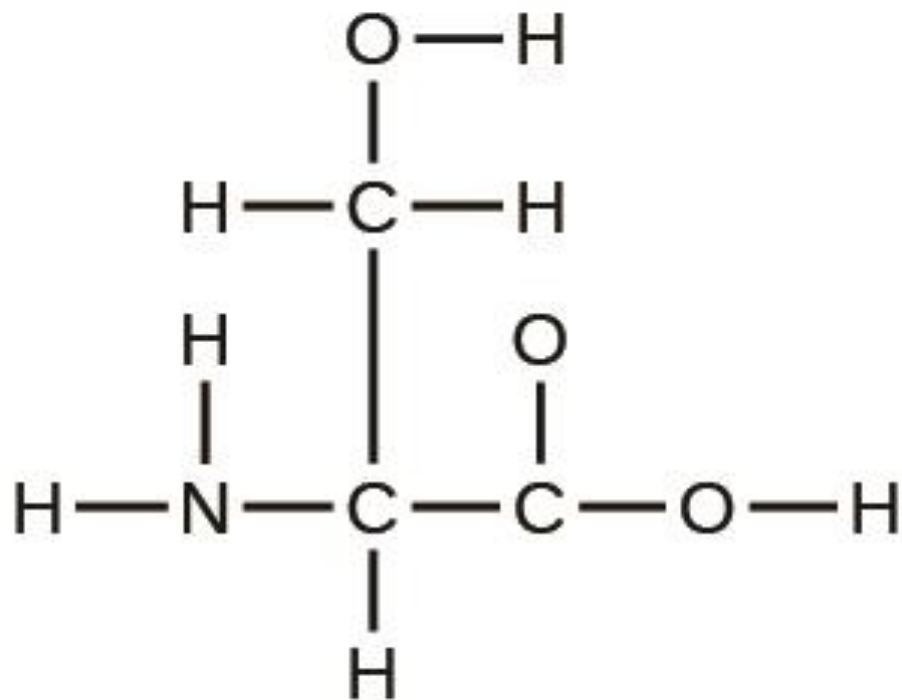
Exercise 26c



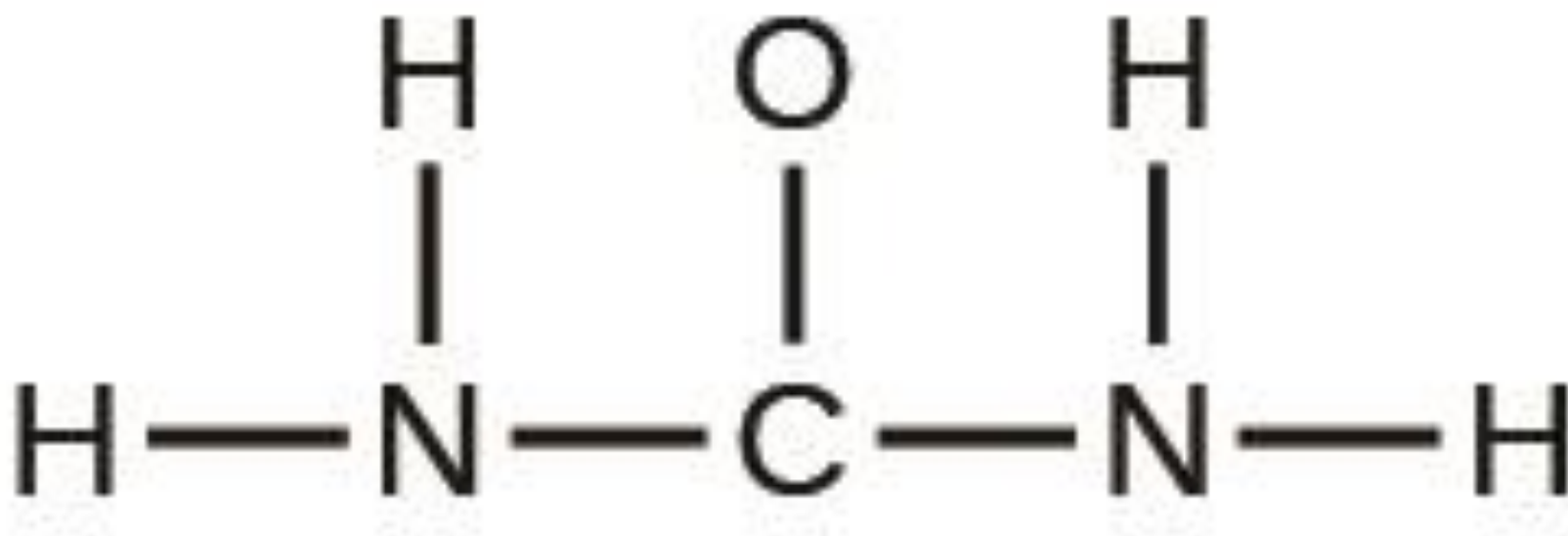
Exercise 26d



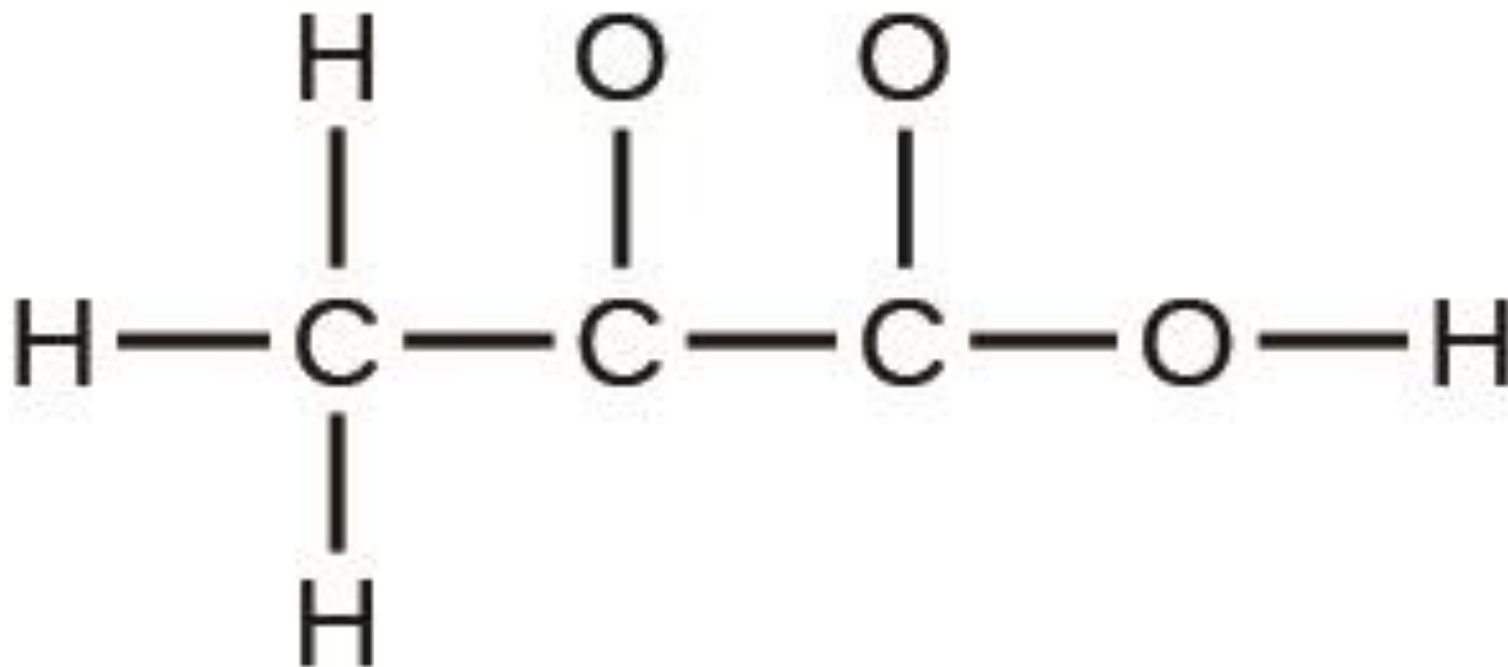
Exercise 39a



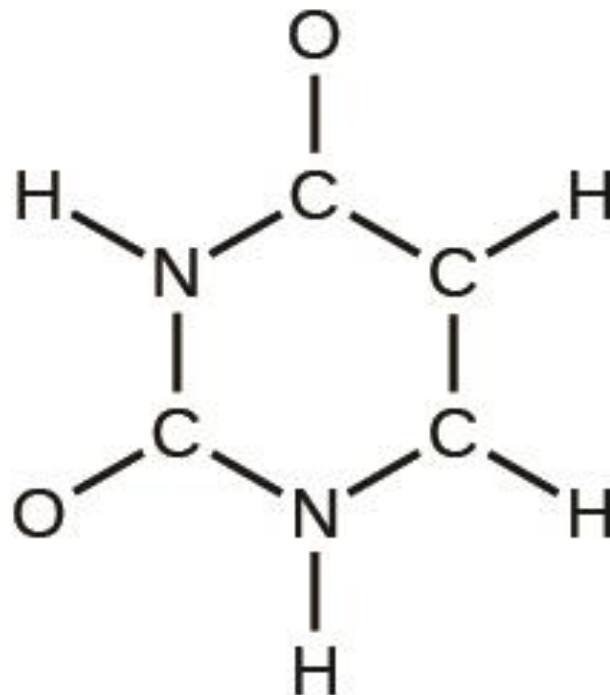
Exercise 39b



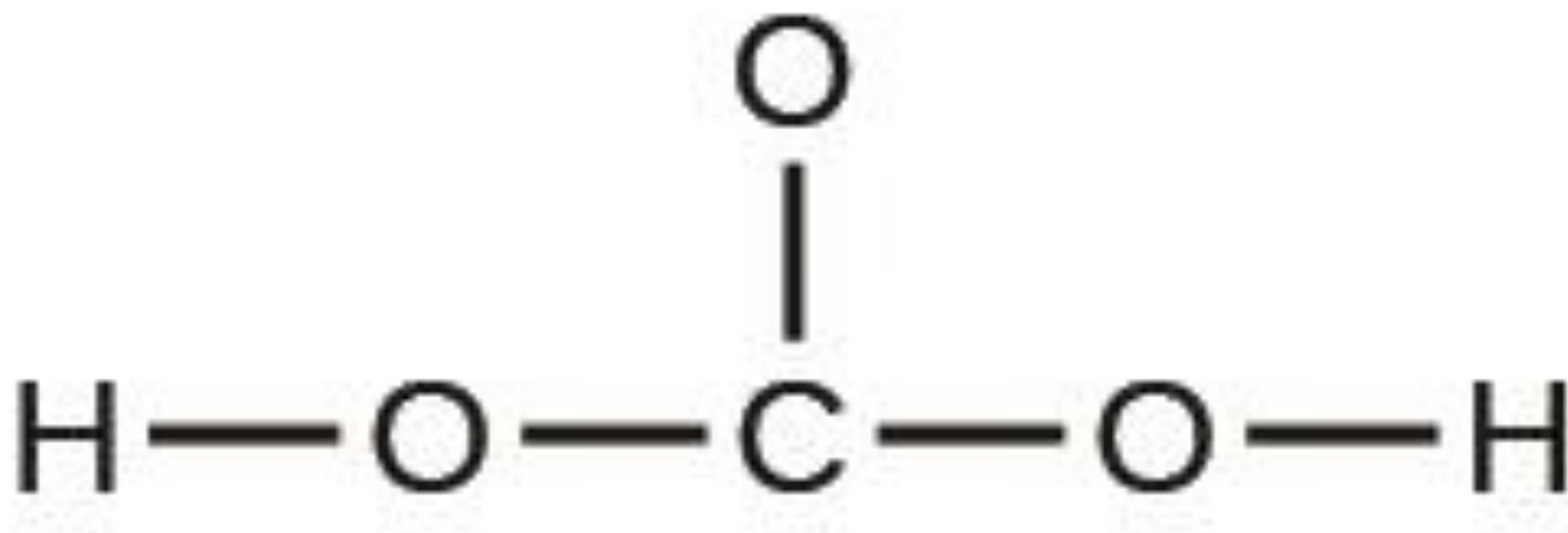
Exercise 39c



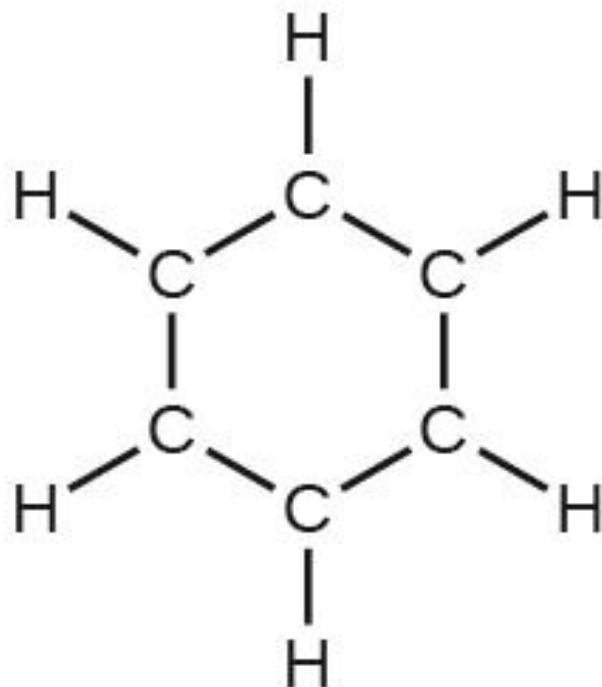
Exercise 39d



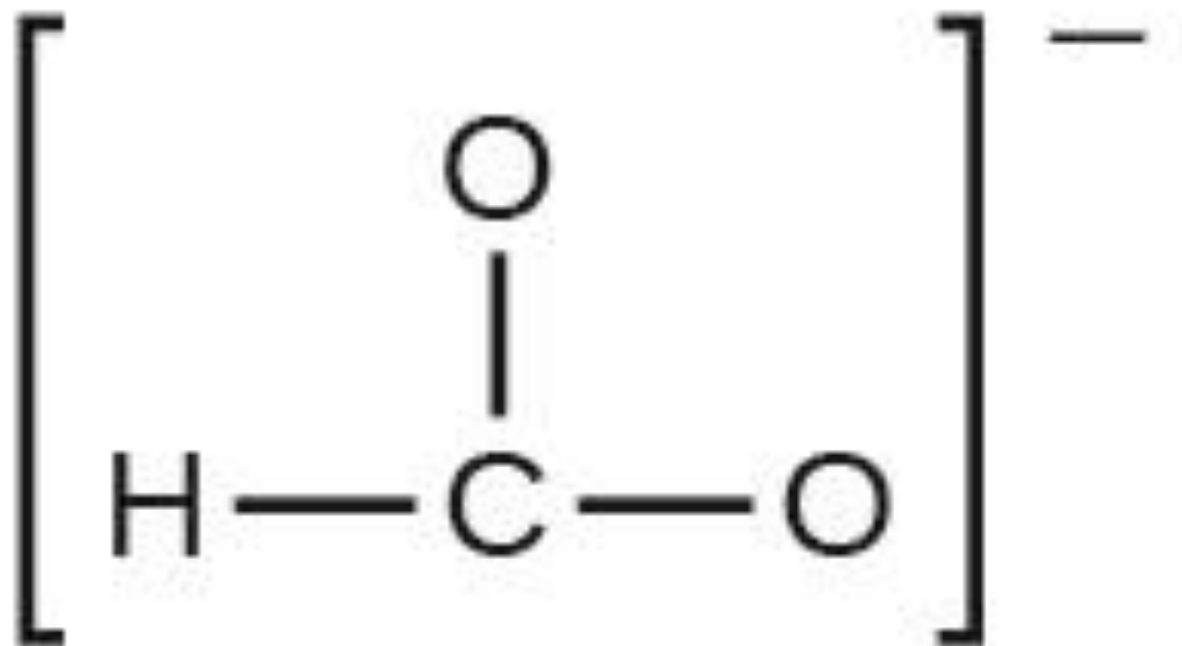
Exercise 39e



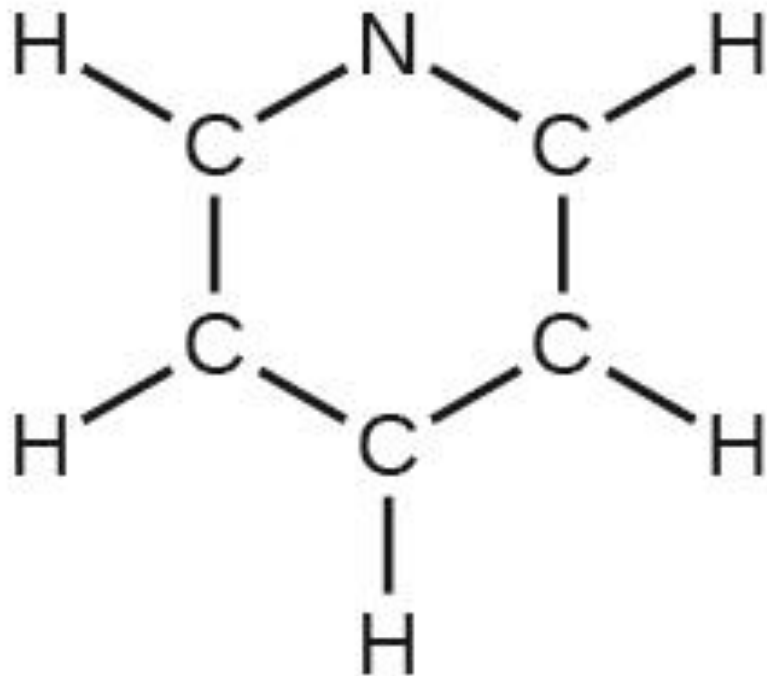
Exercise 44d



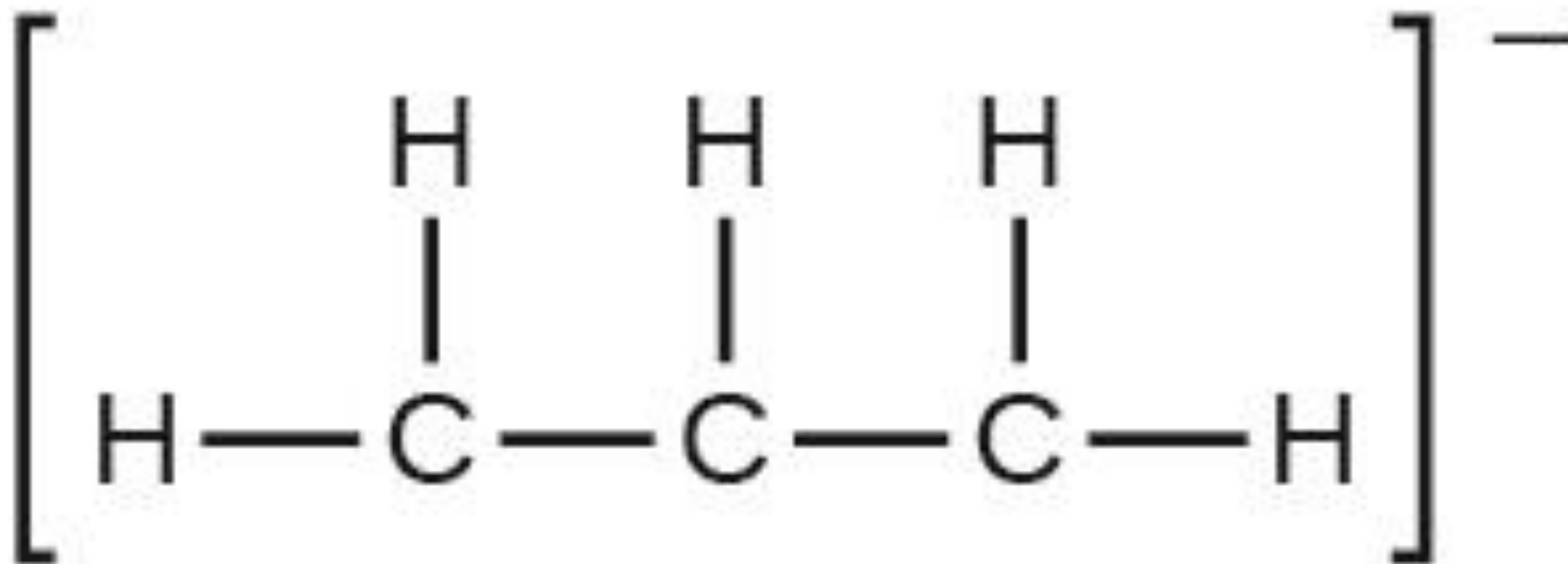
Exercise 44e



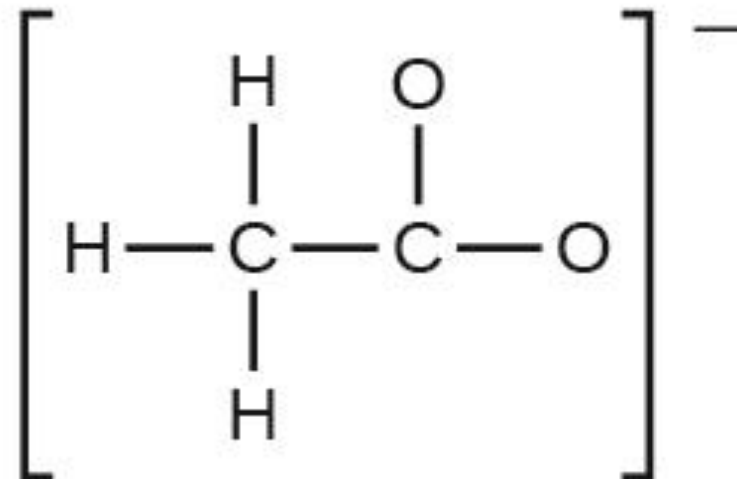
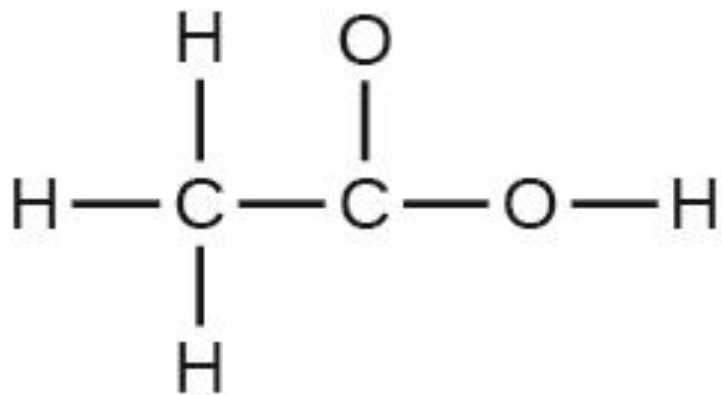
Exercise 45d



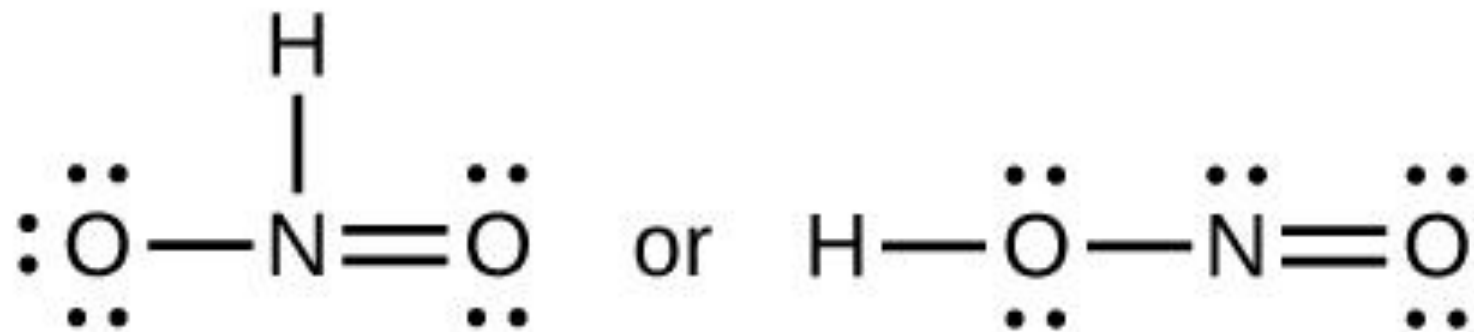
Exercise 45e



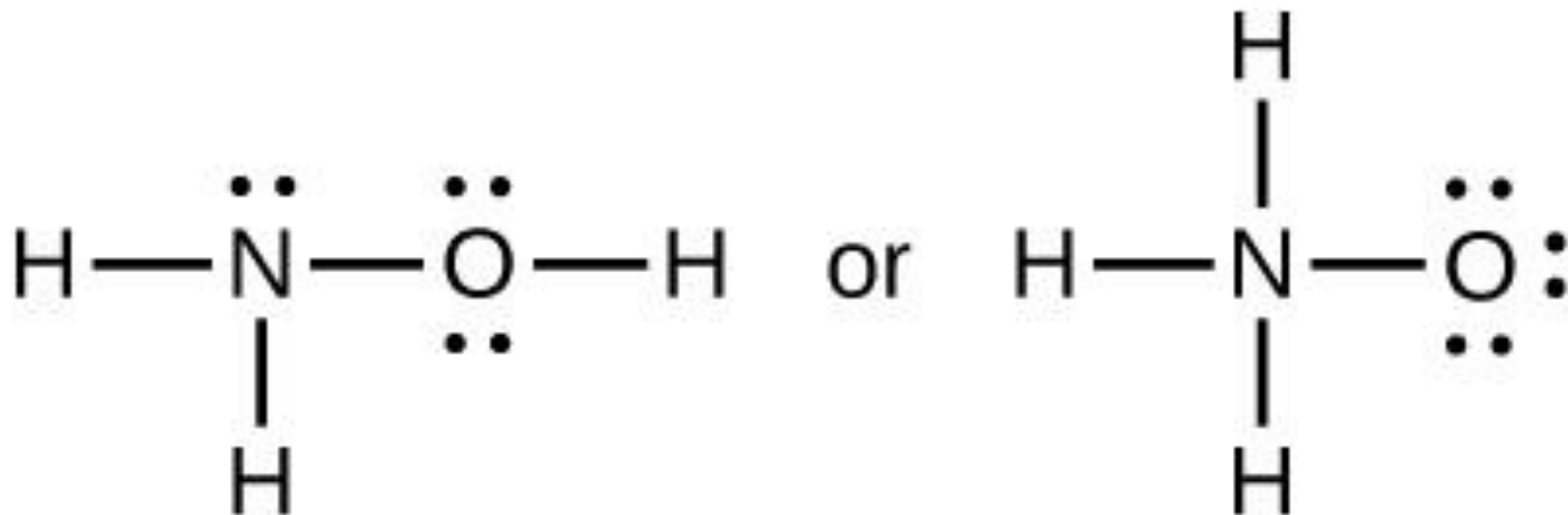
Exercise 48



Exercise 62



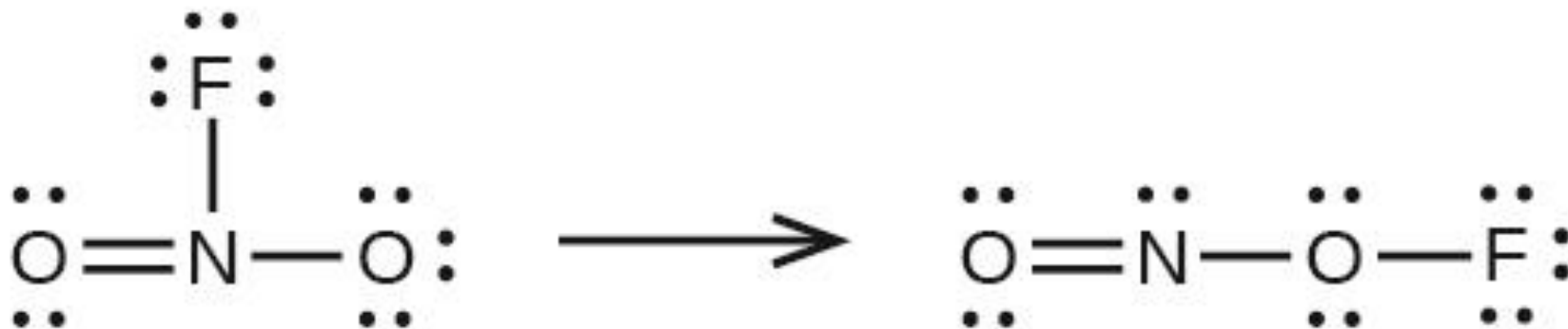
Exercise 67



Exercise 73



Exercise 74



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