# CHAPTER 9 MODELS OF CHEMICAL BONDING

## END-OF-CHAPTER PROBLEMS

- 9.1 a) Larger ionization energy decreases metallic character.
  - b) Larger atomic radius increases metallic character.
  - c) Larger number of outer electrons decreases metallic character.
  - d) Larger effective nuclear charge decreases metallic character.
- 9.2 A has **covalent** bonding, B has **ionic** bonding, and C has **metallic** bonding.
- 9.3 The tendency of main-group elements to form cations decreases from Group 1A(1) to 4A(14), and the tendency to form anions increases from Group 4A(14) to 7A(17). Group 1A(1) and 2A(2) elements form mono- and divalent cations, respectively, while Group 6A(16) and 7A(17) elements form di- and monovalent anions, respectively.
- 9.4 <u>Plan:</u> Metallic behavior increases to the left and down a group in the periodic table. Solution:
  - a) Cs is more metallic since it is further down the alkali metal group than Na.
  - b) **Rb** is more metallic since it is both to the left and down from Mg.
  - c) **As** is more metallic since it is further down Group 5A(15) than N.
- 9.5 a) **O** b) **Be** c) **Se**
- 9.6 <u>Plan:</u> Ionic bonding occurs between metals and nonmetals, covalent bonding between nonmetals, and metallic bonds between metals.

## Solution:

- a) Bond in CsF is **ionic** because Cs is a metal and F is a nonmetal.
- b) Bonding in  $N_2$  is **covalent** because N is a nonmetal.
- c) Bonding in Na(s) is **metallic** because this is a monatomic, metal solid.
- 9.7 a) covalent b) covalent c) ionic
- 9.8 <u>Plan:</u> Lewis electron-dot symbols show valence electrons as dots. Place one dot at a time on the four sides (this method explains the structure in b) and then pair up dots until all valence electrons are used. The group number of the main-group elements (Groups 1A(1)-8A(18)) gives the number of valence electrons. Rb is Group 1A(1), Si is Group 4A(14), and I is Group 7A(17). Solution:
  - a) Rb · b) · Si · c) · I

9.9

- a) •Ba• b) : Kr: c) : Br
- 9.10 <u>Plan:</u> Assuming X is an A-group element, the number of dots (valence electrons) equals the group number. Once the group number is known, the general electron configuration of the element can be written.

- a) Since there are 6 dots in the Lewis electron-dot symbol, element X has 6 valence electrons and is a Group 6A(16) element. Its general electron configuration is [noble gas] $ns^2np^4$ , where n is the energy level.
- b) Since there are 3 dots in the Lewis electron-dot symbol, element X has 3 valence electrons and is a Group 3A(13) element with general electron configuration [noble gas] $ns^2np^1$ .
- 9.11 a) 5A(15);  $ns^2np^3$  b) 4A(14);  $ns^2np^2$
- 9.12 Energy is required to form the cations and anions in ionic compounds but energy is released when the oppositely charged ions come together to form the compound. This energy is the lattice energy and more than compensates for the required energy to form ions from metals and nonmetals.
- 9.13 a) Because the lattice energy is the result of electrostatic attractions among the oppositely charged ions, its magnitude depends on several factors, including ionic size, ionic charge, and the arrangement of ions in the solid. For a particular arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.
  - b) Increasing lattice energy: A < B < C
- 9.14 The lattice energy releases even more energy when the gas is converted to the solid.
- 9.15 The lattice energy drives the energetically unfavorable electron transfer resulting in solid formation.
- 9.16 Plan: Write condensed electron configurations and draw the Lewis electron-dot symbols for the atoms. The group number of the main-group elements (Groups 1A(1)-8A(18)) gives the number of valence electrons. Remove electrons from the metal and add electrons to the nonmetal to attain filled outer levels. The number of electrons lost by the metal must equal the number of electrons gained by the nonmetal.

# Solution:

a) Barium is a metal and loses 2 electrons to achieve a noble gas configuration:

Ba ([Xe]6
$$s^2$$
)  $\rightarrow$  Ba<sup>2+</sup> ([Xe]) + 2e<sup>-</sup>  
• Ba •  $\longrightarrow$   $\left[ Ba \right]^{2+}$  + 2 e-

Chlorine is a nonmetal and gains 1 electron to achieve a noble gas configuration:

$$C1 ([Ne]3s^23p^5) + 1e^- \rightarrow C1^- ([Ne]3s^23p^6)$$

$$: Cl \cdot + 1e^{-} \longrightarrow \left[: Cl :\right]^{-}$$

Two Cl atoms gain the 2 electrons lost by Ba. The ionic compound formed is BaCl<sub>2</sub>.

b) Strontium is a metal and loses 2 electrons to achieve a noble gas configuration:

$$Sr([Kr]5s^2) \rightarrow Sr^{2+}([Kr]) + 2e^{-}$$

Oxygen is a nonmetal and gains 2 electrons to achieve a noble gas configuration:

O ([He]
$$2s^22p^4$$
) + 2e<sup>-</sup>  $\rightarrow$  O<sup>2-</sup> ([He] $2s^22p^6$ )

One O atom gains the two electrons lost by one Sr atom. The ionic compound formed is SrO.

$$\cdot_{\operatorname{Sr}} \stackrel{\cdot}{\longleftarrow} \left[ \begin{array}{c} \operatorname{Sr} \end{array} \right]^{2+} \left[ \begin{array}{c} \vdots \\ \vdots \\ \end{array} \right]^{2-}$$

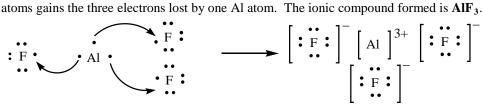
c) Aluminum is a metal and loses 3 electrons to achieve a noble gas configuration:

Al ([Ne]
$$3s^23p^1$$
)  $\rightarrow$  Al<sup>3+</sup> ([Ne]) + 3e<sup>-</sup>

Fluorine is a nonmetal and gains 1 electron to achieve a noble gas configuration:

$$F([He]2s^22p^5) + 1e^- \rightarrow F^-([He]2s^22p^6)$$

Three F atoms gains the three electrons lost by one Al atom. The ionic compound formed is AIF<sub>3</sub>.



d) Rubidium is a metal and loses 1 electron to achieve a noble gas configuration:

$$Rb([Kr]5s^{1}) \rightarrow Rb^{+}([Kr]) + 1e^{-}$$

Oxygen is a nonmetal and gains 2 electrons to achieve a noble gas configuration:

O ([He]
$$2s^22p^4$$
) + 2e<sup>-</sup>  $\rightarrow$  O<sup>2-</sup> ([He] $2s^22p^6$ )

One O atom gains the two electrons lost by two Rb atoms. The ionic compound formed is Rb<sub>2</sub>O.

$$\begin{bmatrix} Rb \end{bmatrix}^{+} \begin{bmatrix} \vdots \\ C \end{bmatrix}^{2-} \begin{bmatrix} Rb \end{bmatrix}^{+}$$

9.17 a) Cesium loses 1 electron to achieve a noble gas configuration:

$$Cs ([Xe]6s^1) \to Cs^+([Xe]) + 1e^-$$

Sulfur gains 2 electrons to achieve a noble gas configuration:

$$S([Ne]3s^23p^4) + 2e^- \rightarrow S^{2-}([Ne]3s^23p^6)$$

One S atom gains the two electrons lost by two Cs atoms. The ionic compound formed is  $Cs_2S$ .

b) Gallium loses 3 electrons to achieve a noble gas configuration:

$$Ga([Ar]3d^{10}4s^24p^1) \rightarrow Ga^{3+}([Ar]3d^{10}) + 3e^{-}$$

Oxygen gains 2 electrons to achieve a noble gas configuration:

$$O([He]2s^22p^4) + 2e^- \rightarrow O^{2-}([He]2s^22p^6)$$

Three O atoms gain the six electrons lost by two Ga atoms. The ionic compound formed is Ga<sub>2</sub>O<sub>3</sub>.

c) Magnesium loses 2 electrons to achieve a noble gas configuration:

$$Mg ([Ne]3s^2) \rightarrow Mg^{2+} ([Ne]) + 2e^{-}$$

Nitrogen gains 3 electrons to achieve a noble gas configuration:

$$N ([He]2s^22p^3) + 3e^- \rightarrow N^{3-} ([He]2s^22p^6)$$

Two N atoms gain the six electrons lost by three Mg atoms. The ionic compound formed is  $Mg_3N_2$ .

d) Lithium loses 1 electron to achieve a noble gas configuration:

$$\text{Li }([\text{He}]2s^1) \to \text{Li}^+([\text{He}]) + 1e^-$$

Bromine gains 1 electron to achieve a noble gas configuration:

Br ([Ar]
$$3d^{10}4s^24p^5$$
) + 1e<sup>-</sup>  $\rightarrow$  Br<sup>-</sup> ([Ar] $3d^{10}4s^24p^6$ )

One Br atoms gains the one electron lost by one Li atom. The ionic compound formed is LiBr.

- 9.18 Plan: Find the charge of the known atom and use that charge to find the ionic charge of element X. For A-group cations, ion charge = the group number; for anions, ion charge = the group number 8. Once the ion charge of X is known, the group number can be determined. Solution:
  - a) X in  $X_2O_3$  is a cation with +3 charge. The oxygen in this compound has a -2 charge. To produce an electrically neutral compound, 2 cations with +3 charge bond with 3 anions with -2 charge: 2(+3) + 3(-2) = 0. Elements in **Group 3A(13)** form +3 ions.
  - b) The carbonate ion,  $CO_3^2$ , has a -2 charge, so X has a +2 charge. **Group 2A(2)** elements form +2 ions.
  - c) X in  $Na_2X$  has a -2 charge, balanced with the +2 overall charge from the two  $Na^+$  ions. Group 6A(16) elements gain 2 electrons to form -2 ions with a noble gas configuration.
- 9.19 a) **7A(17)** b) **6A(16)** c) **3A(13)**
- 9.20 <u>Plan:</u> The magnitude of the lattice energy depends on ionic size and ionic charge. For a particular arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.

## Solution:

- a) **BaS** has the lower lattice energy because the ionic radius of Ba<sup>2+</sup> is larger than Ca<sup>2+</sup>. A larger ionic radius results in a greater distance between ions. The lattice energy decreases with increasing distance between ions.
- b) NaF has the lower lattice energy since the charge on each ion (+1, -1) is half the charge on the Mg<sup>2+</sup> and O<sup>2-</sup> ions. Lattice energy increases with increasing ion charge.
- 9.21 a) **NaCl**; Cl has a larger radius than F.
  - b)  $K_2S$ ; S has a larger radius than O.
- 9.22 The lattice energy in an ionic solid is directly proportional to the product of the ion charges and inversely proportional to the sum of the ion radii. The strong interactions between ions cause most ionic materials to be hard. A very large lattice energy implies a very hard material. The lattice energy is predicted to be high for  $Al_2O_3$  since the ions involved,  $Al^{3+}$  and  $O^{2-}$ , have fairly large charges and are relatively small ions.
- 9.23 When two chlorine atoms are far apart, there is no interaction between them. Once the two atoms move closer together, the nucleus of each atom attracts the electrons on the other atom. As the atoms move closer this attraction increases, but the repulsion of the two nuclei also increases. When the atoms are very close together the repulsion between nuclei is much stronger than the attraction between nuclei and electrons. The final internuclear distance for the chlorine molecule is the distance at which maximum attraction is achieved in spite of the repulsion. At this distance, the energy of the molecule is at its lowest value.
- 9.24 The bond energy is the energy required to overcome the attraction between H atoms and Cl atoms in one mole of HCl molecules in the gaseous state. Energy input is needed to break bonds, so bond energy is always absorbed (endothermic) and  $\Delta H_{\text{bond breaking}}^{\circ}$  is positive. The same amount of energy needed to break the bond is released upon its formation, so  $\Delta H_{\text{bond forming}}^{\circ}$  has the same magnitude as  $\Delta H_{\text{bond breaking}}^{\circ}$ , but opposite in sign (always exothermic and negative).
- 9.25 The strength of the covalent bond is generally inversely related to the size of the bonded atoms. The bonding orbitals in larger atoms are more diffuse, so they form weaker bonds.

- 9.26 Bond strength increases with bond order, so C≡C > C=C > C−C. Two nuclei are more strongly attracted to two shared electron pairs than to one shared electron pair and to three shared electron pairs than to two. The atoms are drawn closer together with more electron pairs in the bond and the bond is stronger.
- 9.27 When benzene boils, the gas consists of C<sub>6</sub>H<sub>6</sub> molecules. The energy supplied disrupts the intermolecular attractions between molecules but not the intramolecular forces of bonding within the molecule.
- 9.28 Plan: Bond strength increases as the atomic radii of atoms in the bond decrease; bond strength also increases as bond order increases.
  Solution:
  - a) **I–I < Br–Br < Cl–Cl**. Atomic radii decrease up a group in the periodic table, so I is the largest and Cl is the smallest of the three.
  - b) S-Br < S-Cl < S-H. H has the smallest radius and Br has the largest, so the bond strength for S-H is the greatest and that for S-Br is the weakest.
  - c) C-N < C=N < C=N. Bond strength increases as the number of electrons in the bond increases. The triple bond is the strongest and the single bond is the weakest.
- 9.29 a) H-F < H-Cl < H-I b) C=O < C-O < C-S c) N-H < N-O < N-S
- 9.30 <u>Plan:</u> Bond strength increases as the atomic radii of atoms in the bond decrease; bond strength also increases as bond order increases.

- a) The C=O bond (bond order = 2) is stronger than the C-O bond (bond order = 1).
- b) O is smaller than C so the O–H bond is shorter and stronger than the C–H bond.
- 9.31 C≡C is a stronger bond than C=C since it has a higher bond order. Since the bond energy is greater, the absorption of IR would occur at shorter wavelength since shorter wavelength has more energy.
- 9.32  $H_2(g) + O_2(g) \rightarrow H-O-O-H(g)$   $\Delta H_{rxn}^{\circ} = \Sigma \Delta H_{bonds\ broken}^{\circ} + \Sigma \Delta H_{bonds\ formed}^{\circ}$   $\Delta H_{rxn}^{\circ} = BE_{H_2}^{} + BE_{O-O}^{} + [2(BE_{OH}) + BE_{O-O}^{}]$  Use negative values for the bond energies of the products.
- 9.33 Reaction between molecules requires the breaking of existing bonds and the formation of new bonds. Substances with weak bonds are more reactive than are those with strong bonds because less energy is required to break weak bonds.
- 9.34 Bond energies are average values for a particular bond in a variety of compounds. Heats of formation are specific for a compound.
- 9.35 Plan: Write the combustion reactions of methane and of formaldehyde. The reactants requiring the smaller amount of energy to break bonds will have the greater heat of reaction. Examine the bonds in the reactant molecules that will be broken. In general, more energy is required to break double bonds than to break single bonds.
  Solution:

For methane:  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$  which requires that 4 C–H bonds and 2 O=O bonds be broken and 2 C=O bonds and 4 O–H bonds be formed.

For formaldehyde:  $CH_2O(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$  which requires that 2 C–H bonds, 1 C=O bond, and 1 O=O bond be broken and 2 C=O bonds and 2 O–H bonds be formed.

Methane contains more C–H bonds and fewer C=O bonds than formaldehyde. Since C–H bonds take less energy to break than C=O bonds, more energy is released in the combustion of methane than of formaldehyde.

9.36 <u>Plan:</u> To find the heat of reaction, add the energy required to break all the bonds in the reactants to the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic. The bond energy values are found in Table 9.2.

# Solution:

Reactant bonds broken:

1 x C=C = (1 mol)(614 kJ/mol) = 614 kJ 4 x C-H = (4 mol)(413 kJ/mol) = 1652 kJ 1 x Cl-Cl = (1 mol)(243 kJ/mol) = 243 kJ  $\Sigma\Delta H^{\circ}_{\text{bonds broken}} = 2509 \text{ kJ}$ 

# Product bonds formed:

1 x C–C = (1 mol)(–347 kJ/mol) = 
$$-347$$
 kJ  
4 x C–H = (4 mol)(–413 kJ/mol) =  $-1652$  kJ  
2 x C–Cl = (2 mol)(–339 kJ/mol =  $-678$  kJ  

$$\Sigma \Delta H_{\text{bonds formed}}^{\circ} = -2677 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_{\text{bonds broken}}^{\circ} + \Sigma \Delta H_{\text{bonds formed}}^{\circ} = 2509 \text{ kJ} + (-2677 \text{ kJ}) = -168 \text{ kJ}$$

9.37 
$$CO_2 + 2NH_3 \rightarrow (H_2N)_2CO + H_2O$$

$$\Delta H_{rxn}^{\circ} = \Sigma \Delta H_{bonds\ broken}^{\circ} + \Sigma \Delta H_{bonds\ formed}^{\circ}$$

$$\Delta H_{rxn}^{\circ} = [(2\ mol\ BE_{C=O} + 6\ BE_{N-H}] + [4\ (BE_{N-H}) + (BE_{C=O}) + 2\ (BE_{C-N}) + 2\ (BE_{O-H})]$$

$$= [2\ mol(799\ kJ/mol) + 6\ mol(391\ kJ/mol)] +$$

$$[4\ mol(-391\ kJ/mol) + 1\ mol(-745\ kJ/mol) + 2\ mol(-305\ kJ/mol) + 2\ mol(-467\ kJ/mol)]$$

$$= 3944\ kJ + (-3853\ kJ)$$

$$= 91\ kJ$$

9.38 <u>Plan:</u> To find the heat of reaction, add the energy required to break all the bonds in the reactants to the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic. The bond energy values are found in Table 9.2.

## Solution:

The reaction:

# Reactant bonds broken:

1 x C-O = (1 mol)(358 kJ/mol) = 358 kJ  
3 x C-H = (3 mol)(413 kJ/mol) = 1239 kJ  
1 x O-H = (1 mol)(467 kJ/mol) = 467 kJ  
1 x C 
$$\equiv$$
 O = (1 mol)(1070 kJ/mol) = 1070 kJ  
 $\Sigma\Delta H^{\circ}_{\text{bonds broken}} = 3134 \text{ kJ}$ 

## Product bonds formed:

3 x C–H = (3 mol)(–413 kJ/mol) = –1239 kJ  
1 x C–C = (1 mol)(–347 kJ/mol) = –347 kJ  
1 x C=O = (1 mol)(–745 kJ/mol) = –745 kJ  
1 x C–O = (1 mol)(–358 kJ/mol) = –358 kJ  
1 x O–H = (1 mol)(–467 kJ/mol) = –467 kJ  

$$\Sigma\Delta H_{\text{bonds formed}}^{\circ} = -3156 \text{ kJ}$$

$$\Delta H_{\rm rxn}^{\circ} = \Sigma \Delta H_{\rm bonds\ broken}^{\circ} + \Sigma \Delta H_{\rm bonds\ formed}^{\circ} = 3134\ kJ + (-3156\ kJ) = -22\ kJ$$

9.39 <u>Plan:</u> To find the heat of reaction, add the energy required to break all the bonds in the reactants to the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic. The bond energy values are found in Table 9.2.

## Solution:

Reactant bonds broken:

1 x C=C = (1 mol)(614 kJ/mol) = 614 kJ  
4 x C-H = (4 mol)(413 kJ/mol) = 1652 kJ  
1 x H-Br = (1 mol)(363 kJ/mol) = 363 kJ  

$$\Sigma \Delta H_{\text{bonds broken}}^{\circ} = 2629 \text{ kJ}$$

#### Product bonds formed:

5 x C–H = (5 mol)(-413 kJ/mol) = -2065 kJ  
1 x C–C = (1 mol)(-347 kJ/mol) = -347 kJ  
1 x C–Br = (1 mol)(-276 kJ/mol) = -276 kJ  

$$\Sigma\Delta H_{\text{bonds formed}}^{\circ} = -2688 \text{ kJ}$$

$$\Delta H_{\rm rxn}^{\circ} = \Sigma \Delta H_{\rm bonds\ broken}^{\circ} + \Sigma \Delta H_{\rm bonds\ formed}^{\circ} = 2629\ kJ + (-2688\ kJ) = -59\ kJ$$

- 9.40 Electronegativity increases from left to right across a period (except for the noble gases) and increases from bottom to top within a group. Fluorine (F) and oxygen (O) are the two most electronegative elements. Cesium (Cs) and francium (Fr) are the two least electronegative elements.
- 9.41 In general, electronegativity and ionization energies are directly related. Electronegativity relates the strength with which an atom attracts bonding electrons and the ionization energy measures the energy needed to remove an electron. Atoms that do not require much energy to have an electron removed do not have much attraction for bonding electrons.
- 9.42 Ionic bonds occur between two elements of very different electronegativity, generally a metal with low electronegativity and a nonmetal with high electronegativity. Although electron sharing occurs to a very small extent in some ionic bonds, the primary force in ionic bonds is attraction of opposite charges resulting from electron transfer between the atoms. A nonpolar covalent bond occurs between two atoms with identical electronegativity values where the sharing of bonding electrons is equal. A polar covalent bond is between two atoms (generally nonmetals) of different electronegativities so that the bonding electrons are unequally shared.

  The H–O bond in water is **polar covalent**. The bond is between two nonmetals so it is covalent and not ionic, but atoms with different electronegativity values are involved.

- 9.43 Electronegativity is the tendency of a bonded atom to hold the bonding electrons more strongly. Electron affinity is the energy involved when an atom acquires an electron.
- 9.44 The difference in EN is a reflection of how strongly one atom in a bond attracts bonding electrons. The greater this difference is, the more likely the bond will be ionic (higher partial ionic character); the smaller the EN difference, the more covalent (lower partial ionic character) the bond.
- 9.45 <u>Plan:</u> Electronegativity increases from left to right across a period (except for the noble gases) and increases from bottom to top within a group.

  Solution:

a)  $\mathbf{Si} < \mathbf{S} < \mathbf{O}$ , sulfur is more electronegative than silicon since it is located further to the right in the table. Oxygen is more electronegative than sulfur since it is located nearer the top of the table. b)  $\mathbf{Mg} < \mathbf{As} < \mathbf{P}$ , magnesium is the least electronegative because it lies on the left side of the periodic table and phosphorus and arsenic on the right side. Phosphorus is more electronegative than arsenic because it is higher in the table.

- 9.46 a) **I < Br < N** b) **Ca < H < F**
- 9.47 <u>Plan:</u> The polar arrow points toward the more electronegative atom. Electronegativity increases from left to right across a period (except for the noble gases) and increases from bottom to top within a group.

  Solution:

7.48 The more electronegative element is partially negative ( $\delta^-$ ) and the less electronegative element is partially positive ( $\delta^+$ ).

a) Br 
$$\stackrel{\delta^{+}}{\longrightarrow}$$
 Cl  $\stackrel{\delta^{-}}{\longrightarrow}$  S<sup>+</sup> S<sup>+</sup> S<sup>-</sup> Cl  $\stackrel{\delta^{+}}{\longrightarrow}$  Cl  $\stackrel{\delta^{+}}{\longrightarrow}$  O  $\stackrel{\delta^{-}}{\longrightarrow}$  S<sup>+</sup> S<sup>-</sup> S<sup>+</sup> S<sup>-</sup> S<sup>+</sup> S<sup>-</sup> S<sup>-</sup> N

9.49 Plan: The more polar bond will have a greater difference in electronegativity,  $\Delta$ EN. Solution:

a) N: EN = 3.0; B: EN = 2.0; 
$$\Delta$$
EN<sub>a</sub> = 3.0 - 2.0 = 1.0  
b) N: EN = 3.0; O: EN = 3.5;  $\Delta$ EN<sub>b</sub> = 3.5 - 3.0 = 0.5  
c) C: EN = 2.5; S: EN = 2.5;  $\Delta$ EN<sub>c</sub> = 2.5 - 2.5 = 0  
d) S: EN = 2.5; O: EN = 3.5;  $\Delta$ EN<sub>d</sub> = 3.5 - 2.5 = 1.0  
e) N: EN = 3.0; H: EN = 2.1;  $\Delta$ EN<sub>e</sub> = 3.0 - 2.1 = 0.9  
f) Cl: EN = 3.0; O: EN = 3.5;  $\Delta$ EN<sub>f</sub> = 3.5 - 3.0 = 0.5  
(a), (d), and (e) have greater bond polarity.

9.50 b) is more polar; ΔEN is 1.0 for F–Cl and 0.2 for Br–Cl
c) is more polar; ΔEN is 1.4 for H–O and 0.3 for Se–H
f) is more polar; ΔEN is 0.5 for S–N and 0.1 for As–H

- 9.51 Plan: Ionic bonds occur between two elements of very different electronegativity, generally a metal with low electronegativity and a nonmetal with high electronegativity. Although electron sharing occurs to a very small extent in some ionic bonds, the primary force in ionic bonds is attraction of opposite charges resulting from electron transfer between the atoms. A nonpolar covalent bond occurs between two atoms with identical electronegativity values where the sharing of bonding electrons is equal. A polar covalent bond is between two atoms (generally nonmetals) of different electronegativities so that the bonding electrons are unequally shared. For polar covalent bonds, the larger the  $\Delta EN$ , the more polar the bond. Solution:
  - a) Bonds in  $S_8$  are **nonpolar covalent**. All the atoms are nonmetals so the substance is covalent and bonds are nonpolar because all the atoms are of the same element and thus have the same electronegativity value.  $\Delta EN = 0$ .
  - b) Bonds in RbCl are **ionic** because Rb is a metal and Cl is a nonmetal. ΔEN is large.
  - c) Bonds in PF<sub>3</sub> are **polar covalent**. All the atoms are nonmetals so the substance is covalent. The bonds between P and F are polar because their electronegativity differs (by 1.9 units for P-F).
  - d) Bonds in SCl<sub>2</sub> are **polar covalent**. S and Cl are nonmetals and differ in electronegativity (by 0.5 unit for S-Cl).
  - e) Bonds in  $F_2$  are **nonpolar covalent**. F is a nonmetal. Bonds between two atoms of the same element are nonpolar since  $\Delta EN = 0$ .
  - f) Bonds in SF<sub>2</sub> are **polar covalent**. S and F are nonmetals that differ in electronegativity (by 1.5 units for S–F).

Increasing bond polarity:  $SCl_2 < SF_2 < PF_3$ 

- 9.52 a) KCl ionic nonpolar covalent c) BF<sub>3</sub> polar covalent b) P<sub>4</sub> d) SO<sub>2</sub> polar covalent e) Br<sub>2</sub> nonpolar covalent f) NO<sub>2</sub> polar covalent  $NO_2 < SO_2 < BF_3$
- 9.53 Plan: Increasing ionic character occurs with increasing  $\Delta EN$ . Electronegativity increases from left to right across a period (except for the noble gases) and increases from bottom to top within a group. The polar arrow points toward the more electronegative atom. Solution:

a) H: EN = 2.1; Cl: EN = 3.0; Br: EN = 2.8; I: EN = 2.5   
 
$$\Delta \text{EN}_{\text{HBr}} = 2.8 - 2.1 = 0.7$$
;  $\Delta \text{EN}_{\text{HCl}} = 3.0 - 2.1 = 0.9$ ;  $\Delta \text{EN}_{\text{HI}} = 2.5 - 2.1 = 0.4$    
 b) H: EN = 2.1; O: EN = 3.5; C: EN = 2.5; F: EN = 4.0   
  $\Delta \text{EN}_{\text{HO}} = 3.5 - 2.1 = 1.4$ ;  $\Delta \text{EN}_{\text{CH}} = 2.5 - 2.1 = 0.4$ ;  $\Delta \text{EN}_{\text{HF}} = 4.0 - 2.1 = 1.9$    
 c) Cl: EN = 3.0; S: EN = 2.5; P: EN = 2.1; Si: EN = 1.8   
  $\Delta \text{EN}_{\text{SCl}} = 3.0 - 2.5 = 0.5$ ;  $\Delta \text{EN}_{\text{PCl}} = 3.0 - 2.1 = 0.9$ ;  $\Delta \text{EN}_{\text{SiCl}} = 3.0 - 1.8 = 1.2$ 

- 9.54 Increasing ionic character occurs with increasing  $\Delta$ EN.
  - P-F > P-Cl > P-Bra)  $\Delta EN_{PCl} = 0.9$ ,  $\Delta EN_{PBr} = 0.7$ ,  $\Delta EN_{PF} = 1.9$  $\delta + \delta - \delta + \delta -$
  - b)  $\Delta EN_{BF} = 2.0$ ,  $\Delta EN_{NF} = 1.0$ ,  $\Delta EN_{CF} = 1.5$ B-F > C-F > N-F
  - $\delta + \delta \delta + \delta \delta + \delta$ c)  $\Delta EN_{SeF} = 1.6$ ,  $\Delta EN_{TeF} = 1.9$ ,  $\Delta EN_{BrF} = 1.2$ Te-F > Se-F > Br-F $\delta + \delta - \delta + \delta - \delta + \delta -$

 $\delta + \delta -$ 

- 9.55 C-C + Cl-Cl  $\rightarrow$  2 C-Cl 347 kJ/mol
  - **d**) The value should be greater than the average of the two bond energies given. This is due to the electronegativity difference.
- 9.56 Molten rock cools from top to bottom. The most stable compound (the one with the largest lattice energy) will solidify first near the top. The less stable compounds will remain in the molten state at the bottom and eventually crystallize there later.
- 9.57 <u>Plan:</u> Write a balanced chemical reaction. The given heat of reaction is the sum of the energy required to break all the bonds in the reactants and the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic. The bond energy values are found in Table 9.2. Use the ratios from the balanced reaction between the heat of reaction and acetylene and between acetylene and CO<sub>2</sub> and O<sub>2</sub> to find the amounts needed. The ideal gas law is used to convert from moles of oxygen to volume of oxygen.

a) 
$$C_2H_2 + 5/2O_2 \rightarrow 2CO_2 + H_2O$$
  $\Delta H_{rxn}^{\circ} = -1259 \text{ kJ/mol}$   $H-C\equiv C-H+5/2O=O \rightarrow 2O=C=O+H-O-H$   $\Delta H_{rxn}^{\circ} = \Sigma \Delta H_{bonds\ broken}^{\circ} + \Sigma \Delta H_{bonds\ formed}^{\circ}$   $\Delta H_{rxn}^{\circ} = [2\ BE_{C-H} + BE_{C\equiv C} + 5/2\ BE_{O=O}] + [4\ (-BE_{C=O}) + 2\ (-BE_{O-H})] -1259\ kJ = [2(413) + BE_{C\equiv C} + 5/2(498)] + [4(-799) + 2(-467)] -1259\ kJ = [826 + BE_{C\equiv C} + 1245] + [-4130)]\ kJ -1259\ kJ = -2059 + BE_{C\equiv C}\ kJ$ 

 $BE_{C=C} = 800. \text{ kJ/mol}$ 

Table 9.2 lists the value as 839 kJ/mol.

b) Heat (kJ) = 
$$(500.0 \text{ g C}_2\text{H}_2) \left( \frac{1 \text{ mol C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2} \right) \left( \frac{-1259 \text{ kJ}}{1 \text{ mol C}_2\text{H}_2} \right)$$
  
=  $-2.4174347 \times 10^4 = -2.417 \times 10^4 \text{ kJ}$ 

c) Mass (g) of CO<sub>2</sub> = 
$$(500.0 \text{ g C}_2\text{H}_2)\left(\frac{1 \text{ mol C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2}\right)\left(\frac{2 \text{ mol CO}_2}{1 \text{ mol C}_2\text{H}_2}\right)\left(\frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2}\right)$$
  
=  $1690.092 = 1690. \text{ g CO}_2$ 

d) Amount (mol) of 
$$O_2 = (500.0 \text{ g C}_2\text{H}_2) \left(\frac{1 \text{ mol C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2}\right) \left(\frac{(5/2) \text{ mol } O_2}{1 \text{ mol C}_2\text{H}_2}\right)$$

$$= 48.0030722 \text{ mol } O_2$$

PV = nRT

Volume (L) of O<sub>2</sub> = 
$$\frac{nRT}{P} = \frac{\left(48.0030722 \text{ mol O}_2\right) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \left(298 \text{ K}\right)}{18.0 \text{ atm}}$$
  
= 65.2145 = **65.2 L O**<sub>2</sub>

9.58 Plan: The heat of formation of MgCl is represented by the equation Mg(s) + 1/2Cl<sub>2</sub>(g) → MgCl(s). Use Hess's law and arrange the given equations so that they sum up to give the equation for the heat of formation of MgCl. You will need to multiply the second equation by ½; you will need to reverse the equation for the lattice energy [MgCl(s) → Mg<sup>+</sup>(g) + Cl<sup>-</sup>(g)] and change the sign of the given lattice energy value. Negative heats of formation are energetically favored.

a) 
$$1) \operatorname{Mg}(s) \to \operatorname{Mg}(g) \qquad \Delta H_{1}^{\circ} = 148 \text{ kJ}$$

$$2) 1/2\operatorname{Cl}_{2}(g) \to \operatorname{Cl}(g) \qquad \Delta H_{2}^{\circ} = 1/2(243 \text{ kJ}) = 121.5 \text{ kJ}$$

$$3) \operatorname{Mg}(g) \to \operatorname{Mg}^{+}(g) + e^{-} \qquad \Delta H_{3}^{\circ} = 738 \text{ kJ}$$

$$4) \operatorname{Cl}(g) + e^{-} \to \operatorname{Cl}^{-}(g) \qquad \Delta H_{4}^{\circ} = -349 \text{ kJ}$$

$$5) \operatorname{Mg}^{+}(g) + \operatorname{Cl}^{-}(g) \to \operatorname{Mg}\operatorname{Cl}(s) \qquad \Delta H_{5}^{\circ} = -783.5 \text{ kJ} \ (= -\Delta H_{\operatorname{lattice}}^{\circ} (\operatorname{Mg}\operatorname{Cl}))$$

$$Mg(s) + 1/2\operatorname{Cl}_{2}(g) \to \operatorname{Mg}\operatorname{Cl}(s) \qquad \Delta H_{f}^{\circ} \ (\operatorname{Mg}\operatorname{Cl}) = ?$$

$$\Delta H_{f}^{\circ} \ (\operatorname{Mg}\operatorname{Cl}) = \Delta H_{1}^{\circ} + \Delta H_{2}^{\circ} + \Delta H_{3}^{\circ} + \Delta H_{4}^{\circ} + \Delta H_{5}^{\circ}$$

$$= 148 \text{ kJ} + 121.5 \text{ kJ} + 738 \text{ kJ} + (-349 \text{ kJ}) + (-783.5 \text{ kJ}) = -125 \text{ kJ}$$

- b) **Yes**, since  $\Delta H_f^o$  for MgCl is negative, MgCl(s) is stable relative to its elements.
- c)  $2MgCl(s) \rightarrow MgCl_2(s) + Mg(s)$

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f (products)}}^{\circ} - \sum n \Delta H_{\text{f (reactants)}}^{\circ}$$

$$\Delta H_{\text{rxn}}^{\circ} = \{1 \Delta H_{\text{f}}^{\circ} \text{ [MgCl}_{2}(s)] + 1 \Delta H_{\text{f}}^{\circ} \text{ [Mg(s)]}\} - \{2 \Delta H_{\text{f}}^{\circ} \text{ [MgCl}(s)]\}$$

$$\Delta H_{\text{rxn}}^{\circ} = [1 \text{ mol}(-641.6 \text{ kJ/mol}) + 1 \text{ mol}(0)] - [2 \text{ mol}(-125 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^{\circ} = -391.6 = -392 \text{ kJ}$$

- d) No,  $\Delta H_f^0$  for MgCl<sub>2</sub> is much more negative than that for MgCl. This makes the  $\Delta H_{rxn}^{\circ}$  value for the above reaction very negative, and the formation of MgCl<sub>2</sub> would be favored.
- 9.59 Plan: Find the bond energy for an H–I bond from Table 9.2. For part a), calculate the wavelength with this energy using the relationship from Chapter 7:  $E = hc/\lambda$ . For part b), calculate the energy for a wavelength of 254 nm and then subtract the energy from part a) to get the excess energy. For part c), speed can be calculated from the excess energy since  $E_k = 1/2mu^2$ . Solution:
  - a) Bond energy for H-I is 295 kJ/mol (Table 9.2).

$$Bond\ energy\ (J/photon) = \left(\frac{295\ kJ}{mol}\right) \left(\frac{10^{3}\ J}{1\ kJ}\right) \left(\frac{1\ mol}{6.022x10^{23}\ photons}\right) = 4.898705x10^{-19}\ J/photon$$

 $E = hc/\lambda$ 

$$\lambda \text{ (m)} = hc/E = \frac{\left(6.626 \text{x} 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \text{x} 10^8 \text{ m/s}\right)}{\left(4.898705 \text{x} 10^{-19} \text{ J}\right)} = 4.057807 \text{x} 10^{-7} \text{ m}$$

$$\lambda \text{ (nm)} = \left(4.057807 \text{x} 10^{-7} \text{ m}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) = 405.7807 = 406 \text{ nm}$$

b) E (HI) =  $4.898705 \times 10^{-19}$  J

$$E (254 \text{ nm}) = hc/\lambda = \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \times 10^8 \text{ m/s}\right)}{254 \text{ nm}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) = 7.82598 \times 10^{-19} \text{ J}$$

Excess energy =  $7.82598x10^{-19} J - 4.898705x10^{-19} J = 2.92728x10^{-19} = 2.93x10^{-19} J$ 

c) Mass (kg) of H = 
$$\left(\frac{1.008 \text{ g H}}{\text{mol}}\right) \left(\frac{\text{mol}}{6.022 \text{x} 10^{23}}\right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) = 1.67386 \text{x} 10^{-27} \text{ kg}$$

$$E_{\rm k} = 1/2mu^2$$
 thus,  $u = \sqrt{\frac{2E}{m}}$ 

$$u = \sqrt{\frac{2(2.92728 \times 10^{-19} \text{ J})}{1.67386 \times 10^{-27} \text{ kg}}} \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}}\right) = 1.8701965 \times 10^4 = 1.87 \times 10^4 \text{ m/s}$$

- 9.60 a) Vibrational motions have frequencies which are in the **IR region** of the electromagnetic
  - b)  $E = \text{hv} = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(4.02 \times 10^{13} \text{ s}^{-1}) = 2.66365 \times 10^{-20} = 2.66 \times 10^{-20} \text{ J (symmetric stretch)}$   $E = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.00 \times 10^{13} \text{ s}^{-1}) = 1.3252 \times 10^{-20} = 1.33 \times 10^{-20} \text{ J (bending)}$   $E = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(7.05 \times 10^{13} \text{ s}^{-1}) = 4.6713 \times 10^{-20} = 4.67 \times 10^{-20} \text{ J (asymmetrical stretch)}$

Bending requires the least amount of energy.

9.61 "Excess bond energy" refers to the difference between the actual bond energy for an X-Y bond and the average of the energies for the X–X and the Y–Y bonds.

Excess bond energy =  $BE_{X-Y} - 1/2 (BE_{X-X} + BE_{Y-Y})$ .

The excess bond energy is zero when the atoms X and Y are identical or have the same electronegativity, as in (a), (b), and (e).

 $\Delta EN_{PH} = 0$ ,  $\Delta EN_{CS} = 0$ ,  $\Delta EN_{BrCl} = 0.2$ ,  $\Delta EN_{BH} = 0.1$ ,  $\Delta EN_{SeSe} = 0$ 

9.62 <u>Plan:</u> Find the appropriate bond energies in Table 9.2. Calculate the wavelengths using  $E = hc/\lambda$ . Solution:

C-Cl bond energy = 339 kJ/mol

Bond energy (J/photon) = 
$$\left(\frac{339 \text{ kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}}\right) = 5.62936 \times 10^{-19} \text{ J/photon}$$

 $E = hc/\lambda$ 

$$\lambda \text{ (m)} = hc/E = \frac{\left(6.626 \text{x} 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \text{x} 10^8 \text{ m/s}\right)}{\left(5.62936 \text{x} 10^{-19} \text{ J}\right)} = 3.5311296 \text{x} 10^{-7} = \mathbf{3.53} \mathbf{x} \mathbf{10}^{-7} \text{ m}$$

 $O_2$  bond energy = 498 kJ/mo

Bond energy (J/photon) = 
$$\left(\frac{498 \text{ kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{1 \text{ mol}}{6.022 \text{x} 10^{23} \text{ photons}}\right) = 8.269678 \text{x} 10^{-19} \text{ J/photon}$$

 $E = hc/\lambda$ 

$$\lambda \text{ (m)} = hc/E = \frac{\left(6.626 \text{x} 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \text{x} 10^8 \text{ m/s}\right)}{\left(8.269678 \text{x} 10^{-19} \text{ J}\right)} = 2.40372 \text{x} 10^{-7} = \textbf{2.40} \textbf{x} \textbf{10}^{-7} \text{ m}$$

9.63 Plan: Write balanced chemical equations for the formation of each of the compounds. Obtain the bond energy of fluorine from Table 9.2 (159 kJ/mol). Determine the average bond energy from  $\Delta H = \text{bonds broken} + \text{bonds formed}$ . Remember that the bonds formed (Xe-F) have negative values since bond formation is exothermic. Solution:

$$\Delta H_{\rm rxn}^{\circ} = \Sigma \Delta H_{\rm bonds\ broken}^{\circ} + \Sigma \Delta H_{\rm bonds\ formed}^{\circ}$$

$$XeF_2$$
  $Xe(g) + F_2(g) \rightarrow XeF_2(g)$ 

$$\Delta H_{\text{rxn}}^{\circ} = -105 \text{ kJ/mol} = [1 \text{ mol } F_2 (159 \text{ kJ/mol})] + [2 (-Xe-F)]$$

$$-264 \text{ kJ/mol} = 2 (-Xe-F)$$

Xe-F = 132 kJ/mol

$$XeF_4$$
  $Xe(g) + 2F_2(g) \rightarrow XeF_4(g)$ 

$$\Delta H_{\text{rxn}}^{\circ} = -284 \text{ kJ/mol} = [2 \text{ mol } F_2 (159 \text{ kJ/mol})] + [4 (-Xe-F)]$$

$$-602 \text{ kJ/mol} = 4 (-\text{Xe-F})$$

$$Xe-F = 150.5 = 150. kJ/mol$$

$$XeF_6$$
  $Xe(g) + 3F_2(g) \rightarrow XeF_6(g)$ 

$$\Delta H_{\text{rxn}}^{\circ} = -402 \text{ kJ/mol} = [3 \text{ mol } F_2 (159 \text{ kJ/mol})] + [6 (-Xe-F)]$$

$$-879 \text{ kJ/mol} = 6 (-\text{Xe-F})$$

$$Xe-F = 146.5 = 146 \text{ kJ/mol}$$

- 9.64 The difference in electronegativity produces a greater than expected overlap of orbitals, which shortens the bond. As  $\Delta$ EN becomes smaller (i.e., as you proceed from HF to HI), this effect lessens and the bond lengths become more predictable.
- a)The presence of the very electronegative fluorine atoms bonded to one of the carbon atoms in 9.65 H<sub>3</sub>C—CF<sub>3</sub> makes the C–C bond polar. This polar bond will tend to undergo heterolytic rather than homolytic cleavage. More energy is required to force heterolytic cleavage.

b) Since one atom gets both of the bonding electrons in heterolytic bond breakage, this results in the formation of ions. In heterolytic cleavage a cation is formed, involving ionization energy; an anion is also formed, involving electron affinity. The bond energy of the O<sub>2</sub> bond is 498 kJ/mol.

 $\Delta H$  = (homolytic cleavage + electron affinity + first ionization energy)

 $\Delta H = (498/2 \text{ kJ/mol} + (-141 \text{ kJ/mol}) + 1314 \text{ kJ/mol}) = 1422 = 1420 \text{ kJ/mol}$ 

It would require 1420 kJ to heterolytically cleave 1 mol of O<sub>2</sub>.

9.66 The bond energies are needed from Table 9.2.  $N_2 = 945 \text{ kJ/mol}$ ;  $O_2 = 498 \text{ kJ/mol}$ ;  $F_2 = 159 \text{ kJ/mol}$ kJ/mol

 $N_2$ :

$$\lambda = hc/E = \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \times 10^8 \text{ m/s}\right)}{\left(945 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right)} = 1.26672 \times 10^{-7} \text{ m}$$

 $O_2$ :

$$\lambda = hc/E = \frac{\left(6.626 \text{x} 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \text{x} 10^8 \text{ m/s}\right)}{\left(498 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \text{x} 10^{23}}\right)} = 2.40372 \text{x} 10^{-7} \text{ m}$$

 $F_2$ :

$$\lambda = hc/E = \frac{\left(6.626 \text{x} 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \text{x} 10^8 \text{ m/s}\right)}{\left(159 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \text{x} 10^{23}}\right)} = 7.528636 \text{x} 10^{-7} = 7.53 \text{x} 10^{-7} \text{ m}$$

 $\Delta H_{\rm rxn}^{\circ} = \Sigma \Delta H_{\rm bonds\ broken}^{\circ} + \Sigma \Delta H_{\rm bonds\ formed}^{\circ}$ 9.67

> For ethane:  $\Delta H_{\text{rxn}}^{\circ} = [1 \text{ mol } (BE_{C-C}) + 6 \text{ mol } (BE_{C-H}) + 1 \text{ mol } (BE_{H-H})] + [8 \text{ mol } (BE_{C-H})]$  $-65.07 \text{ kJ} = [1 \text{ mol}(347 \text{ kJ/mol}) + 6 \text{ mol} (BE_{C-H}) + 1 \text{ mol}(432 \text{ kJ/mol})] + [8 \text{mol}(-415 \text{ kJ/mol})]$

$$BE_{C-H} = \frac{\left(-65.07 - 347 - 432 + 3320\right)kJ}{6 \text{ mol}} = 412.655 = 413 \text{ kJ/mol}$$

For ethene:  $\Delta H_{\text{rxn}}^{\circ} = [1 \text{ mol } (BE_{\text{C-H}}) + 4 \text{ mol } (BE_{\text{C-H}}) + 2 \text{ mol } (BE_{\text{H-H}})] + [8 \text{ mol } (BE_{\text{C-H}})]$ 

 $-202.21 \text{ kJ} = [1 \text{ mol}(614 \text{ kJ/mol}) + 4 \text{ mol} (BE_{C-H}) + 2 \text{ mol}(432 \text{ kJ/mol})]$ 

$$BE_{C-H} = \frac{\left(-202.21 - 614 - 864 + 3320\right) \text{kJ}}{4 \text{ mol}} = 409.9475 = 410. \text{ kJ/mol}$$

For ethyne:  $\Delta H_{\text{rxn}}^{\circ} = [1 \text{ mol } (BE_{C=C}) + 2 \text{ mol } (BE_{C-H}) + 3 \text{ mol } (BE_{H-H})] + [8 \text{ mol } (BE_{C-H})]$ 

 $-376.74 \text{ kJ} = [1 \text{ mol}(839 \text{ kJ/mol}) + 2 \text{ mol} (BE_{C-H}) + 3 \text{ mol}(432 \text{ kJ/mol})]$ 

$$+ [8 \text{ mol}(-415\text{kJ/mol})]$$

$$BE_{C-H} = \frac{(-376.74 - 839 - 1296 + 3320)\text{kJ}}{2 \text{ mol}} = 404.13 = 404 \text{ kJ/mol}$$

9.68 Plan: Convert the bond energy in kJ/mol to units of J/photon. Use the equations E = hv, and  $E = hc/\lambda$  to find the frequency and wavelength of light associated with this energy. Solution:

Bond energy (J/photon) = 
$$\left(\frac{347 \text{ kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}}\right) = 5.762205 \times 10^{-19} \text{ J/photon}$$

$$E = h v \text{ or } v = \frac{E}{h}$$

$$v = \frac{E}{h} = \frac{5.762205 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 8.6963553 \times 10^{14} = 8.70 \times 10^{14} \text{ s}^{-1}$$

 $E = hc/\lambda$  or  $\lambda = hc/E$ 

$$\lambda \text{ (m)} = hc/E = \frac{\left(6.626 \text{x} 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \text{ x} 10^8 \text{ m/s}\right)}{5.762205 \text{x} 10^{-19} \text{ J}} = 3.44972 \text{x} 10^{-7} = \mathbf{3.45 \text{x} 10^{-7} \text{ m}}$$

This is in the ultraviolet region of the electromagnetic spectrum

9.69 
$$v = \frac{E}{h} = \frac{\left(467 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^{3} \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right)}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 1.170374 \times 10^{15} = 1.17 \times 10^{15} \text{ s}^{-1}$$

$$\lambda \text{ (m)} = hc/E = \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right) \left(3.00 \times 10^{8} \text{ m/s}\right)}{\left(467 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^{3} \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right)} = 2.56328 \times 10^{-7} = 2.56 \times 10^{-7} \text{ m}$$

$$E_{\text{photon}} = \left(467 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}}\right) = 7.7548987 \times 10^{-22} = 7.75 \times 10^{-22} \text{ kJ/photon}$$

9.70 Plan: Write the balanced equations for the reactions. Determine the heat of reaction from  $\Delta H = \text{bonds broken} + \text{bonds formed}$ . Remember that the bonds formed have negative values since bond formation is exothermic.

Solution:

$$\overline{a) 2CH_4(g)} + O_2(g) \rightarrow CH_3OCH_3(g) + H_2O(g)$$

$$\Delta H_{\rm rxn}^{\circ} = \Sigma \Delta H_{\rm bonds\ broken}^{\circ} + \Sigma \Delta H_{\rm bonds\ formed}^{\circ}$$

$$\Delta H_{\text{rxn}}^{\circ} = [8 \text{ x } (BE_{C-H}) + 1 \text{ x } (BE_{O-D})] + [6 \text{ x } (BE_{C-H}) + 2 \text{ x } (BE_{C-D}) + 2 \text{ x } (BE_{O-H})]$$

$$\Delta H_{\text{rxn}}^{\circ} = [8 \text{ mol}(413 \text{ kJ/mol}) + 1 \text{ mol}(498 \text{ kJ/mol})]$$

$$+ [6 \text{ mol}(-413 \text{ kJ/mol}) + 2 \text{ mol}(-358 \text{ kJ/mol}) + 2 \text{ mol}(-467 \text{ kJ/mol})]$$

$$\Delta H_{\rm ryn}^{\circ} = -326 \text{ kJ}$$

$$2CH_4(g) + O_2(g) \rightarrow CH_3CH_2OH(g) + H_2O(g)$$

$$\Delta H_{\rm rxn}^{\circ} = \Sigma \Delta H_{\rm bonds\ broken}^{\circ} + \Sigma \Delta H_{\rm bonds\ formed}^{\circ}$$

$$\Delta \textit{H}_{rxn}^{\circ} = [8 \text{ x } (BE_{C-H}) + 1 \text{ x } (BE_{O=O})] + [5 \text{ x } (BE_{C-H}) + 1 \text{ x } (BE_{C-C}) + 1 \text{ x } (BE_{C-O}) + 3 \text{ x } (BE_{O-C}) + 3 \text{ x } (BE_{O-C})$$

 $_{\rm H})]$ 

$$\Delta H_{\text{rxn}}^{\circ} = [8 \text{ mol}(413 \text{ kJ/mol}) + 1 \text{ mol}(498 \text{ kJ/mol})]$$

$$+ [5 \text{ mol}(-413 \text{ kJ/mol}) + 1 \text{ mol}(-347 \text{ kJ/mol}) + 1 \text{ mol}(-358 \text{ kJ/mol}) + 3 \text{ mol}(-467 \text{ kJ/mol})]$$

$$\Delta H_{\rm rxn}^{\circ} = -369 \text{ kJ}$$

b) The formation of gaseous ethanol is more exothermic.

c) The conversion reaction is  $CH_3CH_2OH(g) \rightarrow CH_3OCH_3(g)$ . Use Hess's law:

$$\text{CH}_3\text{CH}_2\text{OH}(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{CH}_4(g) + \text{O}_2(g)$$

$$\Delta H_{\rm rxn}^{\circ} = -(-369 \text{ kJ}) = 369 \text{ kJ}$$

$$2\text{CH}_4(g) + \text{O}_2(g) \rightarrow \text{CH}_3\text{OCH}_3(g) + \text{H}_2\text{O}(g)$$

$$\Delta H_{\rm ryn}^{\circ} = -326 \text{ kJ}$$

$$CH_3CH_2OH(g) \rightarrow CH_3OCH_3(g)$$

$$\Delta H_{\text{rxn}}^{\circ} = -326 \text{ kJ}$$
  
 $\Delta H_{\text{rxn}}^{\circ} = -326 \text{ kJ} + 369 \text{ kJ} = 43 \text{ kJ}$