

# 3

## BIG IDEA 2: BONDING AND STRUCTURE

### Big Idea 2

Chemical and physical properties of materials can be explained by the structure and the arrangement of atoms, ions, or molecules and the forces between them.

The chemical and physical properties you observe can be explained by the structure and arrangement of atoms, ions or molecules and the forces between them. Big Idea 2 is divided into four chapters, Chapters 3, 4, 5, and 6. In Chapter 3, you will learn about the different types of bonds that form, the nature of those bonds, a model that is used to predict the three-dimensional structure of covalently-bonded molecules. These are *intramolecular* forces, attractions *between* atoms *within* a molecule. You will also learn about *intermolecular* forces, the attractions *between* molecules that arise as a result of these bonds. You will apply these ideas as you learn about gases (Chapter 4), liquids and solids (Chapter 5), and solutions (Chapter 6).

You should be able to

- Identify the characteristics of ionic and covalent bonding.
- Identify the relative sizes of ions.
- Identify the effect of lattice energy on melting points of ionic compounds.
- Use electronegativity to predict the polarity of covalent bonds.
- Draw Lewis symbols for atoms and Lewis structures for molecular compounds and polyatomic ions.

- Assign molecular shapes using the VSEPR model for molecules, polyatomic ions, and multi-centered molecules and polyatomic ions, from linear through the octahedral shape.
- Assign hybrid orbitals to central atoms of molecules and polyatomic ions.
- Compare bond lengths and bond strengths in molecules.
- Identify the intermolecular forces in a substance.
- Know the difference between intramolecular forces (chemical bonds) and intermolecular forces (forces of attraction).
- Predict and explain the properties of substances based on their chemical formulas, and to provide explanations based on drawing representations of the substances and their intermolecular forces.

## IONIC BONDING

(Chemistry 8th ed. pages 341–342/9th ed. pages 352–353)

Ionic bonding is the result of electrostatic attraction of oppositely charged ions. Ionic compounds form when an atom which loses electrons easily (atoms with low electron affinity) reacts with an atom that has a high affinity for electrons. Most of the time, an ionic compound is formed when a metal reacts with a nonmetal.

## COULOMB'S LAW

(Chemistry 8th ed. pages 341–342/9th ed. pages 352–353)

Coulomb's law expresses the energy of interaction between a pair of ions. This is directly proportional to the charge on each ion and inversely proportional to the distance between the ions. The greater the charge on the ions, the stronger the ionic bond, and if the charges are equal, then we expect a smaller ion to have a stronger ionic bond. Note that the energy will always be negative because one ion is a cation (positive) and the other an anion (negative).

$$E = (2.31 \times 10^{-19} \text{ J} \cdot \text{nm}) \left( \frac{Q_1 Q_2}{r} \right).$$

$E$  is the energy of interaction between a pair of ions, in joules.

$r$  is the distance in nanometers between ion centers.

$Q_1$  and  $Q_2$  are the charges of the ions.

## IONS: ELECTRON CONFIGURATION AND SIZES

(Chemistry 8th ed. pages 350–353/9th ed. pages 361–365)

### **PREDICTING FORMULAS OF IONIC COMPOUNDS; FORMATION OF IONIC COMPOUNDS**

When a metal and a nonmetal react, each forms an ion with a noble gas configuration in its valence shell. The metal loses all of its

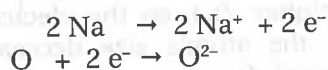
outermost electrons while the nonmetal gains electrons to complete its valence shell.

**EXAMPLE:** Explain how atoms of sodium and oxygen form an ionic compound.

**SOLUTION:** Sodium and oxygen have the following valence electron configurations:



The electronegativity of oxygen is much greater than that of sodium, so electrons are transferred from sodium to oxygen. Oxygen needs two electrons to fill its 2p valence orbitals and to achieve the configuration of neon. Sodium loses one electron to achieve the electron configuration of neon. Two sodium atoms are needed to give one oxygen atom the two electrons necessary to fill its valence orbitals. The oxide ion has an electron configuration like that of neon.



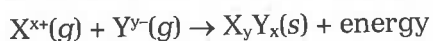
Using electron configurations:



## LATTICE ENERGY

(Chemistry 8th ed. pages 355–357/9th ed. pages 367–369)

Lattice energy is the energy release that occurs when separated gaseous ions are packed together to form an ionic solid.



$$\text{Lattice energy} = k \left( \frac{Q_1 Q_2}{r} \right)$$

$k$  is a proportionality constant dependent on the structure of the solid and the electron configuration of the ions.

$r$  is the distance in nanometers between the ion centers.

$Q_1$  and  $Q_2$  are the charges of the ions.

**EXAMPLE:** Which has the more exothermic lattice energy, NaCl or KCl?

**SOLUTION:** NaCl has the more exothermic lattice energy. The product  $Q_1 \times Q_2$  is the same for both substances so the denominator must be considered.  $\text{Na}^+$  is smaller than  $\text{K}^+$ , so the distance between the centers of the sodium and chloride ions is less than the distance between the potassium and chloride ions. For identical numerators, a smaller denominator gives a more exothermic lattice energy.

## COVALENT BONDING

(Chemistry 8th ed. page 342/9th ed. page 353)

Covalent bonding involves sharing valence electrons between nuclei with similar electronegativities. A covalent or molecular compound is usually formed by bonding two or more nonmetals. There are some metallic compounds that have covalent bonds, such as beryllium chloride,  $\text{BeCl}_2$ , because the electronegativities of the atoms are similar.

## ELECTRONEGATIVITY

(Chemistry 8th ed. pages 344–346/9th ed. pages 356–358)

Electronegativity measures the ability of an atom in a molecule to attract shared electrons to itself. The two factors affecting electronegativity are effective nuclear charge ( $Z_{\text{eff}}$ ) and electron shielding. Going from left to right across a period, there are more protons pulling on electrons (higher  $Z_{\text{eff}}$ ), so the electron shells are pulled closer into the nucleus, the atomic size decreases, and the electronegativity increases. Going down a column, more electron shells are added, shielding the valence electrons from the positively charged nucleus, so the atomic size increases and the electronegativity decreases.

**EXAMPLE:** Place the following atoms in order of increasing electronegativity: Cs, Rb, S, Al, Sr, O.

**SOLUTION:** In order of increasing electronegativity:  $\text{Cs} < \text{Rb} < \text{Sr} < \text{Al} < \text{S} < \text{O}$ .

Electronegativity increases from the lower left to the upper right of the periodic table.

## POLAR BOND

(Chemistry 8th ed. pages 343–349/9th ed. pages 355–360)

The type of bond formed between two atoms is related to the difference in electronegativity between the two atoms. For identical atoms, such as a molecule of hydrogen, the electronegativity difference is zero. There is an equal sharing of electrons between the atoms, and the bond formed is a nonpolar covalent bond. When the difference in electronegativities is very small (less than 0.4), the bond is described as nonpolar. An important nonpolar covalent bond is the C–H bond in organic compounds.

When two atoms have a very large difference (greater than 1.7) in electronegativity, an ionic bond forms. For example, atoms of lithium and chlorine have a large difference in electronegativity and form an ionic compound.

A polar covalent bond results when there is an unequal sharing of electrons. The difference in the electronegativities of atoms in the polar covalent bond is between that of the ionic and nonpolar bonds (greater than 0.3 but less than 1.7). In general, the farther apart two

atoms are on the periodic table, the more polar the bond. Fluorine is the most electronegative atom, so the closer an atom is to fluorine, the more electronegative it is. An example of a polar covalent bond is HF, which has the following charge distribution.



**EXAMPLE:** Which of the following three bonds will be most polar? O-F, N-F, C-F

**SOLUTION:** The most polar bond will be the bond in which the difference in electronegativities is the greatest. Since you are not given electronegativities in this question, you must estimate the differences by looking at how far apart the atoms are on the periodic table. C is further from F than N or O, so the C-F bond is most polar, followed by N-F and O-F.

## BOND POLARITY AND DIPOLE MOMENTS

Fluorine is the most electronegative element in the periodic table. When HF is placed in an electric field, the molecules tend to orient themselves with the fluoride end toward the positive pole and the hydrogen end toward the negative pole. HF is said to have a dipole moment, having two poles. An arrow points to the negative charge center and the tail of the arrow indicates the positive center of charge.



A diatomic molecule with a polar bond has a dipole moment. Molecules with more than two atoms can also have dipolar behavior. This is addressed in the section on molecular shapes where we look at the distribution of charge in the molecule.

## LOCALIZED ELECTRON BONDING MODEL

(Chemistry 8th ed. page 364/9th ed. page 376)

The localized electron model assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms. Lone pairs are pairs of electrons which are localized in an area around one atom. Bonding pairs occupy the space between atoms.

## LEWIS STRUCTURES

(Chemistry 8th ed. pages 365–372/9th ed. pages 376–383)

The Lewis structure shows how the valence electrons are arranged among atoms in a molecule.

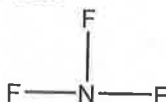
Steps for writing Lewis structures:

1. Sum the total valence electrons from each atom. For a polyatomic ion, add one electron for each negative charge on the anion, or take away one electron for each positive charge on the cation.
2. Place the least electronegative element in the middle. (Hydrogen can never be in the middle because it can form only one bond.) Draw the outer atoms around the central atom. Chemical formulas are often written in the order in which they are connected, such as HCN. The central atom is sometimes written first in a formula, when a central atom has a group of other atoms bonded to it, as in  $\text{SO}_4^{2-}$ .
3. Connect the central atom to the outer atoms using a line to indicate each pair of bonding electrons.
4. Count the valence electrons used in the bonds in step 3 and subtract these from the total valence electrons in step 1 to determine how many valence electrons remain.  
Valence electrons left =  
Total valence electrons (step 1) – Valence electrons used (step 3).
5. Arrange the remaining electrons around the atoms to follow the octet rule for families 4A–7A outer atoms to satisfy the duet rule for hydrogen (hydrogen needs only two electrons to have a filled orbital) and the octet rule for second-row elements and the periods following.
6. Determine the number of valence electrons remaining as in step 4. Place the remaining electrons on the central atom to satisfy the octet rule for elements in the second row and after.
  - a. If there are no electrons remaining to satisfy the central atom, then add a double bond for every pair of electrons you are “short” and readjust the number of electrons on each surrounding atom.
  - b. Elements in periods higher than the second can have more than eight electrons. If  $n > 2$ , then  $d$  orbitals exist and the number of electrons that can surround the element can exceed eight.
7. Check that the valence electrons drawn = the total valence electrons in step 1.

**EXAMPLE:** Draw the Lewis Structure for  $\text{NF}_3$ .

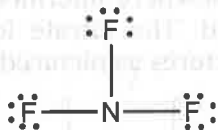
**SOLUTION:** Step 1: Total valence electrons =  $[1 \times \text{N}(5 e^-) + 3 \times \text{F}(7 e^-)] =$   
 $5 e^- + 21 e^- = 26$  valence electrons.

Steps 2 and 3: Place nitrogen in the middle and connect the fluorine atoms to nitrogen using a line to represent a single bond which is a pair of electrons.

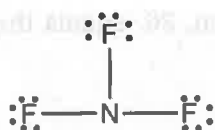


Step 4: Count the valence electrons used. Count two electrons for each single bond ( $2 \times 3$  single bonds = 6 electrons used). Count the electrons left.  $26 - 6 = 20$  electrons left.

Step 5: Satisfy the octet rule for each of the outer fluorine, F, atoms. Each F atom needs six more to complete the octet.



Step 6: Count electrons remaining after satisfying the outer atoms.  $20 - 6(3)$  used = 2 electrons left. Place remaining electrons on central atom, nitrogen, and its octet is completed.



Step 7: Check that electrons drawn, 26, equals the total valence electrons in step 1.

## RESONANCE

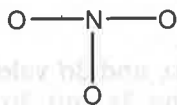
(Chemistry 8th ed. pages 373–374/9th ed. pages 384–385)

Resonance occurs when more than one correct Lewis structure can be drawn for a molecule or ion.

**EXAMPLE:** Draw the Lewis structure for the nitrate ion,  $\text{NO}_3^-$ .

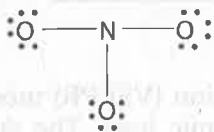
**SOLUTION:** Step 1: Total valence electrons: 5 from N and 6 from each O and 1 from the negative charge on the ion =  $5 + 3(6) + 1 = 24$ .

Step 2: Place nitrogen in the middle and connect the oxygen atoms to nitrogen.



Step 4: Count valence electrons used, 2 for each single bond ( $2 \times 3$  single bonds = 6 electrons used). Count the electrons left.  $24 - 6 = 18$  electrons left.

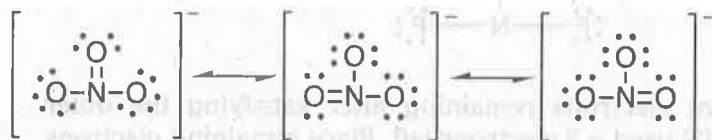
Step 5: Satisfy the octet rule for each of the outer atoms of oxygen. Each O atom needs six more to complete the octet.



Step 6: Count electrons remaining after satisfying the outer atoms.  $18 - 6(3)$  used = 0 electrons left. The central atom, N, still

needs two more electrons to satisfy the octet rule. You can add a double bond for every pair of electrons you are “short.”

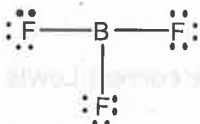
One double bond forms between the N and the O. A double bond is made of two pairs of electrons. However, the nitrate ion does not have one double bond and two single bonds. All of the three bonds are the same length, somewhere intermediate between a single bond and a double bond. The nitrate ion exists as an average of three resonance structures as pictured below.



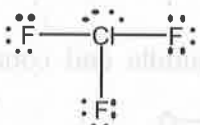
Step 7: Check that electrons drawn, 26, equals the total valence electrons in step 1.

### EXCEPTIONS TO THE OCTET RULE

Elements with a  $Z$  value less than 6 often do not follow the octet rule. For example, boron tends to form compounds in which boron can have fewer than eight electrons, such as boron trifluoride,  $\text{BF}_3$ . Boron can have six electrons around it.



Some elements in period 3 of the periodic table and beyond can exceed the octet rule. For example,  $\text{ClF}_3$ , has 10 electrons around the central atom.



Elements in the third period have  $3s$ ,  $3p$ , and  $3d$  valence orbitals. The valence electrons in chlorine occupy the  $3s$  and  $3p$  orbitals. The  $3d$  orbital is empty and can hold extra electrons. Elements in the second period have only  $2s$  and  $2p$  orbitals. These elements cannot have more than eight electrons in their valence orbitals because they do not have  $d$  orbitals available.

## MOLECULAR STRUCTURE: THE VSEPR MODEL

(Chemistry 8th ed. pages 378–389/9th ed. pages 389–402)

The valence shell electron-pair repulsion (VSEPR) model predicts the geometries of molecules and polyatomic ions. The structure around the central atom is determined by minimizing electron-pair repulsions. Bonding and nonbonding pairs of electron are positioned as far apart as possible. Nonbonding or lone pairs of electrons require more room

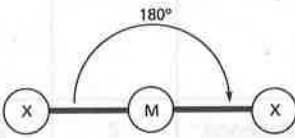
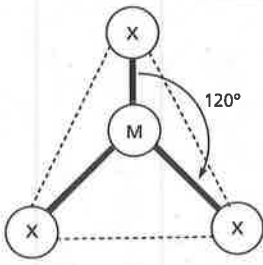
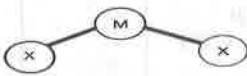


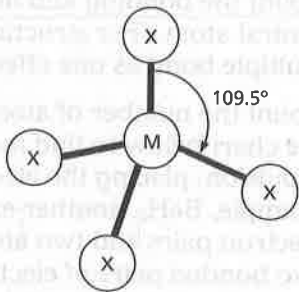
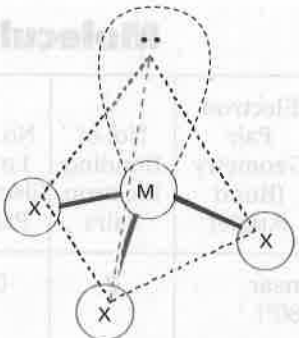
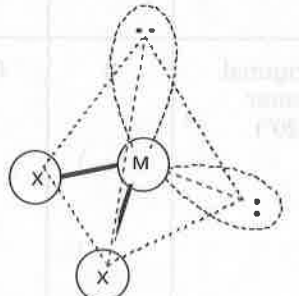
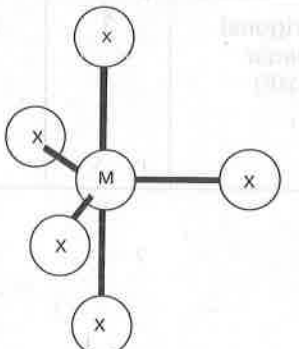
than bonding pairs and tend to compress the angle between bonding pairs.

Steps to apply the VSEPR model:

1. Draw the Lewis structure of the molecule.
2. Count the bonding and nonbonding electron pairs around the central atom. (For structures with multiple bonds, count the multiple bond as one effective pair of electrons.)
3. Count the number of atoms attached to the central atom. Look in the chart below to find the arrangement that minimizes that repulsion, placing the electrons as far apart as possible. For example,  $\text{BeH}_2$ , another exception to the octet rule, has two electron pairs and two atoms attached to the central atom. If the two bonded pairs of electrons are placed  $180^\circ$  apart, the resulting linear geometry has minimal repulsion.

### Molecular Shapes and Bond Angles

No. of Electron Pairs	Electron Pair Geometry (Bond Angle)	No. of Bonding Electron Pairs	No. of Lone Electron Pairs	Molecular Geometry	Formula	2D Structure	Hybrid Orbital
2	Linear ( $180^\circ$ )	2	0	Linear	$\text{BeH}_2$		$sp$
3	Trigonal planar ( $120^\circ$ )	3	0	Trigonal planar	$\text{CO}_3^{2-}$		$sp^2$
3	Trigonal planar ( $120^\circ$ )	3	1	Bent	$\text{NO}_2^-$		$sp^2$

No. of Electron Pairs	Electron Pair Geometry (Bond Angle)	No. of Bonding Electron Pairs	No. of Lone Electron Pairs	Molecular Geometry	Formula	2D Structure	Hybrid Orbital
4	Tetrahedral (109.5°)	4	0	Tetrahedral	CH <sub>4</sub>		$sp^3$
4	Tetrahedral (>109.5°)	3	1	Trigonal pyramidal	NH <sub>3</sub>		$sp^3$
4	Tetrahedral (>>109.5°)	2	2	Bent	H <sub>2</sub> O		$sp^3$
5	Trigonal bipyramidal (90°, 120°)	5	0	Trigonal bipyramidal	PCl <sub>5</sub>		$sp^3d$

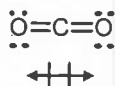
Hybridization beyond  $sp^3$  is beyond scope of course but is included here for completeness and clarity.

No. of Electron Pairs	Electron Pair Geometry (Bond Angle)	No. of Bonding Electron Pairs	No. of Lone Electron Pairs	Molecular Geometry	Formula	2D Structure	Hybrid Orbital
5	Trigonal bipyramidal (90° and >120°)	4	1	Seesaw unsymmetrical tetrahedron	SF <sub>4</sub>		$sp^3d$
5	Trigonal bipyramidal (90° and 180°)	3	2	T-shaped	BrF <sub>3</sub>		$sp^3d$
5	Trigonal bipyramidal (180°)	2	3	Linear	ICl <sub>2</sub> <sup>-</sup>		$sp^3d$
6	Octahedral (90°)	6	6	Octahedral	SF <sub>6</sub>		$sp^3d^2$

No. of Electron Pairs	Electron Pair Geometry (Bond Angle)	No. of Bonding Electron Pairs	No. of Lone Electron Pairs	Molecular Geometry	Formula	2D Structure	Hybrid Orbital
6	Octahedral (90°)	5	1	Square pyramidal	BrF <sub>5</sub>		sp <sup>3</sup> d <sup>2</sup>
6	Octahedral (90°)	4	2	Square planar	ICl <sub>4</sub> <sup>-</sup>		sp <sup>3</sup> d <sup>2</sup>

**EXAMPLE:** Predict the molecular structure of the carbon dioxide molecule. Is this molecule expected to have a dipole moment?

**SOLUTION:** First we must draw the Lewis structure for the CO<sub>2</sub> molecule.



In this structure for CO<sub>2</sub>, there are two effective pairs around the central atom (each double bond is counted as one effective pair). There are two atoms attached to the central atom.

According to the table, a linear arrangement is required.

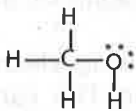
Each C–O bond is polar, but, since the molecule is linear, the dipoles cancel out and the molecule is nonpolar.

**EXAMPLE:** Draw the Lewis structure for PF<sub>5</sub> and identify the molecular geometry.



**SOLUTION:** PF<sub>5</sub> has 40 valence electrons. Connecting 5 F atoms to P, the central atom, uses 10 electrons in five single bonds. The 30 remaining electrons can be used to satisfy the octet rule for each F atom. There are 5 electron pairs around P and 5 atoms attached to P, resulting in a trigonal bipyramidal shape.

**EXAMPLE:** Draw the Lewis structure for  $\text{CH}_3\text{OH}$ .



**SOLUTION:** This molecule has more than one central atom, the carbon and the oxygen. Hydrogen cannot be in the middle since it can form only one bond. Draw the correct Lewis structure and then using the rules for VSEPR, assign the molecular geometry around each central atom. The carbon atom has four electron pairs around it and four atoms attached resulting in tetrahedral geometry. Oxygen also has four electron pairs around it, but only has two atoms attached. This leads to bent geometry around oxygen.

**EXAMPLE:** Arrange the following molecules in order of increasing bond angles:  $\text{H}_2\text{S}$ ,  $\text{CCl}_4$ ,  $\text{NF}_3$ .

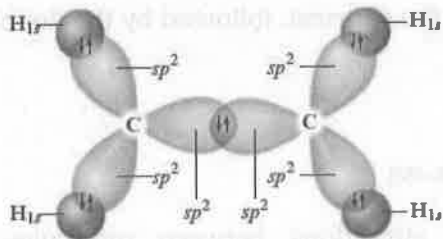
**SOLUTION:** First, draw the correct Lewis structure for each molecule and then assign an approximate bond angle for each.

Each of the four molecules has four electron pairs around the central atom, resulting in a tetrahedral arrangement of the electron pairs about the central atom and approximately a  $109.5^\circ$  bond angle.  $\text{H}_2\text{S}$  has two lone pairs on the central atom;  $\text{NF}_3$  has one lone pair on the central atom. These lone pairs repel more than the bonded electron pairs and will cause the bond angle to be smaller than the expected  $109.5^\circ$ . The more lone pairs, the smaller the bond angle.

In order of increasing bond angles, the answer is  $\text{H}_2\text{S} < \text{NF}_3 < \text{CCl}_4$ .

## HYBRIDIZATION

Hybridization describes the mixing of atomic orbitals to form molecular orbitals of equal energies that share electrons during bond formation. For example, in methane ( $\text{CH}_4$ ), the  $2s$  orbital and three  $2p$  orbitals of carbon mix together to form four  $sp^3$  hybrid orbitals, each with the same energy. The  $sp^3$  orbital of carbon overlaps the  $1s$  orbital of hydrogen, creating a region of high electron density between the two nuclei. These overlapping orbitals form a single bond, also known as a sigma ( $\sigma$ ) bond, similar to the one shown here.



In general, the sum of the superscripts on the hybrid orbitals equals the number of electron groups (multiple bonds count as one group)

around the central atom. The carbon atom in  $\text{CH}_4$  has 4 electron groups around the central atom. The sum of the superscripts in  $sp^3$  equals 4.

Multiple bonds are formed by sharing electrons in unhybridized orbitals above and below the  $\sigma$  bond. The carbon atom in carbon dioxide is  $sp$  hybridized. There are 2 electron groups around the C atom. The sum of the superscripts in  $sp$  is 2. The  $2s$  orbital and one of the  $2p$  orbitals of carbon mix to form  $sp$ , leaving two  $2p$  orbitals unused. There are three electron groups around each oxygen atom (one bonding group and two lone pairs), so the oxygen atoms are  $sp^2$  hybridized. The carbon atom has two unhybridized  $p$  orbitals perpendicular to the  $sp^2$  orbital; the oxygen atoms have one unhybridized  $p$  orbital each. The parallel  $p$  orbitals can share a pair of electrons above and below the carbon-oxygen bonds, forming a pi ( $\pi$ ) bond.

A double bond, such as the one in carbon dioxide, consists of one sigma bond because of the head-on overlap of  $sp^2$  orbitals of each carbon atom and one pi bond due to the parallel  $p$  orbitals. A triple bond consists of one sigma bond and two pi bonds.

The hybrid orbitals are oriented in space according to the VSEPR model. For example, the four  $sp^3$  orbitals have a tetrahedral arrangement (there are 4 electron groups around the central atom).

## BOND LENGTH

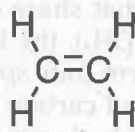
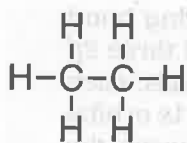
(Chemistry 8th ed. page 363/9th ed. page 375)

As the number of bonds between two atoms increases, the bond grows shorter and stronger.

**EXAMPLE:** Arrange the following molecules in order of decreasing C–C bond length:  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ .

**SOLUTION:** In order of decreasing C–C bond length:  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ .

First, draw the Lewis structure for each molecule.



The C–C triple bond is the shortest, followed by the double bond, and the single bond.

## INTERMOLECULAR FORCES

(Chemistry 8th ed. pages 440–443/9th ed. pages 455–458)

Intermolecular forces are attractions *between* molecules, unlike intramolecular bonds which are attractions *within* a molecule. Molecules with strong intermolecular forces require more energy to

separate from each other, so they will tend to have relatively high melting points, boiling points, and heats of vaporization. When in liquid phase, they will generally have higher viscosity and higher surface tension.

### DIPOLE–DIPOLE ATTRACTIONS

Polar molecules attract each other, lining up so that their positive and negative poles are close to each other. Polar molecules generally have higher boiling points than nonpolar molecules of similar molar mass because they have dipole–dipole attractions in addition to London forces. An example of a polar molecule is  $\text{SO}_2$ .

### HYDROGEN BONDING

Hydrogen bonding is an unusually strong dipole–dipole force among molecules in which hydrogen is bound to a highly electronegative atom such as nitrogen, oxygen, or fluorine. The hydrogen bond occurs between the hydrogen on one of these electronegative atoms and an O, F, or N on another molecule. This is the strongest type of intermolecular force, and results in molecules with higher boiling points than molecules attracted to each other by dipole–dipole forces. Examples of molecules which exhibit H-bonding include  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and HF.

### LONDON DISPERSION FORCES

London dispersion forces exist between all molecules and account for the boiling points of the noble gases. If there were no attractions at all between molecules, then they would never liquefy. The electron cloud can experience temporary shifts that result in one side of the molecule becoming more negative than the other, causing a temporary dipole. This instantaneous dipole can induce a similar dipole on a neighboring atom.

It follows that the greater the charge on the nucleus and the larger the number of electrons in the molecule, the greater the induced dipole. As the atomic number increases down a group, atoms become more polarizable, that is, the electron cloud can become polarized due to the instantaneous dipole. For example, the halogens all experience London dispersion forces, but the force becomes stronger toward the bottom of the group.  $\text{F}_2$  and  $\text{Cl}_2$  are found as gases in nature,  $\text{Br}_2$  is a liquid, and  $\text{I}_2$  is a solid due to increasing London forces as the atomic number and size of the electron cloud increases in the group.

It is important to recognize that, particularly for organic compounds such as hydrocarbons, strength of London dispersion forces depends on the length or surface area of the molecule as much as on the molar mass. A straight chain has more potential contact points than a branched structure with the same formula, therefore has more contact points and stronger London dispersion forces.

**EXAMPLE:** Arrange  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{C}_4\text{H}_{10}$  in order of increasing boiling point.

**SOLUTION:** In order of increasing boiling point  $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_4\text{H}_{10}$ . None of these molecules is polar, so they only exhibit London dispersion forces. The higher the molar mass and the longer the

molecule, the more polarizable the molecule becomes.  $C_4H_{10}$  has the greatest molar mass and longest straight chain of carbons, followed by  $C_2H_6$ , and has the strongest London dispersion forces.

### MULTIPLE-CHOICE QUESTIONS

No calculators are to be used in this section.

- The compound most likely to be ionic is
  - KF
  - $CCl_4$
  - $CO_2$
  - ICI
- Which of the following substances contains both ionic and covalent bonds?
  - $NH_3$
  - $CH_4$
  - NaOH
  - ICI
- The type of bonding within a water molecule is
  - ionic bonding
  - polar covalent bonding
  - nonpolar covalent bonding
  - hydrogen bonding
- Dinitrogen oxide,  $N_2O$ , has two double bonds. The general structure is  $N=N=O$ . The formal charge on the oxygen atom in this molecule is
  - zero
  - positive one (+1)
  - positive two (+2)
  - negative one (-1)
- The Lewis structure of which molecule requires resonance structures?
  - $MgCl_2$
  - $SiO_2$
  - $SO_2$
  - $OCl_2$
- The predicted geometry (shape) of  $PH_3$ , according to the VSEPR theory, is
  - bent or angular
  - trigonal pyramidal
  - tetrahedral
  - trigonal planar

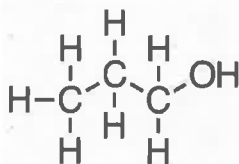


7. Rank the following from lowest to highest boiling temperature:  
 $C_2H_6$   $C_2H_5OH$   $C_2H_5Cl$   
 (A)  $C_2H_6 < C_2H_5OH < C_2H_5Cl$   
 (B)  $C_2H_5OH < C_2H_5Cl < C_2H_6$   
 (C)  $C_2H_5Cl < C_2H_6 < C_2H_5OH$   
 (D)  $C_2H_6 < C_2H_5Cl < C_2H_5OH$
8. The total number of lone pairs in  $PCl_3$  is  
 (A) 1  
 (B) 8  
 (C) 10  
 (D) 12
9. The Lewis structure for carbon dioxide is  
 (A)  $:\ddot{C}=O-O:$   
 (B)  $:\ddot{C}-\ddot{O}-\ddot{O}$   
 (C)  $:\ddot{O}=C=\ddot{O}:$   
 (D)  $:\ddot{O}=C=\ddot{O}:$
10. Which of the following molecules has a dipole moment?  
 $SO_3$   $CCl_4$   $PF_3$   
 (A)  $SO_3$  and  $CCl_4$  only  
 (B)  $CCl_4$  only  
 (C)  $PF_3$  only  
 (D)  $SO_3$ ,  $CCl_4$ , and  $PF_3$
11. A triple bond is comprised of  
 (A) three  $\sigma$  (sigma) bonds  
 (B) two  $\sigma$  (sigma) bonds and one  $\pi$  (pi) bond  
 (C) one  $\sigma$  (sigma) bond and two  $\pi$  (pi) bonds  
 (D) three  $\pi$  (pi) bonds
12. A substance with strong intermolecular forces of attraction would be expected to have  
 (A) a low boiling point  
 (B) a high vapor pressure  
 (C) a high heat of vaporization  
 (D) a low melting point
13. What is the ELECTRON PAIR (or ELECTRON REGION) arrangement around the central atom in the molecule  $IF_5$ ?  
 (A) trigonal pyramidal  
 (B) square planar  
 (C) octahedral  
 (D) square pyramidal
14. In which bond does the oxygen atom possess a partial positive charge?  
 (A) O-H  
 (B) O-F  
 (C) N-O  
 (D) O-C

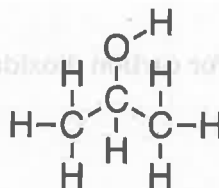
15. The effect of lone pairs on molecular geometry is
- to push other atoms closer together because lone pairs are localized on only one nucleus, so they spread out more
  - to allow the other atoms to be further apart because lone pairs take up less space than bonding pairs
  - to destabilize the molecule by creating a dipole
  - none, because they are just another pair of electrons

### FREE-RESPONSE QUESTIONS

1.



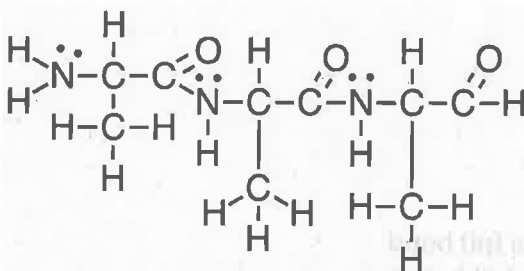
1-propanol



2-propanol

1-propanol boils at 97°C, while 2-propanol boils at 87.5°C. Account for this difference in boiling points.

2.



This polypeptide is both hydrophilic and hydrophobic. Explain what will happen when it is added to water.

## Answers

### MULTIPLE-CHOICE QUESTIONS

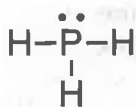
- A** Bonds formed from elements with greater differences in electronegativity are most likely ionic in nature. (Electronegativity increases for elements as you move up and to the right on the periodic table.) (*Chemistry* 8th ed. pages 350–351/9th ed. pages 361–362). LO 2.17
- C** NaOH is an ionic substance (metal to nonmetal). In this case, the anion is a covalently-bonded polyatomic,  $\text{OH}^-$  (*Chemistry* 8th ed. pages 341–343/9th ed. pages 352–356). LO 2.17.
- B** This question is asking you to consider the nature of the bonding between hydrogen and oxygen in water (note the term *within* in the question!). With an electronegativity difference ( $\text{H} = 2.1$  and

O = 3.5) of 1.4, this suggests a bond of a very polar covalent nature due to the uneven sharing of the pair of electrons between hydrogen and oxygen (Note: The force *between* one water molecule and another water molecule is known as a hydrogen bond.) (*Chemistry* 8th ed. pages 346–350/9th ed. pages 358–361). LO 2.13

4. **A** To determine the formal charge on an atom you need to determine the difference in the number of electrons assigned to the atom in the molecule and the number of outermost (valence) electrons on the free atom. In this case, the double bond between nitrogen and oxygen allows oxygen to “own” two (one-half of the four) electrons in the bond, plus totally own the other four electrons. (If this is not clear to you, draw the Lewis structure for this molecule.) Since the number of electrons assigned to oxygen in the molecule and as a free atom is the same, the formal charge is zero. Note that you are not required to use formal charge calculations to explain why certain atoms do not obey the octet rule (*Chemistry* 8th ed. pages 374–378/9th ed. pages 385–389). LO 2.21
5. **C** Watch for *resonance* when it is possible to draw more than one valid Lewis structure. This tends to occur when the same kind of atoms are bonded once as a single bond and again with a multiple bond holding the same kind of atoms together. In this case there is a single bond between sulfur and one of the oxygen atoms, and a double bond between sulfur and the other oxygen atom (*Chemistry* 8th ed. pages 373–374/9th ed. pages 384–385). LO 2.21



6. **B** It is the position of the nuclei upon which we base the shape of a molecule. From the Lewis structure, you can see an unshared pair of electrons on the P; it is this unshared pair which repels the bonded pairs (between P and H) down toward the corners of a tetrahedron. However, the top pair does not contribute to the shape; hence the geometry is a trigonal pyramid (*Chemistry* 8th ed. pages 378–389/9th ed. pages 389–401). LO 2.21

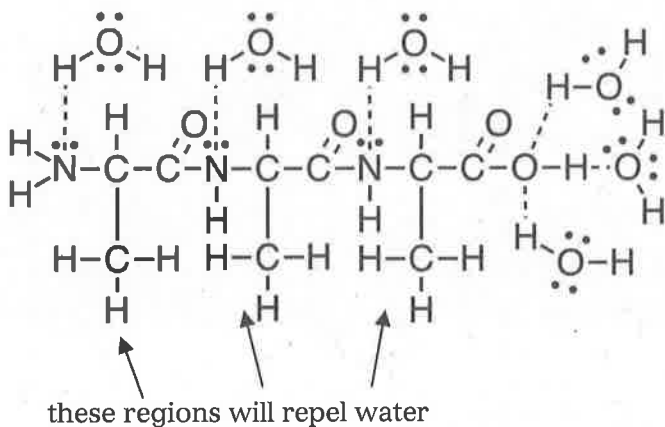


7. **D** Consider the IMF (intermolecular forces) between molecules.  $\text{C}_2\text{H}_6$ , with the lowest boiling temperature is nonpolar and hence has a low IMF.  $\text{C}_2\text{H}_5\text{OH}$  has hydrogen bonding between molecules. Watch for these high IMF when hydrogen is bonded to O, N, or F.  $\text{C}_2\text{H}_5\text{Cl}$  is polar covalent and has intermediate strength IMF between molecules (Measured boiling temperatures are as follows: for  $\text{C}_2\text{H}_6$  it is  $-88.3^\circ\text{C}$ , for  $\text{C}_2\text{H}_5\text{OH}$  it is  $+78.5^\circ\text{C}$ , and for  $\text{C}_2\text{H}_5\text{Cl}$  it is  $+12.3^\circ\text{C}$ .) (*Chemistry* 8th ed. page 443/9th ed. page 458). LO 2.16

8. C A sketch of the Lewis structure will show three lone pairs on each of the chlorine atoms and one more lone pair on the phosphorus atom, for a total of 10 lone pairs (*Chemistry* 8th ed. pages 349–351/9th ed. pages 360–362). LO 2.21
9. C First count the number of total outermost (valence) electrons. Each oxygen has six and the carbon has four, for a total of sixteen. Only response C, with two double bonds, has sixteen valence electrons (*Chemistry* 8th ed. pages 364–372/9th ed. pages 376–383). LO 2.21
10. C In order to have a dipole moment there must be polar covalent bonds present and an asymmetrical distribution of charge. In order to determine this, you must consider both the nature of the bonding (extent of polarity) and the arrangement of these bonds (the molecular shape). If all the vectors, resulting from polar bonds, cancel each other, then there is zero dipole moment. In the case of  $\text{PF}_3$ , the shape is that of a trigonal pyramid, the vectors do not cancel each other, and the molecule is polar (*Chemistry* 8th ed. pages 346–350/9th ed. pages 358–361). LO 2.21
11. C All bonds between atoms start with sharing a pair of electrons in overlapping orbitals. This is called a sigma bond. Multiple bonds occur when electrons in unhybridized orbitals above and below the sigma bond are shared. Each multiple bond is a pi bond, so a triple bond contains one sigma and two pi bonds (*Chemistry* 8th ed. pages 408–410/9th ed. pages 420–422). LO 2.21
12. C A great deal of energy would be required to overcome strong intermolecular forces between the molecules within the substance in order for them to move from liquid to gaseous state (*Chemistry* 8th ed. pages 440–444/9th ed. pages 455–459). LO 2.16
13. C Iodine has 7 valence electrons and each fluorine atom has 7 valence electrons; so  $7 + 5(7) = 42$  electrons. Thus there are five bonding pairs and one lone pair around the central atom. The six pairs or regions of electrons assume an octahedral arrangement (*Chemistry* 8th ed. pages 378–387/9th ed. pages 389–398). LO 2.21
14. B Since fluorine is the most electronegative element in the periodic table, the oxygen atom, when covalently bonded to the fluorine atom, will have a partial positive charge (*Chemistry* 8th ed. pages 344–349/9th ed. pages 356–360). LO 2.17
15. A Lone pairs are only localized around one nucleus, so they spread out close to that nucleus and take up more room (*Chemistry* 8th ed. page 382/9th ed. pages 356–360). LO 2.21

## FREE-RESPONSE QUESTIONS

- Both molecules are able to make hydrogen bonds with their OH groups, so their boiling points are relatively high. Because 1-propanol's OH group is at the end of the carbon chain, the molecule has more contact points available for London dispersion forces of attraction and its boiling point is higher (Chemistry 8th ed. pages 343–349, 353–359, 440–443, 466–471, 474/9th ed. pages 355–360, 365–371, 455–458, 479–483, 486). LO 2.13
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The lone pairs on the nitrogen and oxygen atoms will be attracted to the slightly positive hydrogen atoms of water, forming dipole-dipole attractions (specifically, hydrogen bonds). The nonpolar  $\text{CH}_3$  (methyl) groups will repel the polar water molecules. The molecule may float on the water's surface, with the hydrophobic portion facing up out of the water and the hydrophilic portion facing down. Or it may organize in layers, with the nonpolar portions facing each other, away from the water, and the polar portions facing the water (Chemistry 8th ed. pages 504–505/9th ed. pages 517–518). LO 2.8

