CHAPTER 9 MODELS OF CHEMICAL BONDING

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). 1A(1) and 2A(2) elements form mono- and divalent cations, respectively, while 6A(16) and 7A(17) elements form di- and monovalent anions, respectively.

9.4 Metallic behavior increases to the left and down on the periodic table.
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 than N.

9.5 a) O  b) Be  c) Se

9.6 Ionic bonding occurs between metals and nonmetals, covalent bonding between nonmetals, and metallic bonds between metals.
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 Ionic bonding occurs between metals and nonmetals, covalent bonding between nonmetals, and metallic bonds between metals.
a) Bonding in O\(_3\) would be **covalent** since O is a nonmetal.
b) Bonding in MgCl\(_2\) would be **ionic** since Mg is a metal and Cl is a nonmetal.
c) Bonding in BrO\(_2\) would be **covalent** since both Br and O are nonmetals.

9.9 a) **metallic**  b) **covalent**  c) **ionic**

9.10 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-8A) gives the number of valence electrons. Rb is Group 1A, Si is Group 4A, I is Group 7A.

9.11 a) \(\cdot\text{Ba}\cdot\)  b) \(\cdot\text{Kr}\cdot\)  c) \(\cdot\text{Br}\cdot\)
9.12
a) Sr
b) P
c) S

9.13
a) As
b) Se
c) Ga

9.14
a) Assuming X is an A group element, the number of dots (valence electrons) equals the group number. Therefore, X is a 6A(16) element with 6 valence electrons. Its general electron configuration is \([\text{noble gas}]n^s n^p^4\), where \(n\) is the energy level.
b) X has three valence electrons and is a 3A(13) element with general \(e^-\) configuration \([\text{noble gas}]n^s n^p^1\).

9.15
a) 5A(15); \(n^s n^p^3\)
b) 4A(14); \(n^s n^p^2\)

9.16
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.

9.17
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: \(A < B < C\)

9.18
The lattice energy releases even more energy when the gas is converted to the solid.

9.19
The lattice energy drives the energetically unfavorable electron transfer resulting in solid formation.

9.20
a) Barium is a metal and loses 2 electrons to achieve a noble gas configuration:
\[
\text{Ba} ([\text{Xe}]6s^2) \rightarrow \text{Ba}^+ ([\text{Xe}]) + 2 \text{e}^-
\]

Chlorine is a nonmetal and gains 1 electron to achieve a noble gas configuration:
\[
\text{Cl} ([\text{Ne}]3s^23p^5) + 1 \text{e}^- \rightarrow \text{Cl}^- ([\text{Ne}]3s^23p^6)
\]

Two Cl atoms gain the two electrons lost by Ba. The ionic compound formed is \(\text{BaCl}_2\).
b) \( \text{Sr} ([\text{Kr}]5s^2) \rightarrow \text{Sr}^{2+} ([\text{Kr}]) + 2 e^- \)  
\( \text{O} ([\text{He}]2s^22p^4) \rightarrow \text{O}^2^- ([\text{He}]2s^22p^6) \)

The ionic compound formed is \( \text{SrO} \).

\[
\text{Sr}^{2+} \quad \text{O}^{2-} \quad \text{Sr}_2\text{O}_2
\]

\[ 2 \text{Cs} + \text{S} \rightarrow \text{Cs}_2\text{S} \]
\[
2 \text{Cs} ([\text{Xe}]6s^1) + \text{S} ([\text{Ne}]3s^23p^4) \rightarrow 2 \text{Cs}^+ ([\text{Xe}]) + \text{S}^{2-} ([\text{Ne}]3s^23p^6)
\]

b) \( \text{Sr} ([\text{Kr}]5s^2) \rightarrow \text{Sr}^{2+} ([\text{Kr}]) + 2 e^- \)  
\( \text{O} ([\text{He}]2s^22p^4) \rightarrow \text{O}^2^- ([\text{He}]2s^22p^6) \)

The ionic compound formed is \( \text{SrO} \).

\[
\text{Sr}^{2+} \quad \text{O}^{2-} \quad \text{Sr}_2\text{O}_2
\]

c) \( \text{Al} ([\text{Ne}]3s^23p^1) \rightarrow \text{Al}^{3+} ([\text{Ne}]) + 3 e^- \)  
\( \text{F} ([\text{He}]2s^22p^5) + 1 e^- \rightarrow \text{F}^- ([\text{He}]2s^22p^6) \)

The ionic compound formed is \( \text{AlF}_3 \).

\[
\text{Al}^{3+} \quad \text{F}^- \quad \text{AlF}_3
\]

d) \( \text{Rb} ([\text{Kr}]5s^1) \rightarrow \text{Rb}^+ ([\text{Kr}]) + 1 e^- \)  
\( \text{O} ([\text{He}]2s^22p^4) \rightarrow \text{O}^{2-} ([\text{He}]2s^22p^6) \)

The ionic compound formed is \( \text{Rb}_2\text{O} \).

\[
\text{Rb}^+ \quad \text{O}^{2-} \quad \text{Rb}_2\text{O}
\]
c) X in Na₂X 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.

9.25 a) 7A(17)  b) 6A(16)  c) 3A(13)

9.26 a) BaS would have the higher lattice energy since the charge on each ion is twice the charge on the ions in CsCl and lattice energy is greater when ionic charges are larger.
b) LiCl would have the higher lattice energy since the ionic radius of Li⁺ is smaller than that of Cs⁺ and lattice energy is greater when the distance between ions is smaller.

9.27 a) CaO; O has a smaller radius than S.
b) SrO; Sr has a smaller radius than Ba.

9.28 a) BaS has the lower lattice energy because the ionic radius of Ba²⁺ is larger than Ca²⁺. 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 Mg²⁺ and O²⁻ ions. Lattice energy increases with increasing ion charge.

9.29 a) NaCl; Cl has a larger radius than F.
b) K₂S; S has a larger radius than O.

9.30 Lattice energy: NaCl(s) → Na⁺(aq) + Cl⁻(g)  
Use Hess' Law:  \[ \Delta H^\circ \]
Na(s) → Na(g)  109 kJ
1/2Cl₂(g) → Cl(g)  243/2 = 121.5 kJ
Na(g) → Na⁺(g) + e⁻  496 kJ
Cl(g) + e⁻ → Cl⁻(g)  -349 kJ
NaCl(s) → Na⁺(g) + 1/2Cl⁻(g)  411 kJ (Reaction is reversed and the sign of \[ \Delta H^\circ \] changed).
NaCl(s) → Na⁺(aq) + Cl⁻(g)  788.5 = 788 kJ
The lattice energy for NaCl is less than that of LiF, which is expected since lithium and fluoride ions are smaller than sodium and chloride ions.

9.31 Lattice energy: MgF₂(s) → Mg²⁺(aq) + 2 F⁻(g)  
Use Hess' Law:  \[ \Delta H^\circ \]
Mg(s) → Mg(g)  148 kJ
F₂(g) → 2 F(g)  159 kJ
Mg(g) → Mg⁺(g) + e⁻  738 kJ
Mg⁺(g) → Mg²⁺(g) + e⁻  1450 kJ
2 F(g) + e⁻ → 2 F⁻(g)  2(–328) = -656 kJ
MgF₂(s) → Mg⁺(aq) + 2 F⁻(g)  1123 kJ (Reaction is reversed and the sign of \[ \Delta H^\circ \] changed).
MgF₂(s) → Mg²⁺(aq) + 2 F⁻(g)  2962 kJ
The lattice energy for MgF₂ is greater than that of LiF and NaCl, which is expected since magnesium ions have twice the charge of lithium and sodium ions. Lattice energy increases with increasing ion charge.

9.32 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 Al₂O₃ since the ions involved, Al³⁺ and O²⁻, have fairly large charges and are relatively small ions.
9.33 An analogous Born-Haber cycle has been described in Figure 9.6 for LiF. Use Hess’s Law and solve for the EA of fluorine:

\[ \Delta H^\circ \]

\[ \text{K(s)} \rightarrow \text{K(g)} \]

\[ 90 \text{ kJ} \]

\[ \text{K(g)} \rightarrow \text{K}^+(g) + e^- \]

\[ 419 \text{ kJ} \]

\[ \frac{1}{2} \text{F}_2(g) \rightarrow \text{F}(g) \]

\[ 1/2(159) = 79.5 \text{ kJ} \]

\[ \text{F(g)} + e^- \rightarrow \text{F}^-(g) \]

\[ ? = \text{EA} \]

\[ \text{KF(s)} \rightarrow \text{K}^+(s) + \frac{1}{2} \text{F}_2(g) \]

\[ 569 \text{ kJ} \]

(Reverse the reaction and change the sign of \( \Delta H^\circ \))

\[ \text{KF(s)} \rightarrow \text{K}^+(s) + \text{F}^-(g) \]

\[ 821 \text{ kJ} \]

\[ 821 \text{ kJ} = 90 \text{ kJ} + 419 \text{ kJ} + 79.5 \text{ kJ} + \text{EA} + 569 \text{ kJ} \]

\[ \text{EA} = 821 \text{ kJ} - (90 + 419 + 79.5 + 569) \text{kJ} \]

\[ \text{EA} = -336.5 = -336 \text{ kJ} \]

9.34 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.

9.35 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 \( \Delta H^\circ \text{bond breaking} \) is positive. The same amount of energy needed to break the bond is released upon its formation, so \( \Delta H^\circ \text{bond forming} \) has the same magnitude as \( \Delta H^\circ \text{bond breaking} \) but opposite in sign (always exothermic and negative).

9.36 The strength of the covalent bond is generally inversely related to the size of the bonded atoms. For larger atoms, their bonding orbitals are more diffuse, so they form weaker bonds.

9.37 Bond strength increases with bond order, so \( \text{C≡C} > \text{C=C} > \text{C–C} \). 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.

9.38 When benzene boils, the gas consists of \( \text{C}_6\text{H}_6 \) molecules. The energy supplied disrupts the intermolecular attractions between molecules but not the intramolecular forces of bonding within the molecule.

9.39 a) \( \text{I–I} < \text{Br–Br} < \text{Cl–Cl} \). Bond strength increases as the atomic radii of atoms in the bond decreases. Atomic radii decrease up a group in the periodic table, so I is the largest and Cl is the smallest of the three.
b) \( \text{S–Br} < \text{S–Cl} < \text{S–H} \). Radius of H is the smallest and Br is the largest, so the bond strength for S–H is the greatest and that for S–Br is the weakest.
c) \( \text{C–N} < \text{C=N} < \text{C≡N} \). 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.

9.40 a) \( \text{H–F} < \text{H–Cl} < \text{H–I} \)
b) \( \text{C=O} < \text{C–O} < \text{C–S} \)
c) \( \text{N–H} < \text{N–O} < \text{N–S} \)

9.41 a) For given pair of atoms, in this case carbon and oxygen, bond strength increases with increasing bond order. 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.
9.42 C=C would show absorption of IR at shorter wavelength (higher energy) due to it being a stronger bond than C–C. The C≡C bond would show absorption at a shorter wavelength (higher energy) than the C=C bond since the triple bond has a larger bond energy than the double bond. Bond strength increases as the number of electrons in the bond increases.

9.43 H₂(g) + O₂(g) → H₂O–O–H(g)

\[ \Delta H_{\text{rxn}} = \Delta H^0_{\text{bonds broken}} + \Delta H^0_{\text{bonds formed}} \]

\[ \Delta H_{\text{rxn}} = \text{BE}_{\text{H₂}} + \text{BE}_{\text{O–O}} + [2(\text{BE}_{\text{OH}}) + \text{BE}_{\text{O–O}}] \]

Use negative values for the bond energies of the products.

9.44 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.

9.45 Bond energies are average values for a particular bond in a variety of compounds. Heats of formation are specific for a compound.

9.46 For methane: CH₄(g) + 2 O₂(g) → CO₂(g) + 2 H₂O(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: CH₂O(g) + O₂(g) → CO₂(g) + H₂O(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.

9.47 Methanol has the greater heat of reaction per mole since 3 C–H bonds must be broken in methanol while 5 C–H bonds are broken in the combustion of ethanol. Less energy is required to break the bonds in the reactant molecules in the combustion of methanol.

9.48 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.

Reactant bonds broken: 1(C=O) + 4(C–H) + 1(Cl–Cl)

= (1 mol) (614 kJ/mol) + (4 mol) (413 kJ/mol) + (1 mol) (243 kJ/mol)

= 2509 kJ

Product bonds formed: 1(C–C) + 4(C–H) + 2(C–Cl)

= (1 mol) (–347 kJ/mol) + (4 mol) (–413 kJ/mol) + (2 mol) (–339 kJ/mol)

= –2677 kJ

\[ \Delta H_{\text{rxn}} = \Delta H^0_{\text{bonds broken}} + \Delta H^0_{\text{bonds formed}} = 2509 \text{kJ} + (–2677 \text{kJ}) = –168 \text{kJ} \]

Note: It is correct to report the answer in kJ or kJ/mol as long as the value refers to a reactant or product with a molar coefficient of 1.

9.49 CO₂ + 2 NH₃ → (H₂N)₂CO + H₂O

\[ \Delta H_{\text{rxn}} = \Delta H^0_{\text{bonds broken}} + \Delta H^0_{\text{bonds formed}} \]

\[ \Delta H_{\text{rxn}} = [2(\text{BE}_{\text{C=O}}) + 6 \text{BE}_{\text{N–H}}] + [4(\text{BE}_{\text{NH}}) + (\text{BE}_{\text{C=O}}) + 2(\text{BE}_{\text{C–N}}) + 2(\text{BE}_{\text{O–H}})] \]

\[ = [2(799) + 6(391)] + [4(–391) + (–745) + 2(–305) + 2(–467)] \]

\[ = 3944 – 3853 \]

\[ = 91 \text{kJ} \]

9.50 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.
The reaction:

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{C} \quad \text{H} \\
& + \quad \text{C} \equiv \text{O} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\Delta H^\circ_{\text{bonds broken}} &= 1 \text{ C–O} = 1 \text{ mol (358 kJ/mol)} \\
3 \text{ C–H} &= 3 \text{ mol (413 kJ/mol)} \\
1 \text{ O–H} &= 1 \text{ mol (467 kJ/mol)} \\
1 \text{ C} \equiv \text{O} &= 1 \text{ mol (1070 kJ/mol)} \\
\end{align*}
\]

\[
\begin{align*}
\Delta H^\circ_{\text{bonds formed}} &= 3 \text{ C–H} = 3 \text{ mol (–413 kJ/mol)} \\
1 \text{ C–C} &= 1 \text{ mol (–347 kJ/mol)} \\
1 \text{ C=O} &= 1 \text{ mol (–745 kJ/mol)} \\
1 \text{ C–O} &= 1 \text{ mol (–358 kJ/mol)} \\
1 \text{ O–H} &= 1 \text{ mol (–467 kJ/mol)} \\
\end{align*}
\]

\[
\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{bonds broken}} + \Delta H^\circ_{\text{bonds formed}} = 3134 \text{ kJ} + (–3156 \text{ kJ}) = –22 \text{ kJ}
\]

9.51 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.

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
& + \quad \text{H} \quad \text{Br} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Bonds broken: 
\[
\begin{align*}
1(\text{C=C}) &+ 4(\text{C–H}) + 1(\text{H–Br}) = 614 + 4(413) + 363 = +2629 \text{ kJ}
\end{align*}
\]

Bonds formed: 
\[
\begin{align*}
1(\text{C–C}) &+ 5(\text{C–H}) + 1(\text{C–Br}) = (–347) + 5(–413) + (–276) = –2688 \text{ kJ}
\end{align*}
\]

\[
\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{bonds broken}} + \Delta H^\circ_{\text{bonds formed}} = 2629 + (–2688) = –59 \text{ kJ}
\]

9.52 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.

9.53 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.

9.54 The H–O bond in water is polar covalent, because the two atoms differ in electronegativity which results in an unequal sharing of the bonding electrons. A nonpolar covalent bond occurs between two atoms with identical electronegativity values where the sharing of bonding electrons is equal. 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.

9.55 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.

9.56 The difference in E.N. is a reflection of how strongly one atom attracts bonding electrons. The greater this difference is, the more likely the bond will be ionic; the smaller the E.N. difference, the more covalent the bond.
Electronegativity increases from left to right across a period (except for the noble gases) and increases from bottom to top within a group.

a) Si < S < 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) Mg < As < 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.

9.58 a) I < Br < N
b) Ca < H < F

9.59 Electronegativity generally increases up a group and left to right across a period.

a) N > P > Si, nitrogen is above P in Group 5(A)15 and P is to the right of Si in period 3.

b) As > Ga > Ca, all three elements are in Period 4, with As the right-most element.

9.60 a) Cl > Br > P
b) F > O > I

9.61 The arrow points toward the more electronegative atom.

a) N — B  b) N — O  c) C — S

d) S — O  e) N — H  f) Cl — O

9.62 The more electronegative element is partially negative (δ⁻) and the less electronegative element is partially positive (δ⁺).

a) Br — Cl  b) F — Cl  c) H — O

d) Se — H  e) As — H  f) S — N

9.63 The more polar bond will have a greater difference in electronegativity, ΔEN.

a) N: EN = 3.0; B: EN = 2.0; ΔEN₂ = 1.0  b) N: EN = 3.0; O: EN = 3.5; ΔEN₃ = 0.5
c) C: EN = 2.5; S: EN = 2.5; ΔEN₄ = 0  d) S: EN = 2.5; O: EN = 3.5; ΔEN₅ = 1.0
e) N: EN = 3.0; H: EN = 2.1; ΔEN₆ = 0.9  f) Cl: EN = 3.0; O: EN = 3.5; ΔEN₇ = 0.5

(a), (d), and (e) have greater bond polarity.

9.64 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.

9.65 a) Bonds in S₈ 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. ΔEN = 0.
b) Bonds in RbCl are ionic because Rb is a metal and Cl is a nonmetal. ΔEN is large.
c) Bonds in PF₃ 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 SCl₂ are polar covalent. S and Cl are nonmetals and differ in electronegativity. (By 0.5 unit for S—Cl)
e) Bonds in F₂ are nonpolar covalent. F is a nonmetal. Bonds between two atoms of the same element are nonpolar since ΔEN = 0.
f) Bonds in SF$_2$ are polar covalent. S and F are nonmetals that differ in electronegativity. (By 1.5 units for S–F)

**Increasing bond polarity:**

$\text{SCl}_2 < \text{SF}_2 < \text{PF}_3$

9.66 a) KCl ionic  
   b) P$_4$ nonpolar covalent  
   c) BF$_3$ polar covalent
   d) SO$_2$ polar covalent  
   e) Br$_2$ nonpolar covalent  
   f) NO$_2$ polar covalent

$\text{NO}_2 < \text{SO}_2 < \text{BF}_3$

9.67 Increasing ionic character occurs with increasing $\Delta$EN.

a) $\Delta$EN$_{\text{HBr}} = 0.7$, $\Delta$EN$_{\text{HCl}} = 0.9$, $\Delta$EN$_{\text{HI}} = 0.4$

b) $\Delta$EN$_{\text{HO}} = 1.4$, $\Delta$EN$_{\text{CH}} = 0.4$, $\Delta$EN$_{\text{HF}} = 1.9$

c) $\Delta$EN$_{\text{SCl}} = 0.5$, $\Delta$EN$_{\text{PCl}} = 0.9$, $\Delta$EN$_{\text{SiCl}} = 1.2$

9.68 Increasing ionic character occurs with increasing $\Delta$EN.

a) $\Delta$EN$_{\text{PCl}} = 0.9$, $\Delta$EN$_{\text{PBr}} = 0.7$, $\Delta$EN$_{\text{PF}} = 1.9$  
   $\text{P–F} > \text{P–Cl} > \text{P–Br}$
   $\delta^+ \delta^- \delta^+ \delta^- \delta^+ \delta^-$

b) $\Delta$EN$_{\text{BF}} = 2.0$, $\Delta$EN$_{\text{NF}} = 1.0$, $\Delta$EN$_{\text{CF}} = 1.5$  
   $\text{B–F} > \text{C–F} > \text{N–F}$
   $\delta^+ \delta^- \delta^+ \delta^- \delta^+ \delta^-$

c) $\Delta$EN$_{\text{SeF}} = 1.6$, $\Delta$EN$_{\text{TeF}} = 1.9$, $\Delta$EN$_{\text{BrF}} = 1.2$  
   $\text{Te–F} > \text{Se–F} > \text{Br–F}$
   $\delta^+ \delta^- \delta^+ \delta^- \delta^+ \delta^-$

9.69 C–C + Cl–Cl → 2 C–Cl

$347 \text{ kJ/mol}$  $243 \text{ kJ/mol}$

**d)** The value should be greater than the average of the two bond energies given. This is due to the electronegativity difference.

9.70 a) A solid metal is a shiny solid that conducts heat, is malleable, and melts at high temperatures. (Other answers include relatively high boiling point and good conductor of electricity.)

b) Metals lose electrons to form positive ions and metals form basic oxides.

9.71 a) Potassium is a larger atom than sodium, so its electrons are held more loosely and thus its metallic bond strength is weaker.

b) Be has two valence electrons per atom compared with Li, which has one. The metallic bond strength is stronger for the Be.

c) The boiling point is high due to the large amount of energy needed to separate the metal ions from each other in the electron sea.

9.72 When metallic magnesium is deformed, the atoms are displaced and pass over one another while still being tightly held by the attraction of the “sea of electrons.” When ionic MgF$_2$ is deformed, the ions are displaced so that repulsive forces between neighboring ions of like charge cause shattering of the crystals.

9.73 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.
9.74 a) \( \text{C}_2\text{H}_2 + 5/2 \text{O}_2 \rightarrow 2 \text{CO}_2 + \text{H}_2\text{O} \)  \( \Delta H_{\text{rxn}} = -1259 \text{ kJ/mol} \)

\[ \begin{align*}
\text{H–C} & \equiv \text{C–H} + \frac{5}{2} \text{O=O} \\
& \rightarrow 2 \text{O=C=O} + \text{H–O–H}
\end{align*} \]

\( \Delta H_{\text{rxn}} = [2 \text{BE}_{\text{C–H}} + \text{BE}_{\text{C=O}} + \frac{5}{2} \text{BE}_{\text{O=O}} ] + [4 (\text{BE}_{\text{C–O}}) + 2 (\text{BE}_{\text{O–H}})] \\
-1259 \text{ kJ} = [2(413) + \text{BE}_{\text{C=O}} + 5/2 (498)] + [4(–799) + 2(–467)] \\
-1259 \text{ kJ} = [826 + \text{BE}_{\text{C=O}} + 1245] + [-4130] \text{ kJ}
\]

\( \text{BE}_{\text{C=O}} = 800. \text{ kJ/mol} \)

Table 9.2 lists the value as 839 kJ/mol

b) heat \( (\text{kJ}) = \)

\[ 22 \times \left( \frac{500.0 \text{ g C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2} \right) \left( \frac{1 \text{ mol C}_2\text{H}_2}{1 \text{ mol C}_2\text{H}_2} \right) \left( \frac{1259 \text{ kJ}}{1 \text{ mol C}_2\text{H}_2} \right) \]

\[ = -2.4174347 \times 10^4 = -2.417 \times 10^4 \text{ kJ} \]

c) \( \text{CO}_2 \) produced \( (\text{g}) = \)

\[ 22 \times \left( \frac{500.0 \text{ g C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2} \right) \left( \frac{1 \text{ mol C}_2\text{H}_2}{1 \text{ mol C}_2\text{H}_2} \right) \left( \frac{2 \text{ mol CO}_2}{1 \text{ mol C}_2\text{H}_2} \right) \left( \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} \right) \]

\[ = 1690.092 = 1690 \text{ g CO}_2 \]

d) \( \text{mol O}_2 = \)

\[ 22 \times \left( \frac{500.0 \text{ g C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2} \right) \left( \frac{1 \text{ mol C}_2\text{H}_2}{1 \text{ mol C}_2\text{H}_2} \right) \left( \frac{5/2 \text{ mol O}_2}{1 \text{ mol C}_2\text{H}_2} \right) \]

\[ = 48.00307 \text{ mol O}_2 \text{ (unrounded)} \]

\[ \text{V} = \frac{\text{nRT}}{P} = \frac{\left( 48.00307 \text{ mol O}_2 \right)(0.08206 \text{ L•atm/mol•K})(298 \text{ K})}{18.0 \text{ atm}} \]

\[ = 65.2145 = 65.2 \text{ L O}_2 \]

9.75 a) \( \cdot \text{Br} + 3 \cdot \text{F} \rightarrow \cdot \text{F} + \cdot \text{Br} \)

b) \( \cdot \text{Al} + 3 \cdot \text{F} \rightarrow \cdot \text{F} + \cdot \text{Al} \)

9.76 a) 1) \( \text{Mg}(\text{s}) \rightarrow \text{Mg}(\text{g}) \) \( \Delta H^\circ = 148 \text{ kJ} \)

2) \( 1/2 \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g}) \) \( \Delta H^\circ = 1/2 (243 \text{ kJ}) \)

3) \( \text{Mg}(\text{g}) \rightarrow \text{Mg}^+ (\text{g}) + \text{e}^- \) \( \Delta H^\circ = 738 \text{ kJ} \)

4) \( \text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^- (\text{g}) \) \( \Delta H^\circ = -349 \text{ kJ} \)

5) \( \text{Mg}^+(\text{g}) + \text{Cl}^- (\text{g}) \rightarrow \text{MgCl}(\text{s}) \) \( \Delta H^\circ = -783.5 \text{ kJ} (= \Delta H^\circ_{\text{latex}} \text{ (MgCl)}) \)

6) \( \text{Mg}(\text{g}) + 1/2 \text{Cl}_2(\text{g}) \rightarrow \text{MgCl}(\text{s}) \) \( \Delta H^\circ (\text{MgCl}) = ? \)

\( \Delta H^\circ (\text{MgCl}) = \Delta H^\circ_{\text{Mg}} + \Delta H^\circ_{\text{Cl}} + \Delta H^\circ_{\text{MgCl}} + \Delta H^\circ_{\text{Cl}_2} \)

\[ = 148 \text{ kJ} + 1/2 (243 \text{ kJ}) + 738 \text{ kJ} + \left( -349 \text{ kJ} \right) + \left( -783.5 \text{ kJ} \right) = -125 \text{ kJ} \]

b) Yes, since \( \Delta H^\circ \) for MgCl is negative, MgCl(s) is stable relative to its elements.

c) 2 \( \text{MgCl}(\text{s}) \rightarrow \text{MgCl}_2(\text{s}) + \text{Mg}(\text{s}) \)

\( \Delta H^\circ = \left[ 1 \text{ mol (} \Delta H^\circ_{\text{MgCl}} \text{, MgCl}_2(\text{s})) + 1 \text{ mol (} \Delta H^\circ_{\text{Mg}}, \text{Mg}(\text{s})) \right] - \left[ 2 \text{ mol (} \Delta H^\circ_{\text{Mg}}, \text{MgCl}(\text{s})) \right] \)

\[ = \left[ 1 \text{ mol (} -641.6 \text{ kJ/mol) + 1 mol (0))} - \left[ 2 \text{ mol (} -125 \text{ kJ/mol}) \right] \right] \]

\[ = -391.6 = -392 \text{ kJ} \]

d) No, \( \Delta H^\circ_{\text{MgCl}} \) for MgCl is much more negative than that for MgCl. This makes the \( \Delta H^\circ \) value for the above reaction very negative, and the formation of MgCl\(_2\) would be favored.
9.77 a) \( \Delta H^\circ = \sum (n)BE_{\text{reactants}} + \sum (m)BE_{\text{products}} \)
\[
= [1 \text{ mol } (BE_{\text{H-H}}) + 1 \text{ mol } (BE_{\text{Cl-Cl}})] + [2 \text{ mol } (BE_{\text{H-Cl}})]
= [1 \text{ mol } (432 \text{ kJ/mol}) + 1 \text{ mol } (243 \text{ kJ/mol})] + [2 \text{ mol } (-427 \text{ kJ/mol})]
= -179 \text{ kJ}
\]

b) \( \Delta H^\circ = \sum (n)BE_{\text{reactants}} + \sum (m)BE_{\text{products}} \)
\[
= [1 \text{ mol } (BE_{\text{H-I}}) + 1 \text{ mol } (BE_{\text{I-I}})] + [2 \text{ mol } (BE_{\text{H-I}})]
= [1 \text{ mol } (432 \text{ kJ/mol}) + 1 \text{ mol } (151 \text{ kJ/mol})] + [2 \text{ mol } (-295 \text{ kJ/mol})]
= -7 \text{ kJ}
\]

c) \( \Delta H^\circ = \sum (n)BE_{\text{reactants}} + \sum (m)BE_{\text{products}} \)
\[
= [2 \text{ mol } (BE_{\text{H-H}}) + 1 \text{ mol } (BE_{\text{O-O}})] + [4 \text{ mol } (BE_{\text{H-O}})]
= [2 \text{ mol } (432 \text{ kJ/mol}) + 1 \text{ mol } (498 \text{ kJ/mol})] + [4 \text{ mol } (-467 \text{ kJ/mol})]
= -506 \text{ kJ}
\]
Reactions (a) and (c) are strongly exothermic and are a potential explosive hazard. Reaction (c) should occur most explosively.

9.78 a) Find the bond energy for an H–I bond from Table 9.2. Calculate wavelength from this energy using the relationship from Chapter 7: \( E = hc / \lambda \).
Bond energy for H–I is 295 kJ/mol (Table 9.2).
\[
\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{295 \text{ kJ/mol}} \left( 1 \text{ mol } \right) \left( 10^3 \text{ J} \right) \left( \frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 405.7807 = 406 \text{ nm}
\]

b) Calculate the energy for a wavelength of 254 nm and then subtract the energy from part a) to get the excess energy.
\[
E (254 \text{ nm}) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{254 \text{ nm}} \left( 3.00 \times 10^8 \text{ m/s} \right) \left( 1 \text{ nm} \right) = 7.82598 \times 10^{-19} \text{ J}
\]
Excess energy = 7.82598 \times 10^{-19} \text{ J} – 4.8987 \times 10^{-19} \text{ J} = 2.93 \times 10^{-19} \text{ J}

c) Speed can be calculated from the excess energy since \( E_k = \frac{1}{2} mu^2 \).
\[
E_k = \frac{1}{2} mu^2 \text{ thus, } u = \sqrt{\frac{2}{m} \left( \frac{1.008 \text{ g H}}{6.022 \times 10^{23} \text{ mol}} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right)} = 1.67386 \times 10^{-27} \text{ kg}
\]
\[
u = \frac{2(2.92728 \times 10^{-19} \text{ J})}{1.67386 \times 10^{-27} \text{ kg}} = 1.8701965 \times 10^4 = 1.87 \times 10^4 \text{ m/s}
\]

9.79 a) Vibrational motions have frequencies which are in the IR region of the electromagnetic spectrum.
b) \( E = hv = (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (4.02 \times 10^{13} \text{ s}^{-1}) = 2.66365 \times 10^{-20} \text{ J} \) (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} \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} \text{ J} \) (asymmetrical stretch)
Bending requires the least amount of energy.

9.80 “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 = \( BE_{X,Y} - \frac{1}{2} (BE_{X,X} + BE_{Y,Y}) \).
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).
\[
\Delta EN_{\text{PH}} = 0, \Delta EN_{CS} = 0, \Delta EN_{\text{BeCl}} = 0.2, \Delta EN_{\text{BH}} = 0.1, \Delta EN_{\text{SeSe}} = 0
\]
9.81 Rb ([Kr]5s¹) has one valence electron, so the metallic bonding would be fairly weak, resulting in a soft, low-melting material. Cd ([Kr]5s²4d¹⁰) has two valence electrons so the metallic bonding is stronger. V ([Ar]4s³3d⁵) has five valence electrons, so its metallic bonding is the strongest, that is, its hardness, melting point and other metallic properties would be greatest.

9.82 Find the appropriate bond energies in Table 9.2. Calculate the wavelengths using \( E = \frac{hc}{\lambda} \).

C–Cl bond energy = 339 kJ/mol

\[
\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 3.00 \times 10^8 \text{ m/s}}{339 \text{ kJ/mol} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} \times \frac{6.022 \times 10^{23}}{\text{mol}}} = 3.53 \times 10^{-7} \text{ m}
\]

O₂ bond energy = 498 kJ/mol

\[
\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 3.00 \times 10^8 \text{ m/s}}{498 \text{ kJ/mol} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} \times \frac{6.022 \times 10^{23}}{\text{mol}}} = 2.40 \times 10^{-7} \text{ m}
\]

9.83 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.

\[
\begin{align*}
\text{XeF}_2 & : \text{Xe}(g) + \text{F}_2(g) \rightarrow \text{XeF}_2(g) \\
\Delta H &= [1 \text{ mol F}_2 (159 \text{ kJ/mol})] + [2 (-\text{Xe–F})] = -105 \text{ kJ/mol} \\
\text{Xe–F} &= 132 \text{ kJ/mol} \\
\text{XeF}_4 & : \text{Xe}(g) + 2 \text{ F}_2(g) \rightarrow \text{XeF}_4(g) \\
\Delta H &= [2 \text{ mol F}_2 (159 \text{ kJ/mol})] + [4 (-\text{Xe–F})] = -284 \text{ kJ/mol} \\
\text{Xe–F} &= 150.5 \text{ kJ/mol} \\
\text{XeF}_6 & : \text{Xe}(g) + 3 \text{ F}_2(g) \rightarrow \text{XeF}_6(g) \\
\Delta H &= [3 \text{ mol F}_2 (159 \text{ kJ/mol})] + [6 (-\text{Xe–F})] = -402 \text{ kJ/mol} \\
\text{Xe–F} &= 146.5 \text{ kJ/mol}
\end{align*}
\]

9.84 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.

9.85 a) The presence of the very electronegative fluorine atoms bonded to one of the carbons 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 O₂ bond is 498 kJ/mol. \( \Delta H = \text{homolytic cleavage + electron affinity + first ionization energy} \) \( \Delta H = (498/2 \text{ kJ/mol} + (-141 \text{ kJ/mol} + 1314 \text{ kJ/mol}) = 1422 = 1420 \text{ kJ/mol} \)

It would require 1420 kJ to heterolytically cleave 1 mol of O₂.

9.86 The bond energies are needed from Table 9.2. \( \text{N}_2 = 945 \text{ kJ/mol} \); \( \text{O}_2 = 498 \text{ kJ/mol} \); \( \text{F}_2 = 159 \text{ kJ/mol} \)

\[
\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 3.00 \times 10^8 \text{ m/s}}{945 \text{ kJ/mol} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} \times \frac{6.022 \times 10^{23}}{\text{mol}}} = 1.26672 \times 10^{-7} = 1.27 \times 10^{-7} \text{ m}
\]
9.87 a) To compare the two energies, the ionization energy must be converted to the energy to remove an electron from an atom. The energy needed to remove an electron from a single gaseous Ag atom (J) = 
\[
\left( \frac{731 \text{ kJ}}{\text{mol}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) \left( \frac{\text{mol}}{6.022 \times 10^{23}} \right) = 1.21388 \times 10^{-18} = 1.21 \times 10^{-18} \text{ J} > 7.59 \times 10^{-19} \text{ J}
\]
It requires less energy to remove an electron from the surface of solid silver.
b) The electrons in solid silver are held less tightly than the electrons in gaseous silver because the electrons in metals are delocalized, meaning they are shared among all the metal nuclei. The delocalized attraction of many nuclei to an electron (solid silver) is weaker than the localized attraction of one nucleus to an electron (gaseous silver).

9.88 Use Hess’ Law. \( \Delta H_f^o \) of SiO\(_2\) is found in Appendix B.

1) \( \text{Si}(s) \rightarrow \text{Si}(g) \) \( \Delta H_f^o = 454 \text{ kJ} \)
2) \( \text{Si}(g) \rightarrow \text{Si}^{2+}(g) + 4e^- \) \( \Delta H_f^o = 9949 \text{ kJ} \)
3) \( \text{O}_2(g) \rightarrow 2 \text{O}^{2-}(g) \) \( \Delta H_f^o = 498 \text{ kJ} \)
4) \( 2 \text{O}^{2-}(g) + 4 e^- \rightarrow 2 \text{O}^{2-}(g) \) \( \Delta H_f^o = 2(737) \text{ kJ} \)
5) \( \text{Si}^{2+}(g) + 2 \text{O}^{2-}(g) \rightarrow \text{SiO}_2(s) \) \( \Delta H_f^o = \Delta H_{\text{lattice}}^o (\text{SiO}_2) = ? \)
6) \( \text{Si}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) \) \( \Delta H_f^o (\text{SiO}_2) = -910.9 \text{ kJ} \)
\( \Delta H_f^o = - \left( \Delta H_f^o + \Delta H_f^o + \Delta H_f^o + \Delta H_{\text{lattice}}^o \right) \)
\( -910.9 \text{ kJ} = (454 \text{ kJ} + 9949 \text{ kJ} + 498 \text{ kJ} + 2(737) \text{ kJ} + \Delta H_{\text{lattice}}^o ) \)
\( \Delta H_{\text{lattice}}^o = -13285.9 = -13286 \text{ kJ} \)

9.89 \( \Delta H_{\text{rxn}}^o = \Sigma (n) \text{BE reactants} + \Sigma \text{BE products} \)
For ethane: \( \Delta H_{\text{rxn}}^o = [1 \text{ mol (BE}_\text{C-C}) + 6 \text{ mol (BE}_\text{C-H}) + 1 \text{ mol (BE}_\text{H-H})] + [8 \text{ mol (BE}_\text{C-H})] \)
\( -65.07 \text{ kJ} = [1 \text{ mol (347 kJ/mol) + 6 mol (BE}_\text{C-H}) + 1 \text{ mol (432 kJ/mol})] + [8(-415 kJ/mol)] \)
\( \text{BE}_\text{C-H} = \frac{-65.07 - 347 - 432 + 3320}{6 \text{ mol}} = 412.655 = 413 \text{ kJ/mol} \)

For ethene: \( \Delta H_{\text{rxn}}^o = [1 \text{ mol (BE}_\text{C-C}) + 4 \text{ mol (BE}_\text{C-H}) + 2 \text{ mol (BE}_\text{H-H})] + [8 \text{ mol (BE}_\text{C-H})] \)
\( -202.21 \text{ kJ} = [1 \text{ mol (614 kJ/mol) + 4 mol (BE}_\text{C-H}) + 2 \text{ mol (432 kJ/mol})] + [8 \text{ mol (-415 kJ/mol)]} \)
\( \text{BE}_\text{C-H} = \frac{-202.21 - 614 - 864 + 3320}{4 \text{ mol}} = 409.9475 = 410 \text{ kJ/mol} \)
For ethyne: \( \Delta H^\circ_{\text{rxn}} = [1 \text{ mol} (\text{BE}_\text{C=C}) + 2 \text{ mol} (\text{BE}_\text{C-H}) + 3 \text{ mol} (\text{BE}_\text{H-H})] + [8 \text{ mol} (\text{BE}_\text{C-H})] \)

\( -376.74 \text{ kJ} = [1 \text{ mol} (839 \text{ kJ/mol}) + 2 \text{ mol} (\text{BE}_\text{C-H}) + 3 \text{ mol} (432 \text{ kJ/mol})] + [8 \text{ mol} (-415 \text{ kJ/mol})] \)

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

9.90 Use the equations \( E = h\nu \), and \( E = \frac{hc}{\lambda} \).

\[ \nu = \frac{E}{h} = \frac{\left(347 \text{ kJ/mol}\right) \left(10^7 \text{ J/1 kJ}\right) \left(6.022 \times 10^{23}\text{ mol}\right)}{6.626 \times 10^{-34} \text{ J}\text{s}} = 8.696356 \times 10^{14} = 8.70 \times 10^{14} \text{ s}^{-1} \]

\[ \lambda = \frac{hc}{E} = \frac{\left(6.626 \times 10^{-34} \text{ J}\text{s}\right) \left(3.00 \times 10^8 \text{ m/s}\right) \left(10^3 \text{ J/1 kJ}\right) \left(6.022 \times 10^{23}\text{ mol}\right)}{347 \text{ kJ/mol}} = 3.44972 \times 10^{-7} = 3.45 \times 10^{-7} \text{ m} \]

This is in the ultraviolet region of the electromagnetic spectrum.

9.91

\[ \nu = \frac{E}{h} = \frac{\left(467 \text{ kJ/mol}\right) \left(10^7 \text{ J/1 kJ}\right) \left(6.022 \times 10^{23}\text{ mol}\right)}{6.626 \times 10^{-34} \text{ J}\text{s}} = 1.170374 \times 10^{15} = 1.17 \times 10^{15} \text{ s}^{-1} \]

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

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

9.92 a) \( 2 \text{CH}_4(\ell) + \text{O}_2(\ell) \rightarrow \text{CH}_3\text{OCH}_3(\ell) + \text{H}_2\text{O}(\ell) \)

\( \Delta H^\circ_{\text{rxn}} = \Sigma \text{BE}_{\text{reactants}} + \Sigma \text{BE}_{\text{products}} \)

\( \Delta H^\circ_{\text{rxn}} = [8 \times (\text{BE}_{\text{C-H}}) + (\text{BE}_{\text{O}=\text{O}})] + [6 \times (\text{BE}_{\text{C-H}}) + 2 \times (\text{BE}_{\text{C-O}}) + 2 \times (\text{BE}_{\text{O-H}})] \)

\( \Delta H^\circ_{\text{rxn}} = [8 \times (413 \text{ kJ}) + 498 \text{ kJ}] + [6 \times (-413 \text{ kJ}) + 2 \times (-358 \text{ kJ}) + 2 \times (-467)] \)

\( \Delta H^\circ_{\text{rxn}} = -326 \text{ kJ} \)

b) The formation of gaseous ethanol is more exothermic.

c) \( \Delta H^\circ_{\text{rxn}} = -326 \text{ kJ} - (-369 \text{ kJ}) = 43 \text{ kJ} \)

9.93 a) \( \text{CH}_2=\text{CH}_2(\ell) + \text{H}_2\text{O}(\ell) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\ell) \)

Using bond energies: \( \Delta H^\circ_{\text{rxn}} = \Sigma \text{BE}_{\text{reactants}} + \Sigma \text{BE}_{\text{products}} \)

\( \Delta H^\circ_{\text{rxn}} = [4 \times (\text{BE}_{\text{C-H}}) + (\text{BE}_{\text{C-C}}) + 2 \times (\text{BE}_{\text{O-H}})] + [5 \times (\text{BE}_{\text{C-H}}) + (\text{BE}_{\text{C-C}}) + (\text{BE}_{\text{C-O}}) + 3 \times (\text{BE}_{\text{O-H}})] \)

\( \Delta H^\circ_{\text{rxn}} = [4 \times (413 \text{ kJ}) + 614 \text{ kJ} + 2 \times (467 \text{ kJ})] + [5 \times (-413 \text{ kJ}) + (-347 \text{ kJ}) + (-358 \text{ kJ}) + 3 \times (-467)] \)

\( \Delta H^\circ_{\text{rxn}} = -37 \text{ kJ} \)

Using heats of formation: \( \Delta H^\circ = \Sigma \Delta H_{\text{products}}^* - \Sigma \Delta H_{\text{reactants}}^* \)

\( \Delta H^\circ = [1 \text{ mol} \times \Delta H_{\text{CH}_3\text{CH}_2\text{OH}(\ell))} - [1 \text{ mol} \times \Delta H_{\text{CH}_2=\text{CH}_2(\ell)} + 1 \text{ mol} \times \Delta H_{\text{H}_2\text{O}(\ell)}] \)

\( \Delta H^\circ = [-235.1 \text{ kJ}] - [52.47 \text{ kJ} + (-241.826 \text{ kJ})] \)

\( \Delta H^\circ = -45.744 = -45.7 \text{ kJ} \)
b) \[ \text{C}_2\text{H}_4\text{O}(l) + \text{H}_2\text{O}(l) \rightarrow \text{C}_2\text{H}_6\text{O}_2(l) \]

\[ \Delta H_{\text{rxn}} = \Sigma \text{BE}_{\text{reactants}} + \Sigma \text{BE}_{\text{products}} \]

\[ \Delta H_{\text{rxn}} = \left[ 4 \times \text{(BE}_\text{C-H}) + \text{(BE}_\text{C-C}) + 2\text{(BE}_\text{C-O}) + 2\text{(BE}_\text{O-H}) \right] \]

\[ + \left[ 4\text{(BE}_\text{C-H}) + \text{(BE}_\text{C-C}) + 2\text{(BE}_\text{C-O}) + 2\text{(BE}_\text{O-H}) \right] \]

\[ \Delta H_{\text{rxn}} = \left[ 4(413 \text{ kJ}) + 347 \text{ kJ} + 2(358 \text{ kJ}) + 2(467 \text{ kJ}) \right] \]

\[ + \left[ 4(-413 \text{ kJ}) + (-347 \text{ kJ}) + 2(-358 \text{ kJ}) + 2(-467 \text{ kJ}) \right] \]

\[ \Delta H_{\text{rxn}} = 0 \text{ kJ} \]

c) In the hydrolysis in part b), the \( \Delta H_{\text{rxn}} \) appears to be 0 kJ using bond energies since the number and types of bonds broken and the number and types of bonds formed are the same. Since the bond energy values used are average values, this method does not differentiate between an O-H bond in water, for example and an O-H bond in ethylene glycol.