

# CHAPTER 8 MODELS OF CHEMICAL BONDING

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## END-OF-CHAPTER PROBLEMS

- 8.1 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.
- 8.4 Plan: 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 15 than N.
- 8.6 Plan: 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<sub>2</sub> is **covalent** because N is a nonmetal.  
c) Bonding in Na(s) is **metallic** because this is a monatomic, metal solid.
- 8.8 Plan: Ionic bonding occurs between metals and nonmetals, covalent bonding between nonmetals, and metallic bonds between metals.  
Solution:  
a) Bonding in O<sub>3</sub> would be **covalent** since O is a nonmetal.  
b) Bonding in MgCl<sub>2</sub> would be **ionic** since Mg is a metal and Cl is a nonmetal.  
c) Bonding in BrO<sub>2</sub> would be **covalent** since both Br and O are nonmetals.
- 8.10 Plan: 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 elements in Groups 1-2 and the group number – 10 of the main-group elements in Groups 13-18 gives the number of valence electrons. Rb is Group 1, Si is a Group 14 element, and I is a Group 17 element.  
Solution:
- a) Rb •      b) • Si •      c) • I •
- 8.12 Plan: 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 elements in Groups 1-2 and the group number – 10 of the main-group elements in Groups 13-18 gives the number of valence electrons. Sr is a Group 1 element, P is a Group 15 element, and S is a Group 16 element.  
Solution:
- a) • Sr •      b) • P •      c) • S •

- 8.14 Plan: Assuming X is a main-group element, the number of dots (valence electrons) equals the group number if this number is 1 or 2. If the number of dots (valence electrons) is 3 or more, then we add 10 to calculate the group number. Once the group number is known, the general electron configuration of the element can be written.

Solution:

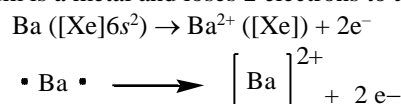
a) Since there are 6 dots in the Lewis electron-dot symbol, element X has 6 valence electrons and is a Group 16 element. Its general electron configuration is **[noble gas] $ns^2np^4$** , where  $n$  is the energy level.

b) Since there are 3 dots in the Lewis electron-dot symbol, element X has 3 valence electrons and is a Group 13 element with general electron configuration **[noble gas] $ns^2np^1$** .

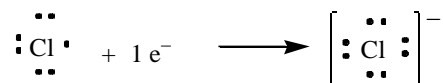
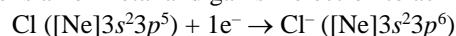
- 8.20 Plan: Write condensed electron configurations and draw the Lewis electron-dot symbols for the atoms. The group number of the elements in Groups 1-2 and the group number – 10 of the main-group elements in Groups 13-18 gives the number of valence electrons. Remove electrons from the metal and add 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:

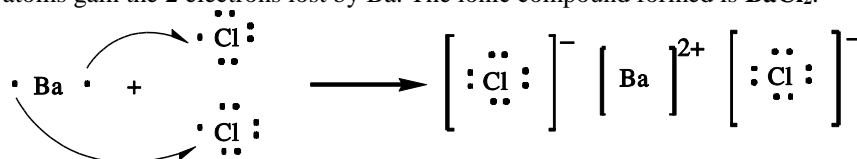
a) Barium is a metal and loses 2 electrons to achieve a noble gas configuration:



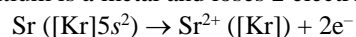
Chlorine is a nonmetal and gains 1 electron to achieve a noble gas configuration:



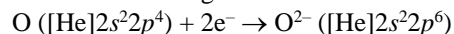
Two Cl atoms gain the 2 electrons lost by Ba. The ionic compound formed is **BaCl<sub>2</sub>**.



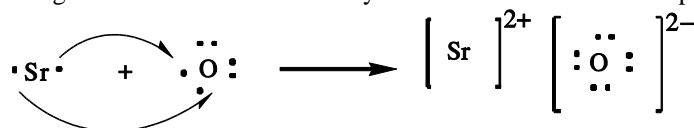
b) Strontium is a metal and loses 2 electrons to achieve a noble gas configuration:



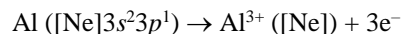
Oxygen is a nonmetal and gains 2 electrons to achieve a noble gas configuration:



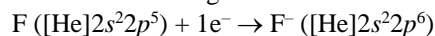
One O atom gains the two electrons lost by one Sr atom. The ionic compound formed is **SrO**.



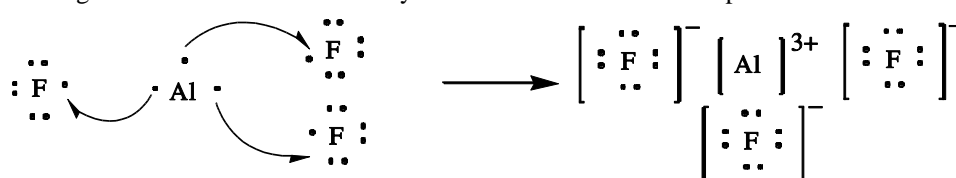
c) Aluminum is a metal and loses 3 electrons to achieve a noble gas configuration:



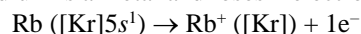
Fluorine is a nonmetal and gains 1 electron to achieve a noble gas configuration:



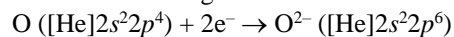
Three F atoms gain the three electrons lost by one Al atom. The ionic compound formed is **AlF<sub>3</sub>**.



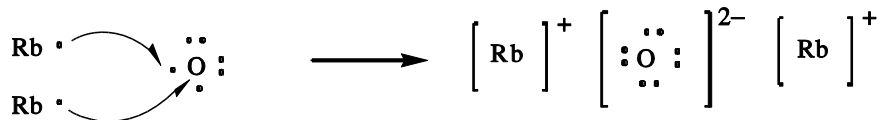
d) Rubidium is a metal and loses 1 electron to achieve a noble gas configuration:



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



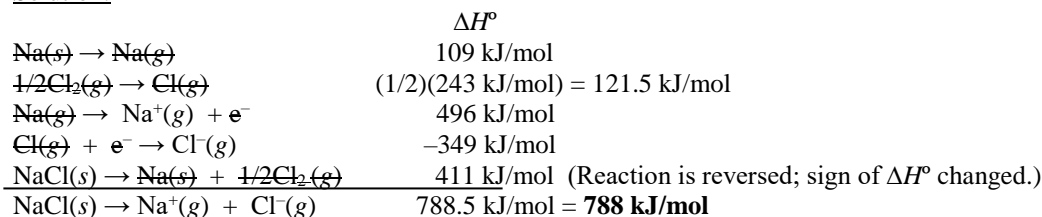
One O atom gains the two electrons lost by two Rb atoms. The ionic compound formed is **Rb<sub>2</sub>O**.



- 8.22 Plan: Find the charge of the known atom and use that charge to find the ionic charge of element X.  
For cations of groups 1 and 2, ion charge = the group number; for cations of groups 13 and higher, ion charge = the group number – 10. For anions, ion charge = the group number – 18. Once the ion charge of X is known, the group number can be determined.  
Solution:  
a) X in  $\text{XF}_2$  is a cation with +2 charge since the anion is  $\text{F}^-$  and there are two fluoride ions in the compound. **Group 2** metals form +2 ions.  
b) X in  $\text{MgX}$  is an anion with – 2 charge since  $\text{Mg}^{2+}$  is the cation. Elements in **Group 16** form –2 ions ( $16 - 18 = -2$ ).  
c) X in  $\text{X}_2\text{SO}_4$  must be a cation with +1 charge since the polyatomic sulfate ion has a charge of –2. X comes from **Group 1**.
- 8.24 Plan: Find the charge of the known atom and use that charge to find the ionic charge of element X.  
For cations of groups 1 and 2, ion charge = the group number; for cations of groups 13 and higher, ion charge = the group number – 10. For anions, ion charge = the group number – 18. Once the ion charge of X is known, the group number can be determined.  
Solution:  
a) X in  $\text{X}_2\text{O}_3$  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 13** form +3 ions.  
b) The carbonate ion,  $\text{CO}_3^{2-}$ , has a –2 charge, so X has a +2 charge. **Group 2** elements form +2 ions.  
c) X in  $\text{Na}_2\text{X}$  has a –2 charge, balanced with the +2 overall charge from the two  $\text{Na}^+$  ions. **Group 16** elements gain 2 electrons to form –2 ions with a noble gas configuration.
- 8.26 Plan: 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** would have the higher lattice energy since the charge on each ion (+2 for Ba and –2 for S) is twice the charge on the ions in  $\text{CsCl}$  (+1 for Cs and –1 for Cl) and lattice energy is greater when ionic charges are larger.  
b) **LiCl** would have the higher lattice energy since the ionic radius of  $\text{Li}^+$  is smaller than that of  $\text{Cs}^+$  and lattice energy is greater when the distance between ions is smaller.
- 8.28 Plan: 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  $\text{Ba}^{2+}$  is larger than  $\text{Ca}^{2+}$ . 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  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions. Lattice energy increases with increasing ion charge.

- 8.30 Plan: The lattice energy of NaCl is represented by the equation  $\text{NaCl}(s) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g)$ . Use Hess's law and arrange the given equations so that they sum up to give the equation for the lattice energy. You will need to reverse the last equation (and change the sign of  $\Delta H^\circ$ ); you will also need to multiply the second equation ( $\Delta H^\circ$ ) by  $\frac{1}{2}$ .

Solution:

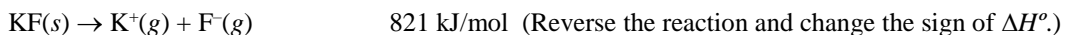
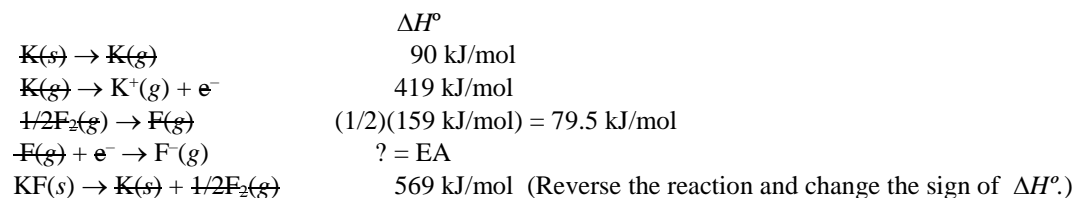


The lattice energy for NaCl is less than that of LiF, which is expected since lithium and fluoride ions are smaller than sodium and chloride ions, resulting in a larger lattice energy for LiF.

- 8.33 Plan: The electron affinity of fluorine is represented by the equation  $\text{F}(g) + e^- \rightarrow \text{F}^-(g)$ . Use Hess's law and arrange the given equations so that they sum up to give the equation for the lattice energy,  $\text{KF}(s) \rightarrow \text{K}^+(g) + \text{F}^-(g)$ . You will need to reverse the last two given equations (and change the sign of  $\Delta H^\circ$ ); you will also need to multiply the third equation ( $\Delta H^\circ$ ) by  $\frac{1}{2}$ . Solve for EA.

Solution:

An analogous Born-Haber cycle has been described in Figure 8.7 for LiF. Use Hess's law and solve for the EA of fluorine:



$$821 \text{ kJ/mol} = 90 \text{ kJ/mol} + 419 \text{ kJ/mol} + 79.5 \text{ kJ/mol} + \text{EA} + 569 \text{ kJ/mol}$$

$$\text{EA} = 821 \text{ kJ/mol} - (90 + 419 + 79.5 + 569) \text{ kJ/mol}$$

$$\text{EA} = -336.5 \text{ kJ/mol} = \textbf{-336 kJ/mol}$$

- 8.34 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.
- 8.35 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  $\Delta_{\text{bond breaking}} H^\circ$  is positive. The same amount of energy needed to break the bond is released upon its formation, so  $\Delta_{\text{bond forming}} H^\circ$  has the same magnitude as  $\Delta_{\text{bond breaking}} H^\circ$ , but opposite in sign (always exothermic and negative).

- 8.39 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)  $\text{S-Br} < \text{S-Cl} < \text{S-H}$ . 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)  $\text{C-N} < \text{C=N} < \text{C}\equiv\text{N}$ . 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.

- 8.41 Plan: Bond strength increases as the atomic radii of atoms in the bond decrease; bond strength also increases as bond order increases.

Solution:

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.

- 8.43 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.

- 8.45 Plan: Write the combustion reactions of methane and of methanal. 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:  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$  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 methanal:  $\text{CH}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$  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 methanal.

- 8.47 Plan: 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 8.2.

Solution:

Reactant bonds broken:

$$1 \times \text{C}=\text{C} = 1(614 \text{ kJ/mol}) = 614 \text{ kJ/mol}$$

$$4 \times \text{C}-\text{H} = 4(413 \text{ kJ/mol}) = 1652 \text{ kJ/mol}$$

$$1 \times \text{Cl}-\text{Cl} = (243 \text{ kJ/mol}) = 243 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds broken}} H^\circ = 2509 \text{ kJ/mol}$$

Product bonds formed:

$$1 \times \text{C}-\text{C} = (-347 \text{ kJ/mol}) = -347 \text{ kJ/mol}$$

$$4 \times \text{C}-\text{H} = 4(-413 \text{ kJ/mol}) = -1652 \text{ kJ/mol}$$

$$2 \times \text{C}-\text{Cl} = 2(-339 \text{ kJ/mol}) = -678 \text{ kJ/mol}$$

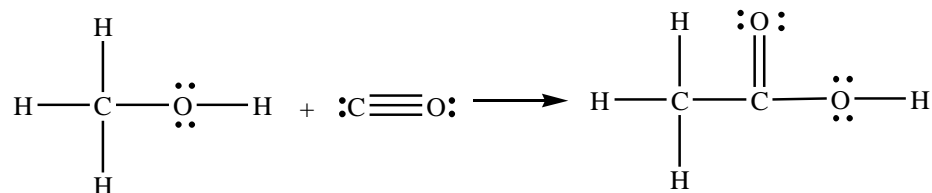
$$\Sigma \Delta_{\text{bonds formed}} H^\circ = -2677 \text{ kJ/mol}$$

$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ = 2509 \text{ kJ/mol} + (-2677 \text{ kJ/mol}) = \mathbf{-168 \text{ kJ/mol}}$$

- 8.49 Plan: 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 8.2.

Solution:

The reaction:



Reactant bonds broken:

$$1 \times \text{C}-\text{O} = (358 \text{ kJ/mol}) = 358 \text{ kJ/mol}$$

$$3 \times \text{C}-\text{H} = 3(413 \text{ kJ/mol}) = 1239 \text{ kJ/mol}$$

$$1 \times \text{O}-\text{H} = (467 \text{ kJ/mol}) = 467 \text{ kJ/mol}$$

$$1 \times \text{C}\equiv\text{O} = \underline{(1070 \text{ kJ/mol})} = 1070 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds broken}} H^\circ = 3134 \text{ kJ/mol}$$

Product bonds formed:

$$3 \times \text{C}-\text{H} = 3(-413 \text{ kJ/mol}) = -1239 \text{ kJ/mol}$$

$$1 \times \text{C}-\text{C} = (-347 \text{ kJ/mol}) = -347 \text{ kJ/mol}$$

$$1 \times \text{C}=\text{O} = (-745 \text{ kJ/mol}) = -745 \text{ kJ/mol}$$

$$1 \times \text{C}-\text{O} = (-358 \text{ kJ/mol}) = -358 \text{ kJ/mol}$$

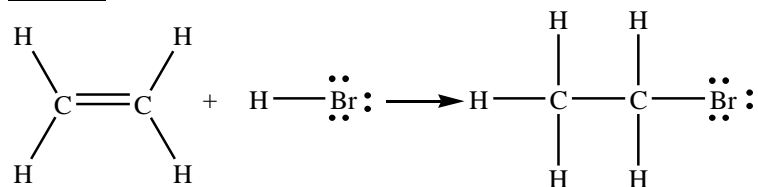
$$1 \times \text{O}-\text{H} = \underline{(-467 \text{ kJ/mol})} = -467 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds formed}} H^\circ = -3156 \text{ kJ/mol}$$

$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ = 3134 \text{ kJ/mol} + (-3156 \text{ kJ/mol}) = \mathbf{-22 \text{ kJ/mol}}$$

- 8.50 Plan: 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 8.2.

Solution:



Reactant bonds broken:

$$1 \times \text{C}=\text{C} = (614 \text{ kJ/mol}) = 614 \text{ kJ/mol}$$

$$4 \times \text{C}-\text{H} = 4(413 \text{ kJ/mol}) = 1652 \text{ kJ/mol}$$

$$1 \times \text{H}-\text{Br} = (363 \text{ kJ/mol}) = \underline{363 \text{ kJ/mol}}$$

$$\Sigma \Delta_{\text{bonds broken}} H^\circ = 2629 \text{ kJ/mol}$$

Product bonds formed:

$$5 \times \text{C}-\text{H} = 5(-413 \text{ kJ/mol}) = -2065 \text{ kJ/mol}$$

$$1 \times \text{C}-\text{C} = (-347 \text{ kJ/mol}) = -347 \text{ kJ/mol}$$

$$1 \times \text{C}-\text{Br} = \underline{(-276 \text{ kJ/mol})} = -276 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds formed}} H^\circ = -2688 \text{ kJ/mol}$$

$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ = 2629 \text{ kJ/mol} + (-2688 \text{ kJ/mol}) = \mathbf{-59 \text{ kJ/mol}}$$

- 8.51 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.

8.53 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.

8.56 Plan: 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) **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.

8.58 Plan: Electronegativity increases from left to right across a period (except for the noble gases) and increases from bottom to top within a group.

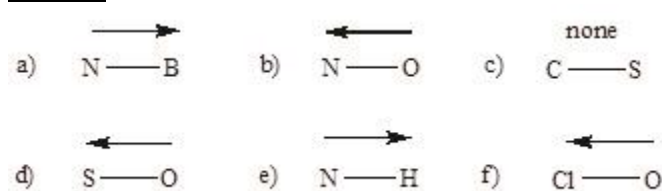
Solution:

a) **N > P > Si**, nitrogen is above P in Group 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 rightmost element.

8.60 Plan: The polar arrow points toward the less 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:



8.62 Plan: The more polar bond will have a greater difference in electronegativity,  $\Delta\chi$ .

Solution:

a) N:  $\chi = 3.0$ ; B:  $\chi = 2.0$ ;  $\Delta_a\chi = 3.0 - 2.0 = 1.0$

b) N:  $\chi = 3.0$ ; O:  $\chi = 3.5$ ;  $\Delta_b\chi = 3.5 - 3.0 = 0.5$

c) C:  $\chi = 2.5$ ; S:  $\chi = 2.5$ ;  $\Delta_c\chi = 2.5 - 2.5 = 0$

d) S:  $\chi = 2.5$ ; O:  $\chi = 3.5$ ;  $\Delta_d\chi = 3.5 - 2.5 = 1.0$

e) N:  $\chi = 3.0$ ; H:  $\chi = 2.1$ ;  $\Delta_e\chi = 3.0 - 2.1 = 0.9$

f) Cl:  $\chi = 3.0$ ; O:  $\chi = 3.5$ ;  $\Delta_f\chi = 3.5 - 3.0 = 0.5$

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

8.64 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  $\Delta\chi$ , the more polar the bond.

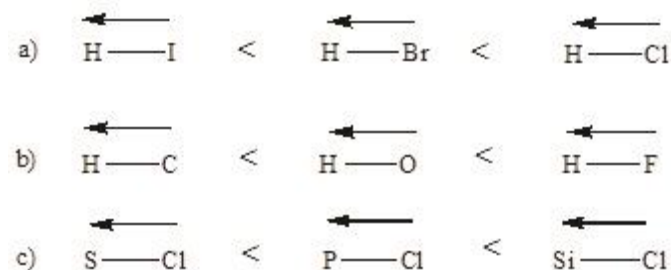
Solution:

- 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.  $\Delta\chi = 0$ .
- b) Bonds in  $RbCl$  are **ionic** because Rb is a metal and Cl is a nonmetal.  $\Delta\chi$  is large.
- c) Bonds in  $PF_3$  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  $SCl_2$  are **polar covalent**. S and Cl are nonmetals and differ in electronegativity (by 0.5 units 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  $\Delta\chi = 0$ .
- 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:  $SCl_2 < SF_2 < PF_3$**

- 8.66 **Plan:** Increasing ionic character occurs with increasing  $\Delta\chi$ . 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 less electronegative atom.

**Solution:**

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



- 8.69 **Plan:** To be the central atom in a compound, an atom must be able to simultaneously bond to at least two other atoms.

**Solution:**

**He, F, and H** cannot serve as central atoms in a Lewis structure. Helium ( $1s^2$ ) is a noble gas, and as such, it does not need to bond to any other atoms. Hydrogen ( $1s^1$ ) and fluorine ( $1s^2 2s^2 2p^5$ ) only need one electron to complete their valence shells. Thus, they can only bond to one other atom, and they do not have d orbitals available to expand their valence shells.

- 8.71 **Plan:** For an element to obey the octet rule it must be surrounded by eight electrons. To determine the number of electrons present, (1) count the individual electrons actually shown adjacent to a particular atom (lone pairs), and (2) add two times the number of bonds to that atom: number of electrons = individual electrons + 2(number of bonds).

**Solution:**

- (a)  $0 + 2(4) = 8$ ; (b)  $2 + 2(3) = 8$ ; (c)  $0 + 2(5) = 10$ ; (d)  $2 + 2(3) = 8$ ; (e)  $0 + 2(4) = 8$ ;  
 (f)  $2 + 2(3) = 8$ ; (g)  $0 + 2(3) = 6$ ; (h)  $8 + 2(0) = 8$ .

**All the structures obey the octet rule except: c and g.**

- 8.73 **Plan:** Count the valence electrons and draw Lewis structures.

**Solution:**

Total valence electrons:  $\text{SiF}_4$ :  $[1 \times \text{Si}(4e^-)] + [4 \times \text{F}(7e^-)] = 32$ ;  $\text{SeCl}_2$ :  $[1 \times \text{Se}(6e^-)] + [2 \times \text{Cl}(7e^-)] = 20$ ;  $\text{COF}_2$ :  $[1 \times \text{C}(4e^-)] + [1 \times \text{O}(6e^-)] + [2 \times \text{F}(7e^-)] = 24$ . The Si, Se, and the C are the central atoms, because these are the elements in their respective compounds with the lower group number (in addition, we are told C is central). Place the other atoms around the central atoms and connect each to the central atom with a single bond.  $\text{SiF}_4$ : At this

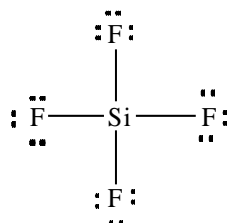


point, eight electrons ( $2e^-$  in four Si-F bonds) have been used with  $32 - 8 = 24$  remaining; the remaining electrons are placed around the fluorine atoms (three pairs each). All atoms have an octet.

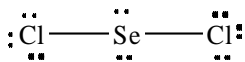
$\text{SeCl}_2$ : The two bonds use  $4e^-$  ( $2e^-$  in two Se-Cl bonds) leaving  $20 - 4 = 16e^-$ . These  $16e^-$  are used to complete the octets on Se and the Cl atoms.

$\text{COF}_2$ : The three bonds to the C use  $6e^-$  ( $2e^-$  in three bonds) leaving  $24 - 6 = 18e^-$ . These  $18e^-$  are distributed to the surrounding atoms first to complete their octets. After the  $18e^-$  are used, the central C is two electrons short of an octet. Forming a double bond to the O (change a lone pair on O to a bonding pair on C) completes the C octet.

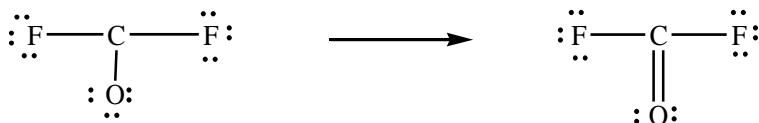
(a)  $\text{SiF}_4$



(b)  $\text{SeCl}_2$



(c)  $\text{COF}_2$



8.75 Plan: Count the valence electrons and draw Lewis structures.

Solution:

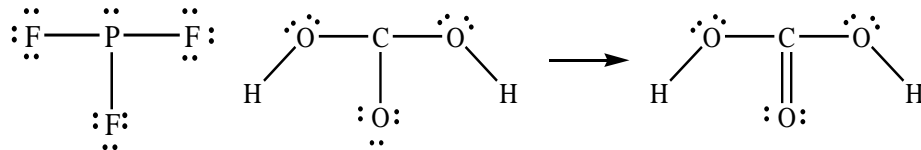
a)  $\text{PF}_3$ :  $[1 \times \text{P}(5e^-)] + [3 \times \text{F}(7e^-)] = 26$  valence electrons. P is the central atom. Draw single bonds from P to the three F atoms, using  $2e^- \times 3 \text{ bonds} = 6e^-$ . Remaining  $e^-$ :  $26 - 6 = 20e^-$ . Distribute the  $20e^-$  around the P and F atoms to complete their octets.

b)  $\text{H}_2\text{CO}_3$ :  $[2 \times \text{H}(1e^-)] + [1 \times \text{C}(4e^-)] + 3 \times \text{O}(6e^-)] = 24$  valence electrons. C is the central atom with the H atoms attached to the O atoms. Place appropriate single bonds between all atoms using  $2e^- \times 5 \text{ bonds} = 10e^-$  so that  $24 - 10 = 14e^-$  remain. Use these  $14e^-$  to complete the octets of the O atoms (the H atoms already have their two electrons). After the  $14e^-$  are used, the central C is two electrons short of an octet. Forming a double bond to the O that does not have an H bonded to it (change a lone pair on O to a bonding pair on C) completes the C octet.

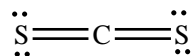
c)  $\text{CS}_2$ :  $[1 \times \text{C}(4e^-)] + [2 \times \text{S}(6e^-)] = 16$  valence electrons. C is the central atom. Draw single bonds from C to the two S atoms, using  $2e^- \times 2 \text{ bonds} = 4e^-$ . Remaining  $e^-$ :  $16 - 4 = 12e^-$ . Use these  $12e^-$  to complete the octets of the surrounding S atoms; this leaves C four electrons short of an octet. Form a double bond from each S to the C by changing a lone pair on each S to a bonding pair on C.

a)  $\text{PF}_3$  (26 valence  $e^-$ )

b)  $\text{H}_2\text{CO}_3$  (24 valence  $e^-$ )



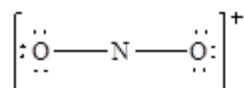
c)  $\text{CS}_2$  (16 valence  $e^-$ )



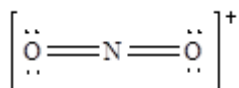
8.77 Plan: The problem asks for resonance structures, so there must be more than one answer for each part.

Solution:

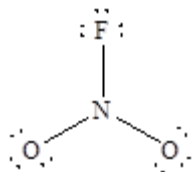
- a)  $\text{NO}_2^+$  has  $[1 \times \text{N}(5e^-)] + [2 \times \text{O}(6e^-)] - 1e^-$  (+ charge) = 16 valence electrons. Draw a single bond from N to each O, using  $2e^- \times 2 \text{ bonds} = 4e^-$ ;  $16 - 4 = 12e^-$  remain. Distribute these  $12e^-$  to the O atoms to complete their octets.



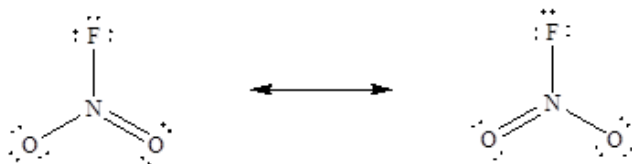
This leaves N  $4e^-$  short of an octet. Form a double bond from each O to the N by changing a lone pair on each O to a bonding pair on N. No resonance is required as all atoms can achieve an octet with double bonds.



- b)  $\text{NO}_2\text{F}$  has  $[1 \times \text{N}(5e^-)] + [2 \times \text{O}(6e^-)] + [1 \times \text{F}(7e^-)] = 24$  valence electrons. Draw a single bond from N to each surrounding atom, using  $2e^- \times 3 \text{ bonds} = 6e^-$ ;  $24 - 6 = 18e^-$  remain. Distribute these  $18e^-$  to the O and F atoms to complete their octets.



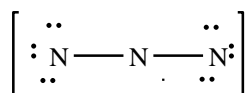
This leaves N  $2e^-$  short of an octet. Form a double bond from either O to the N by changing a lone pair on O to a bonding pair on N. There are two resonance structures since a lone pair from either of the two O atoms can be moved to a bonding pair with N:



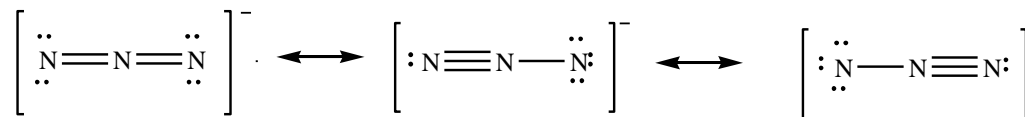
8.79 Plan: Count the valence electrons and draw Lewis structures. Additional structures are needed to show resonance.

Solution:

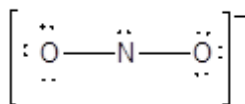
- a)  $\text{N}_3^-$  has  $[3 \times \text{N}(5e^-)] + [1 e^- (\text{from charge})] = 16$  valence electrons. Place a single bond between the nitrogen atoms. This uses  $2e^- \times 2 \text{ bonds} = 4$  electrons, leaving  $16 - 4 = 12$  electrons (6 pairs). Giving three pairs on each end nitrogen gives them an octet, but leaves the central N with only four electrons as shown below:



The central N needs four electrons. There are three options to do this: (1) each of the end N atoms could form a double bond to the central N by sharing one of its pairs; (2) one of the end N atoms could form a triple bond by sharing two of its lone pairs; (3) the other end N atom could form the triple bond instead.



- b)  $\text{NO}_2^-$  has  $[1 \times \text{N}(5e^-)] + [2 \times \text{O}(6e^-)] + [1 e^- (\text{from charge})] = 18$  valence electrons. The nitrogen should be the central atom with each of the oxygen atoms attached to it by a single bond ( $2e^- \times 2 \text{ bonds} = 4$  electrons). This leaves  $18 - 4 = 14$  electrons (seven pairs). If three pairs are given to each O and one pair is given to the N, then both O atoms have an octet, but the N atom only has six.



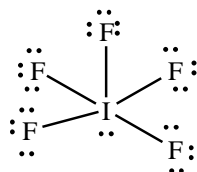
To complete an octet the N atom needs to gain a pair of electrons from one O atom or the other (form a double bond). The resonance structures are:



- 8.81 Plan: Initially, the method used in the preceding problems may be used to establish a Lewis structure. The total of the formal charges must equal the charge on an ion or be equal to 0 for a compound. The formal charge only needs to be calculated once for a set of identical atoms. Formal charge (FC) = no. of valence electrons – [no. of unshared valence electrons + ½ no. of shared valence electrons].

Solution:

a)  $\text{IF}_5$  has  $[1 \times \text{I}(7e^-)] + [5 \times \text{F}(7e^-)] = 42$  valence electrons. The presence of five F atoms around the central I means that the I atom will have a minimum of ten electrons; thus, this is an exception to the octet rule. The five I–F bonds use  $2e^- \times 5 \text{ bonds} = 10$  electrons leaving  $42 - 10 = 32$  electrons (16 pairs). Each F needs three pairs to complete an octet. The five F atoms use fifteen of the sixteen pairs, so there is one pair left for the central I. This gives:



Calculating formal charges:

FC = no. of valence electrons – [no. of unshared valence electrons + ½ no. of shared valence electrons].

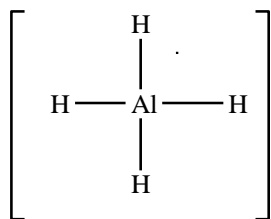
For iodine:  $\text{FC}_\text{I} = 7 - [2 + \frac{1}{2}(10)] = 0$

For each fluorine:  $\text{FC}_\text{F} = 7 - [6 + \frac{1}{2}(2)] = 0$

Total formal charge = 0 = charge on the compound.

b)  $\text{AlH}_4^-$  has  $[1 \times \text{Al}(3e^-)] + [4 \times \text{H}(1e^-)] + [1e^- \text{ (from charge)}] = 8$  valence electrons.

The four Al–H bonds use all the electrons and Al has an octet.



FC = no. of valence electrons – [no. of unshared valence electrons + ½ no. of shared valence electrons].

For aluminum:  $\text{FC}_\text{Al} = 3 - [0 + \frac{1}{2}(8)] = -1$

For each hydrogen:  $\text{FC}_\text{H} = 1 - [0 + \frac{1}{2}(2)] = 0$

- 8.83 Plan: Initially, the method used in the preceding problems may be used to establish a Lewis structure. The total of the formal charges must equal the charge on an ion or be equal to 0 for a compound. The formal charge only needs to be calculated once for a set of identical atoms. Formal charge (FC) = no. of valence electrons – [no. of unshared valence electrons + ½ no. of shared valence electrons].

Solution:

a)  $\text{CN}^-$ :  $[1 \times \text{C}(4e^-)] + [1 \times \text{N}(5e^-)] + [1e^- \text{ from charge}] = 10$  valence electrons. Place a single bond between the carbon and nitrogen atoms. This uses  $2e^- \times 1 \text{ bond} = 2$  electrons, leaving  $10 - 2 = 8$  electrons (four pairs). Giving three pairs of electrons to the nitrogen atom completes its octet but that leaves only one pair of electrons for the carbon atom which will not have an octet. The nitrogen could form a triple bond by sharing two of its lone pairs

with the carbon atom. A triple bond between the two atoms plus a lone pair on each atom satisfies the octet rule and uses all ten electrons.

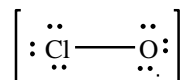


FC = no. of valence electrons – [no. of unshared valence electrons + ½ no. of shared valence electrons].

$$\text{FC}_{\text{C}} = 4 - [2 + \frac{1}{2}(6)] = -1; \quad \text{FC}_{\text{N}} = 5 - [2 + \frac{1}{2}(6)] = 0$$

Check: The total formal charge equals the charge on the ion (–1).

b)  $\text{ClO}^-$ :  $[1 \times \text{Cl}(7e^-)] + [1 \times \text{O}(6e^-)] + [1e^- \text{ from charge}] = 14$  valence electrons. Place a single bond between the chlorine and oxygen atoms. This uses  $2e^- \times 1 \text{ bond} = 2$  electrons, leaving  $14 - 2 = 12$  electrons (six pairs). Giving three pairs of electrons each to the carbon and oxygen atoms completes their octets.



FC = no. of valence electrons – [no. of unshared valence electrons + ½ no. of shared valence electrons].

$$\text{FC}_{\text{Cl}} = 7 - [6 + \frac{1}{2}(2)] = 0 \quad \text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

Check: The total formal charge equals the charge on the ion (–1).

8.85 Plan: The general procedure is similar to the preceding problems, plus the oxidation number determination.

Solution:

a)  $\text{BrO}_3^-$  has  $[1 \times \text{Br}(7e^-)] + 3 \times \text{O}(6e^-)] + [1e^- \text{ (from charge)}] = 26$  valence electrons.

Placing the O atoms around the central Br and forming three Br–O bonds uses  $2e^- \times 3 \text{ bonds} = 6$  electrons and leaves  $26 - 6 = 20$  electrons (ten pairs). Placing three pairs on each O ( $3 \times 3 = 9$  total pairs) leaves one pair for the Br and yields structure I below. In structure I, all the atoms have a complete octet. Calculating formal charges:

$$\text{FC}_{\text{Br}} = 7 - [2 + \frac{1}{2}(6)] = +2 \quad \text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

The  $\text{FC}_{\text{O}}$  is acceptable, but  $\text{FC}_{\text{Br}}$  is larger than is usually acceptable. Forming a double bond between any one of the O atoms gives structure II. Calculating formal charges:

$$\text{FC}_{\text{Br}} = 7 - [2 + \frac{1}{2}(8)] = +1 \quad \text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1 \quad \text{FC}_{\text{O}} = 6 - [4 + \frac{1}{2}(4)] = 0$$

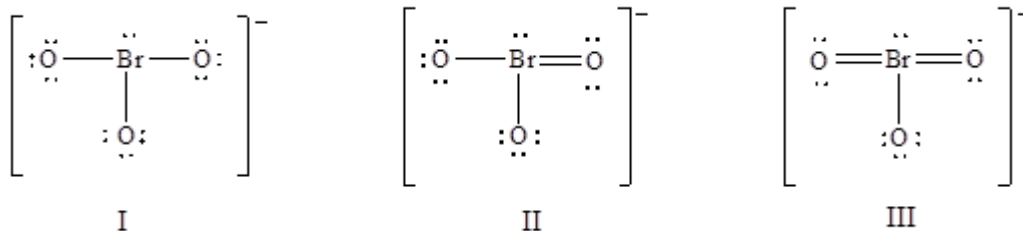
(Double bonded O)

The  $\text{FC}_{\text{Br}}$  can be improved further by forming a second double bond to one of the other O atoms (structure III).

$$\text{FC}_{\text{Br}} = 7 - [2 + \frac{1}{2}(10)] = 0 \quad \text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1 \quad \text{FC}_{\text{O}} = 6 - [4 + \frac{1}{2}(4)] = 0$$

(Double bonded O atoms)

Structure III has the most reasonable distribution of formal charges.



Oxidation number = (No. of valence  $e^-$ ) – (no. of shared  $e^-$  + no. of unshared  $e^-$ )

(Note: when there are electrons in a bond, they are transferred completely to the more electronegative atom)

The oxidation numbers are: oxidation number of Br = +5 and oxidation number of O = –2.

+5 –2

$\text{BrO}_3^-$

Check: The total formal charge equals the charge on the ion (–1).

b)  $\text{SO}_3^{2-}$  has  $[1 \times \text{S}(6e^-)] + [3 \times \text{O}(6e^-)] + [2e^- \text{ (from charge)}] = 26$  valence electrons.

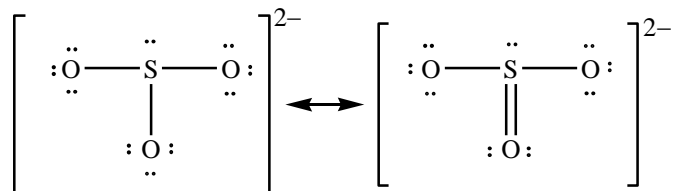
Placing the O atoms around the central S and forming three S–O bonds uses  $2e^- \times 3 \text{ bonds} = 6$  electrons and leaves  $26 - 6 = 20$  electrons (ten pairs). Placing three pairs on each O ( $3 \times 3 = 9$  total pairs) leaves one pair for the S and yields structure I below. In structure I all the atoms have a complete octet. Calculating formal charges:

$$\text{FC}_{\text{S}} = 6 - [2 + \frac{1}{2}(6)] = +1; \quad \text{FC}_{\text{O}} = 6 - [6 + \frac{1}{2}(2)] = -1$$

The FCO is acceptable, but  $\text{FC}_\text{S}$  is larger than is usually acceptable. Forming a double bond between any one of the O atoms (structure II) gives:

$$\text{FC}_\text{S} = 6 - [2 + \frac{1}{2}(8)] = 0 \quad \text{FC}_\text{O} = 6 - [6 + \frac{1}{2}(2)] = -1 \quad \text{FC}_\text{O} = 6 - [4 + \frac{1}{2}(4)] = 0$$

(Double bonded O)



Structure II has the more reasonable distribution of formal charges.  $+4 \quad -2$

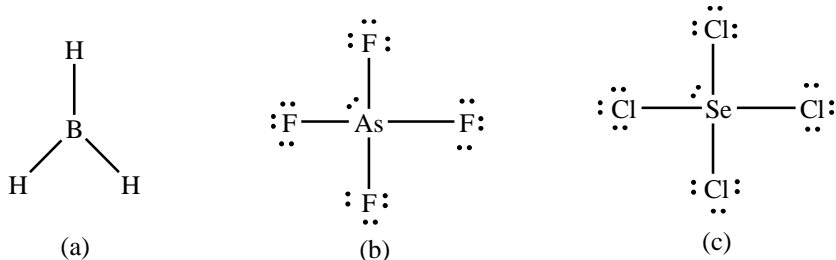
The oxidation numbers (O.N.) are: O.N.<sub>S</sub> = +4 and O.N.<sub>O</sub> = -2.  $\text{SO}_3^{2-}$

Check: The total formal charge equals the charge on the ion (-2).

- 8.87 Plan: The octet rule states that when atoms bond, they share electrons to attain a filled outer shell of eight electrons. If an atom has fewer than eight electrons, it is electron deficient; if an atom has more than eight electrons around it, the atom has an expanded octet.

Solution:

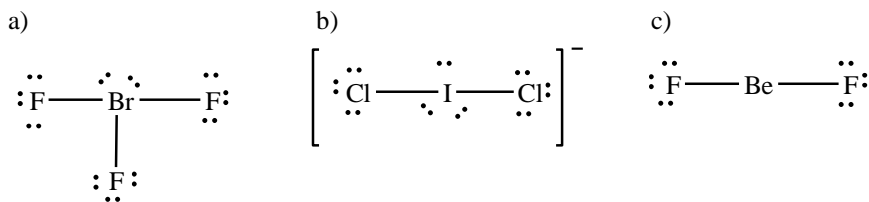
- a)  $\text{BH}_3$  has  $[1 \times \text{B}(3e^-)] + [3 \times \text{H}(1e^-)] = 6$  valence electrons. These are used in three B–H bonds. The B has six electrons instead of an octet; this molecule is **electron deficient**.
- b)  $\text{AsF}_4^-$  has  $[1 \times \text{As}(5e^-)] + [4 \times \text{F}(7e^-)] + [1e^- \text{ (from charge)}] = 34$  valence electrons. Four As–F bonds use eight electrons leaving  $34 - 8 = 26$  electrons (13 pairs). Each F needs three pairs to complete its octet and the remaining pair goes to the As. The As has an **expanded octet** with ten electrons. The F cannot expand its octet.
- c)  $\text{SeCl}_4$  has  $[1 \times \text{Se}(6e^-)] + 4 \times \text{Cl}(7e^-) = 34$  valence electrons. The  $\text{SeCl}_4$  is isoelectronic (has the same electron structure) as  $\text{AsF}_4^-$ , and so its Lewis structure looks the same. Se has an **expanded octet** of ten electrons.



- 8.89 Plan: The octet rule states that when atoms bond, they share electrons to attain a filled outer shell of eight electrons. If an atom has fewer than eight electrons, it is electron deficient; if an atom has more than eight electrons around it, the atom has an expanded octet.

Solution:

- a)  $\text{BrF}_3$  has  $[1 \times \text{Br}(7e^-)] + [3 \times \text{F}(7e^-)] = 28$  valence electrons. Placing a single bond between Br and each F uses  $2e^- \times 3 \text{ bonds} = 6e^-$ , leaving  $28 - 6 = 22$  electrons (eleven pairs). After the F atoms complete their octets with three pairs each, the Br gets the last two lone pairs. The Br has an **expanded octet** of ten electrons.
- b)  $\text{ICl}_2^-$  has  $[1 \times \text{I}(7e^-)] + [2 \times \text{Cl}(7e^-)] + [1e^- \text{ (from charge)}] = 22$  valence electrons. Placing a single bond between I and each Cl uses  $2e^- \times 2 \text{ bond} = 4e^-$ , leaving  $22 - 4 = 18$  electrons (nine pairs). After the Cl atoms complete their octets with three pairs each, the iodine finishes with the last three lone pairs. The iodine has an expanded octet of ten electrons.
- c)  $\text{BeF}_2$  has  $[1 \times \text{Be}(2e^-)] + [2 \times \text{F}(7e^-)] = 16$  valence electrons. Placing a single bond between Be and each of the F atoms uses  $2e^- \times 2 \text{ bonds} = 4e^-$ , leaving  $16 - 4 = 12$  electrons (six pairs). The F atoms complete their octets with three pairs each, and there are no electrons left for the Be. Formal charges work against the formation of double bonds. Be, with only four electrons, is **electron deficient**.



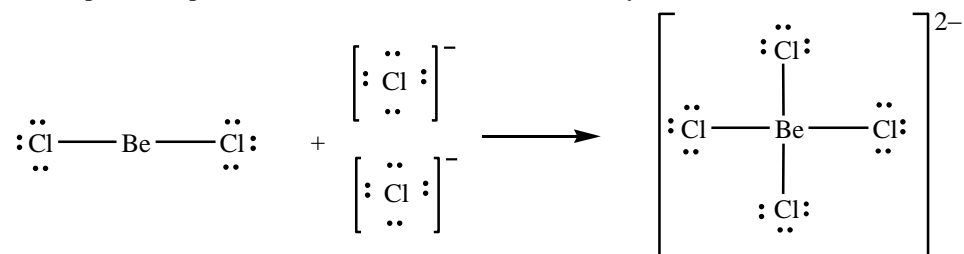
8.91 Plan: Draw Lewis structures for the reactants and products.

Solution:

Beryllium chloride has the formula  $\text{BeCl}_2$ .  $\text{BeCl}_2$  has  $[1 \times \text{Be}(2e^-)] + [2 \times \text{Cl}(7e^-)] = 16$  valence electrons. Four of these electrons are used to place a single bond between Be and each of the Cl atoms, leaving  $16 - 4 = 12$  electrons (six pairs). These six pairs are used to complete the octets of the Cl atoms, but Be does not have an octet – it is electron deficient.

Chloride ion has the formula  $\text{Cl}^-$  with an octet of electrons.

$\text{BeCl}_4^{2-}$  has  $[1 \times \text{Be}(2e^-)] + [4 \times \text{Cl}(7e^-)] + [2e^- \text{ (from charge)}] = 32$  valence electrons. Eight of these electrons are used to place a single bond between Be and each Cl atom, leaving  $32 - 8 = 24$  electrons (twelve pairs). These twelve pairs complete the octet of the Cl atoms (Be already has an octet).



8.94 Plan: Use the structures in the text to determine the formal charges.

Formal charge (FC) = no. of valence electrons – [no. of unshared valence electrons +  $\frac{1}{2}$  no. of shared valence electrons].

Solution:

Structure A:  $\text{FC}_\text{C} = 4 - [0 + \frac{1}{2}(8)] = 0$ ;  $\text{FC}_\text{O} = 6 - [4 + \frac{1}{2}(4)] = 0$ ;  $\text{FC}_\text{Cl} = 7 - [6 + \frac{1}{2}(2)] = 0$

Total FC = 0

Structure B:  $\text{FC}_\text{C} = 4 - [0 + \frac{1}{2}(8)] = 0$ ;  $\text{FC}_\text{O} = 6 - [6 + \frac{1}{2}(2)] = -1$ ;

$\text{FC}_\text{Cl}(\text{double bonded}) = 7 - [4 + \frac{1}{2}(4)] = +1$ ;  $\text{FC}_\text{Cl}(\text{single bonded}) = 7 - [6 + \frac{1}{2}(2)] = 0$

Total FC = 0

Structure C:  $\text{FC}_\text{C} = 4 - [0 + \frac{1}{2}(8)] = 0$ ;  $\text{FC}_\text{O} = 6 - [6 + \frac{1}{2}(2)] = -1$ ;

$\text{FC}_\text{Cl}(\text{double bonded}) = 7 - [4 + \frac{1}{2}(4)] = +1$ ;  $\text{FC}_\text{Cl}(\text{single bonded}) = 7 - [6 + \frac{1}{2}(2)] = 0$

Total FC = 0

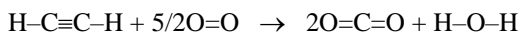
Structure A has the most reasonable set of formal charges.

8.95 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

8.99 Plan: 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 8.2. Use the ratios from the balanced reaction between the heat of reaction and acetylene and between acetylene and  $\text{CO}_2$  and  $\text{O}_2$  to find the amounts needed. The ideal gas law is used to convert from moles of oxygen to volume of oxygen.

Solution:



$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ$$

$$\Delta_r H^\circ = [2\text{BE}_{\text{C-H}} + \text{BE}_{\text{C}\equiv\text{C}} + 5/2\text{BE}_{\text{O=O}}] + [4(-\text{BE}_{\text{C=O}}) + 2(-\text{BE}_{\text{O-H}})]$$

$$-1259 \text{ kJ/mol} = [2(413 \text{ kJ/mol}) + \text{BE}_{\text{C}\equiv\text{C}} + 5/2(498 \text{ kJ/mol})] + [4(-799 \text{ kJ/mol}) + 2(-467 \text{ kJ/mol})]$$

$$-1259 \text{ kJ/mol} = [826 \text{ kJ/mol} + \text{BE}_{\text{C}\equiv\text{C}} + 1245 \text{ kJ/mol}] + [-4130 \text{ kJ/mol}]$$

$$-1259 \text{ kJ/mol} = -2059 \text{ kJ/mol} + \text{BE}_{\text{C}\equiv\text{C}}$$

$$\text{BE}_{\text{C}\equiv\text{C}} = \mathbf{800. \text{ kJ/mol}}$$

Table 8.2 lists the value as 839 kJ/mol.

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

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

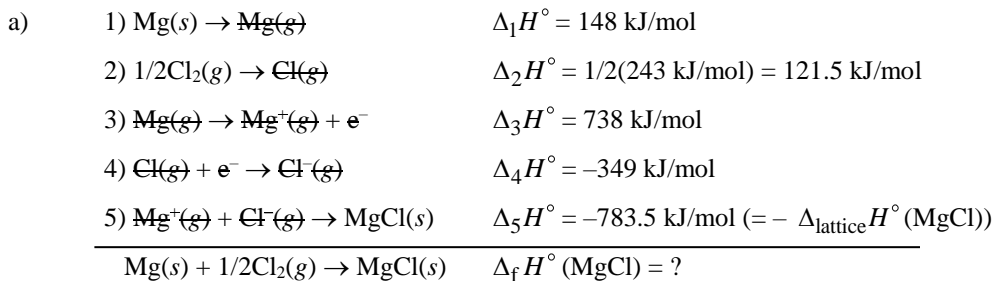
$$\text{d) Amount (mol) of O}_2 = (500.0 \text{ g C}_2\text{H}_2) \left( \frac{1 \text{ mol C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2} \right) \left( \frac{(5/2) \text{ mol O}_2}{1 \text{ mol C}_2\text{H}_2} \right) = 48.0030722 \text{ mol O}_2$$

$$pV = nRT$$

$$\text{Volume (L) of O}_2 = \frac{nRT}{p} = \frac{(48.0030722 \text{ mol O}_2) \left( 8.3144 \frac{\text{L} \cdot \text{kPa}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K})}{1823 \text{ kPa}} = 65.2423 \text{ L} = \mathbf{65.2 \text{ L O}_2}$$

- 8.101 Plan: The heat of formation of MgCl is represented by the equation  $\text{Mg(s)} + 1/2\text{Cl}_2(\text{g}) \rightarrow \text{MgCl(s)}$ . 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  $1/2$ ; you will need to reverse the equation for the lattice energy  $[\text{MgCl(s)} \rightarrow \text{Mg}^+(\text{g}) + \text{Cl}^-(\text{g})]$  and change the sign of the given lattice energy value. Negative heats of formation are energetically favored.

Solution:



$$\begin{aligned} \Delta_f H^\circ (\text{MgCl}) &= \Delta_1 H^\circ + \Delta_2 H^\circ + \Delta_3 H^\circ + \Delta_4 H^\circ + \Delta_5 H^\circ \\ &= 148 \text{ kJ/mol} + 121.5 \text{ kJ/mol} + 738 \text{ kJ/mol} + (-349 \text{ kJ/mol}) + (-783.5 \text{ kJ/mol}) \\ &= \mathbf{-125 \text{ kJ/mol}} \end{aligned}$$

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



$$\Delta_r H^\circ = \Sigma m \Delta_{\text{f(products)}} H^\circ - \Sigma n \Delta_{\text{f(reactants)}} H^\circ$$

$$\Delta_r H^\circ = \{1 \Delta_f H^\circ [\text{MgCl}_2(\text{s})] + 1 \Delta_f H^\circ [\text{Mg(s)}]\} - \{2 \Delta_f H^\circ [\text{MgCl(s)}]\}$$

$$\Delta_r H^\circ = [(-641.6 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [2(-125 \text{ kJ/mol})]$$

$$\Delta_r H^\circ = -391.6 \text{ kJ/mol} = \mathbf{-392 \text{ kJ/mol}}$$

d) **No**,  $\Delta_f H^\circ$  for  $\text{MgCl}_2$  is much more negative than that for MgCl. This makes the  $\Delta_r H^\circ$  value for the above reaction very negative, and the formation of  $\text{MgCl}_2$  would be favored.

- 8.103 Plan: Find the bond energy for an H–I bond from Table 8.2. For part a), calculate the wavelength with this energy using the relationship from Chapter 6:  $E = hc/\lambda$ . 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 8.2).

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

$$E = hc/\lambda$$

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

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

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

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

$$\text{Excess energy} = 7.82598 \times 10^{-19} \text{ J} - 4.898705 \times 10^{-19} \text{ J} = 2.92728 \times 10^{-19} \text{ J} = \mathbf{2.93 \times 10^{-19} \text{ J}}$$

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

$$E_k = 1/2mu^2 \text{ thus, } u = \sqrt{\frac{2E}{m}}$$

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

- 8.106 Plan: Find the appropriate bond energies in Table 8.2. Calculate the wavelengths using  $E = hc/\lambda$ .

Solution:

C–Cl bond energy = 339 kJ/mol

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

$$E = hc/\lambda$$

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

O<sub>2</sub> bond energy = 498 kJ/mol

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

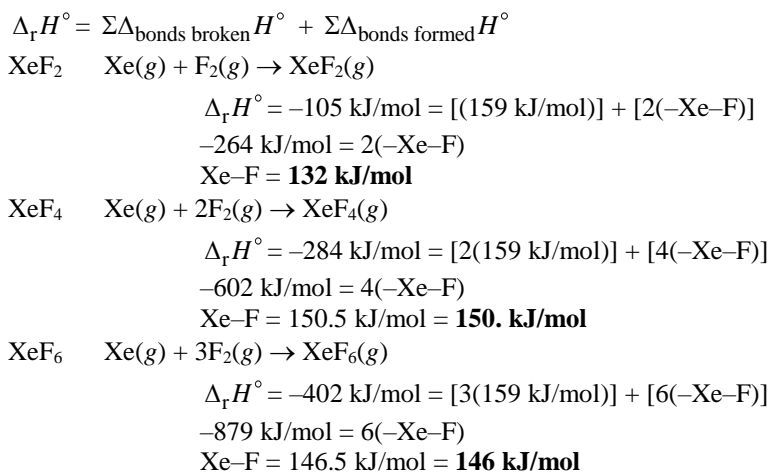
$$E = hc/\lambda$$

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



- 8.107 Plan: Write balanced chemical equations for the formation of each of the compounds. Obtain the bond energy of fluorine from Table 8.2 (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:



- 8.109 a) The presence of the very electronegative fluorine atoms bonded to one of the carbon atoms in 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.

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

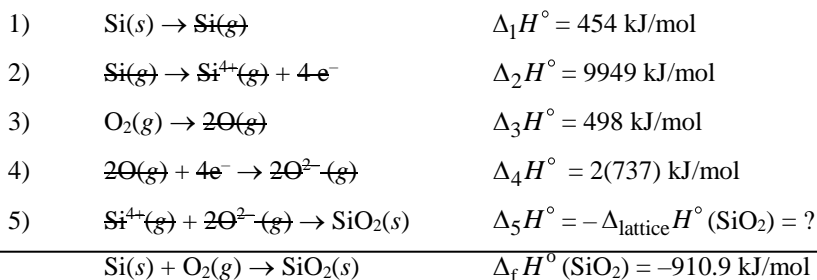
$$\Delta H = (498/2 \text{ kJ/mol} + (-141 \text{ kJ/mol}) + 1314 \text{ kJ/mol}) = 1422 \text{ kJ/mol} = \mathbf{1420 \text{ kJ/mol}}$$

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

- 8.112 Plan: The heat of formation of SiO<sub>2</sub> is represented by the equation Si(s) + O<sub>2</sub>(g) → SiO<sub>2</sub>(s). Use Hess's law and arrange the given equations so that they sum up to give the equation for the heat of formation. The lattice energy of SiO<sub>2</sub> is represented by the equation SiO<sub>2</sub>(s) → Si<sup>4+</sup>(g) + 2O<sup>2-</sup>(g). You will need to reverse the lattice energy equation (and change the sign of  $\Delta H^\circ$ ); you will also need to multiply the fourth given equation by 2.

Solution:

Use Hess' law.  $\Delta H_f^\circ$  of SiO<sub>2</sub> is found in Appendix B.



$$\Delta_f H^\circ = [\Delta_1 H^\circ + \Delta_2 H^\circ + \Delta_3 H^\circ + \Delta_4 H^\circ + (-\Delta_{\text{lattice}} H^\circ)]$$

$$-910.9 \text{ kJ/mol} = [454 \text{ kJ/mol} + 9949 \text{ kJ/mol} + 498 \text{ kJ/mol} + 2(737) \text{ kJ/mol} + (-\Delta_{\text{lattice}} H^\circ)]$$

$$-\Delta_{\text{lattice}} H^\circ = -13,285.9 \text{ kJ/mol}$$

$$\Delta_{\text{lattice}} H^\circ = \mathbf{13,286 \text{ kJ/mol}}$$

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

Solution:

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

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

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

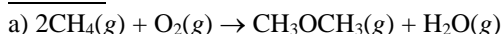
$$E = hc/\lambda \text{ or } \lambda = hc/E$$

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

This is in the **ultraviolet** region of the electromagnetic spectrum.

- 8.116 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:



$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ$$

$$\Delta_r H^\circ = [8 \times (\text{BE}_{\text{C-H}}) + 1 \times (\text{BE}_{\text{O-O}})] + [6 \times (\text{BE}_{\text{C-H}}) + 2 \times (\text{BE}_{\text{C-O}}) + 2 \times (\text{BE}_{\text{O-H}})]$$

$$\Delta_r H^\circ = [8 (413 \text{ kJ/mol}) + (498 \text{ kJ/mol})] + [6(-413 \text{ kJ/mol}) + 2(-358 \text{ kJ/mol}) + 2(-467 \text{ kJ/mol})]$$

$$\Delta_r H^\circ = \mathbf{-326 \text{ kJ/mol}}$$



$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ$$

$$\Delta_r H^\circ = [8 \times (\text{BE}_{\text{C-H}}) + 1 \times (\text{BE}_{\text{O-O}})] + [5 \times (\text{BE}_{\text{C-H}}) + 1 \times (\text{BE}_{\text{C-C}}) + 1 \times (\text{BE}_{\text{C-O}}) + 3 \times (\text{BE}_{\text{O-H}})]$$

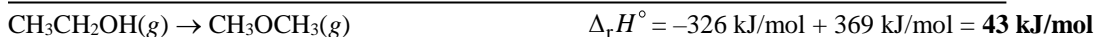
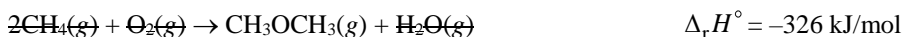
$$\Delta_r H^\circ = [8(413 \text{ kJ/mol}) + (498 \text{ kJ/mol})] + [5(-413 \text{ kJ/mol}) + (-347 \text{ kJ/mol}) + (-358 \text{ kJ/mol}) + 3(-467 \text{ kJ/mol})]$$

$$\Delta_r H^\circ = \mathbf{-369 \text{ kJ/mol}}$$

b) The formation of gaseous **ethanol** is more exothermic.

c) The conversion reaction is  $\text{CH}_3\text{CH}_2\text{OH}(\text{g}) \rightarrow \text{CH}_3\text{OCH}_3(\text{g})$ .

Use Hess's law:



- 8.118 Plan: The Lewis structures are needed to do this problem. A single bond (bond order = 1) is weaker and longer than a double bond (bond order = 2) which is weaker and longer than a triple bond (bond order = 3). 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 8.2.

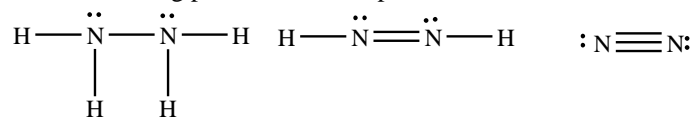
Solution:

a) The H atoms cannot be central, and they are evenly distributed on the N atoms.

$\text{N}_2\text{H}_4$  has  $[2 \times \text{N}(5e^-)] + [4 \times \text{H}(1e^-)]$  = fourteen valence electrons, ten of which are used in the bonds between the atoms. The remaining two pairs are used to complete the octets of the N atoms.

$\text{N}_2\text{H}_2$  has  $[2 \times \text{N}(5e^-)] + (2 \times \text{H}(1e^-)) =$  twelve valence electrons, six of which are used in the bonds between the atoms. The remaining three pairs of electrons are not enough to complete the octets of both N atoms, so one lone pair is moved to a bonding pair between the N atoms.

$\text{N}_2$  has  $[2 \times \text{N}(5e^-)] =$  ten valence electrons, two of which are used to place a single bond between the two N atoms. Since only four pairs of electrons remain and six pairs are required to complete the octets, two lone pairs become bonding pairs to form a triple bond.



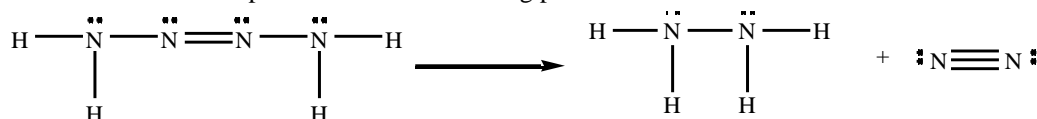
Hydrazine

Diazene

Nitrogen

The **single (bond order = 1) N–N bond is weaker and longer** than any of the others are. The **triple bond (bond order = 3) is stronger and shorter** than any of the others. The **double bond (bond order = 2) has an intermediate strength and length**.

b)  $\text{N}_4\text{H}_4$  has  $[4 \times \text{N}(5e^-)] + [4 \times \text{H}(1e^-)] =$  twenty-four valence electrons, fourteen of which are used for single bonds between the atoms. When the remaining five pairs are distributed to complete the octets, one N atom lacks two electrons. A lone pair is moved to a bonding pair for a double bond.



Reactant bonds broken:

$$4 \text{ N-H} = 4 (391 \text{ kJ/mol}) = 1564 \text{ kJ/mol}$$

$$2 \text{ N-N} = 2 (160 \text{ kJ/mol}) = 320 \text{ kJ/mol}$$

$$1 \text{ N=N} = (418 \text{ kJ/mol}) = 418 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds broken}} H^\circ = 2302 \text{ kJ/mol}$$

Product bonds formed:

$$4 \text{ N-H} = 4 (-391 \text{ kJ/mol}) = -1564 \text{ kJ/mol}$$

$$1 \text{ N-N} = (-160 \text{ kJ/mol}) = -160 \text{ kJ/mol}$$

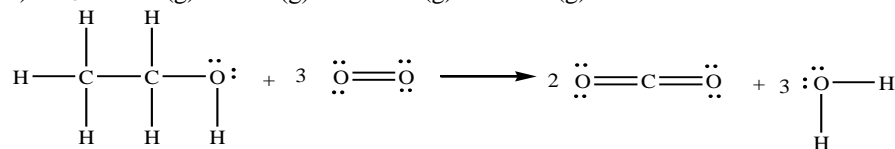
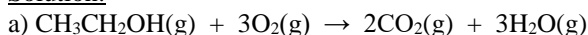
$$1 \text{ N}\equiv\text{N} = (-945 \text{ kJ/mol}) = -945 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds formed}} H^\circ = -2669 \text{ kJ/mol}$$

$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ = 2302 \text{ kJ/mol} + (-2669 \text{ kJ/mol}) = -367 \text{ kJ/mol}$$

- 8.122 Plan: Ethanol burns (combusts) with  $\text{O}_2$  to produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . To find the heat of reaction in part a), 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 8.2. The heat of vaporization of ethanol must be included for part b). The enthalpy change in part c) is the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants. The calculation for part d) is the same as in part a).

Solution:



Reactant bonds broken:

$$1 \times \text{C-C} = (347 \text{ kJ/mol}) = 347 \text{ kJ/mol}$$

$$5 \times \text{C-H} = (5)(413 \text{ kJ/mol}) = 2065 \text{ kJ/mol}$$

$$1 \times \text{C-O} = (358 \text{ kJ/mol}) = 358 \text{ kJ/mol}$$

$$1 \times \text{O-H} = (467 \text{ kJ/mol}) = 467 \text{ kJ/mol}$$

$$3 \times \text{O=O} = (3)(498 \text{ kJ/mol}) = 1494 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds broken}} H^\circ = 4731 \text{ kJ/mol}$$

Product bonds formed:

$$4 \times \text{C=O} = (4)(-799 \text{ kJ/mol}) = -3196 \text{ kJ/mol}$$

$$6 \times \text{O-H} = (6)(-467 \text{ kJ/mol}) = -2802 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds formed}} H^\circ = -5998 \text{ kJ/mol}$$

$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ = 4731 \text{ kJ/mol} + (-5998 \text{ kJ/mol}) = \mathbf{-1267 \text{ kJ/mol}}$  (for each mole of ethanol burned).

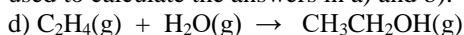
b) If it takes 40.5 kJ/mol to vaporize the ethanol, part of the heat of combustion must be used to convert liquid ethanol to gaseous ethanol. The new value becomes:

$$\Sigma \Delta_{\text{combustion(liquid)}} H^\circ = -1267 \text{ kJ/mol} + (1) \left[ \frac{40.5 \text{ kJ}}{1 \text{ mol}} \right] = -1226.5 \text{ kJ/mol} = \mathbf{-1226 \text{ kJ/mol}}$$
 (of liquid ethanol burned)

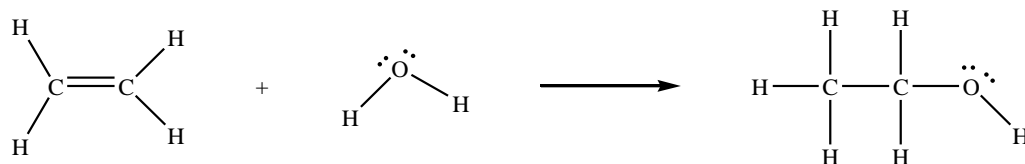
c)  $\Delta_r H^\circ = \Sigma m \Delta_f H^\circ (\text{products}) - \Sigma n \Delta_f H^\circ (\text{reactants})$

$$\begin{aligned} \Delta_r H^\circ &= \{ 2 \Delta_f H^\circ [\text{CO}_2(\text{g})] + 3 \Delta_f H^\circ [\text{H}_2\text{O}(\text{g})] \} - \{ 1 \Delta_f H^\circ [\text{C}_2\text{H}_5\text{OH}(\text{l})] + 3 \Delta_f H^\circ [\text{O}_2(\text{g})] \} \\ &= \{ (2)(-393.5 \text{ kJ/mol}) + (3)(-241.826 \text{ kJ/mol}) \} - [(-277.63 \text{ kJ/mol}) + 3 (0 \text{ kJ/mol})] \\ &= -1234.848 \text{ kJ/mol} = \mathbf{-1234.8 \text{ kJ/mol}} \end{aligned}$$

The two answers differ by less than 10 kJ/mol. This is a very good agreement since average bond energies were used to calculate the answers in a) and b).



The Lewis structures for the reaction are:



Reactant bonds broken:

$$\begin{aligned} 1 \times \text{C}=\text{C} &= (1)(614 \text{ kJ/mol}) = 614 \text{ kJ/mol} \\ 4 \times \text{C}-\text{H} &= (4)(413 \text{ kJ/mol}) = 1652 \text{ kJ/mol} \\ 2 \times \text{O}-\text{H} &= (2)(467 \text{ kJ/mol}) = 934 \text{ kJ/mol} \\ \hline \Sigma \Delta_{\text{bonds broken}} H^\circ &= 3200 \text{ kJ/mol} \end{aligned}$$

Product bonds formed:

$$\begin{aligned} 1 \times \text{C}-\text{C} &= (-347 \text{ kJ/mol}) = -347 \text{ kJ/mol} \\ 5 \times \text{C}-\text{H} &= (5)(-413 \text{ kJ/mol}) = -2065 \text{ kJ/mol} \\ 1 \times \text{C}-\text{O} &= (-358 \text{ kJ/mol}) = -358 \text{ kJ/mol} \\ 1 \times \text{O}-\text{H} &= (-467 \text{ kJ/mol}) = -467 \text{ kJ/mol} \\ \hline \Sigma \Delta_{\text{bonds formed}} H^\circ &= -3237 \text{ kJ/mol} \end{aligned}$$

$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ = 3200 \text{ kJ/mol} + (-3237 \text{ kJ/mol}) = \mathbf{-37 \text{ kJ/mol}}$$

- 8.124 Plan: Determine the empirical formula from the percent composition (assuming 100 g of compound). Use the titration data to determine the mole ratio of acid to the NaOH. This ratio gives the amount of acidic H atoms in the formula of the acid. Finally, combine this information to construct the Lewis structure.

Solution:

$$\text{Moles of H} = (2.24 \text{ g H}) \left( \frac{1 \text{ mol}}{1.008 \text{ g H}} \right) = 2.222 \text{ mol H}$$

$$\text{Moles of C} = (26.7 \text{ g C}) \left( \frac{1 \text{ mol}}{12.01 \text{ g C}} \right) = 2.223 \text{ mol C}$$

$$\text{Moles of O} = (71.1 \text{ g O}) \left( \frac{1 \text{ mol}}{16.00 \text{ g O}} \right) = 4.444 \text{ mol O}$$

The preliminary formula is  $\text{H}_{2.222}\text{C}_{2.223}\text{O}_{4.444}$ .

Dividing all subscripts by the smallest subscript to obtain integer subscripts:

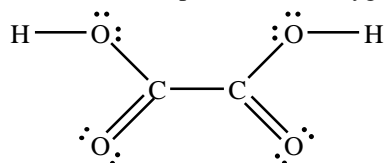
$$\frac{H_{2.222}}{2.222} \frac{C_{2.223}}{2.222} \frac{O_{4.444}}{2.222} = HCO_2$$

The empirical formula is  $HCO_2$ .

To determine the molecular formula, calculate the amount of NaOH required for the titration:

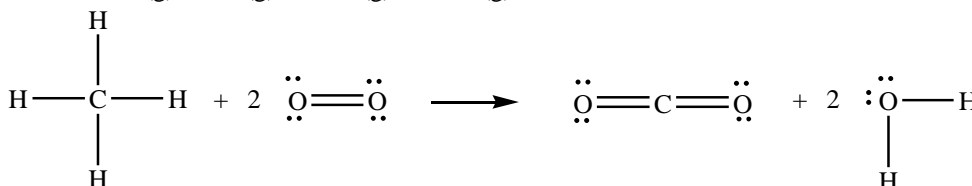
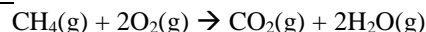
$$\text{mmoles of NaOH} = (50.0 \text{ mL}) \left( \frac{0.040 \text{ mol NaOH}}{\text{L}} \right) \left( \frac{1000 \text{ mmol}}{\text{mol}} \right) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) = 2.0 \text{ mmol NaOH}$$

Thus, the ratio is 2.0 mmole base/1.0 mmole acid, or each acid molecule has two hydrogen atoms to react (diprotic). The empirical formula indicates a monoprotic acid, so the formula must be doubled to:  $H_2C_2O_4$ .  $H_2C_2O_4$  has  $[2 \times H(1e^-)] + [2 \times C(4e^-)] + [4 \times O(6e^-)] = 34$  valence electrons to be used in the Lewis structure. Fourteen of these electrons are used to bond the atoms with single bonds, leaving  $34 - 14 = 20$  electrons or ten pairs of electrons. When these ten pairs of electrons are distributed to the atoms to complete octets, neither C atom has an octet; a lone pair from the oxygen without hydrogen is changed to a bonding pair on C.



- 8.127 Plan: Write the balanced chemical equations for the reactions and draw the Lewis structures. 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 8.2. Divide the heat of reaction by the amount of moles of oxygen gas appearing in each reaction to get the heat of reaction per mole of oxygen.

Solution:



Reactant bonds broken:

$$4 \times \text{C-H} = (4)(413 \text{ kJ/mol}) = 1652 \text{ kJ/mol}$$

$$2 \times \text{O=O} = (2)(498 \text{ kJ/mol}) = 996 \text{ kJ/mol}$$

$$\Sigma \Delta H^\circ_{\text{bonds broken}} = 2648 \text{ kJ/mol}$$

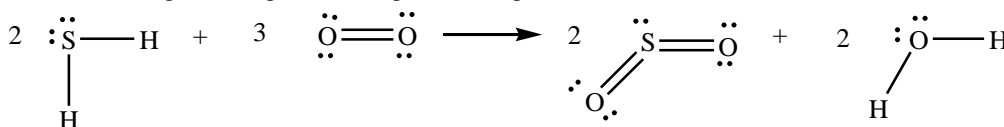
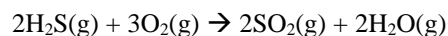
Product bonds formed:

$$2 \times \text{C=O} = (2)(-799 \text{ kJ/mol}) = -1598 \text{ kJ/mol}$$

$$4 \times \text{O-H} = (4)(-467 \text{ kJ/mol}) = -1868 \text{ kJ/mol}$$

$$\Sigma \Delta H^\circ_{\text{bonds formed}} = -3466 \text{ kJ/mol}$$

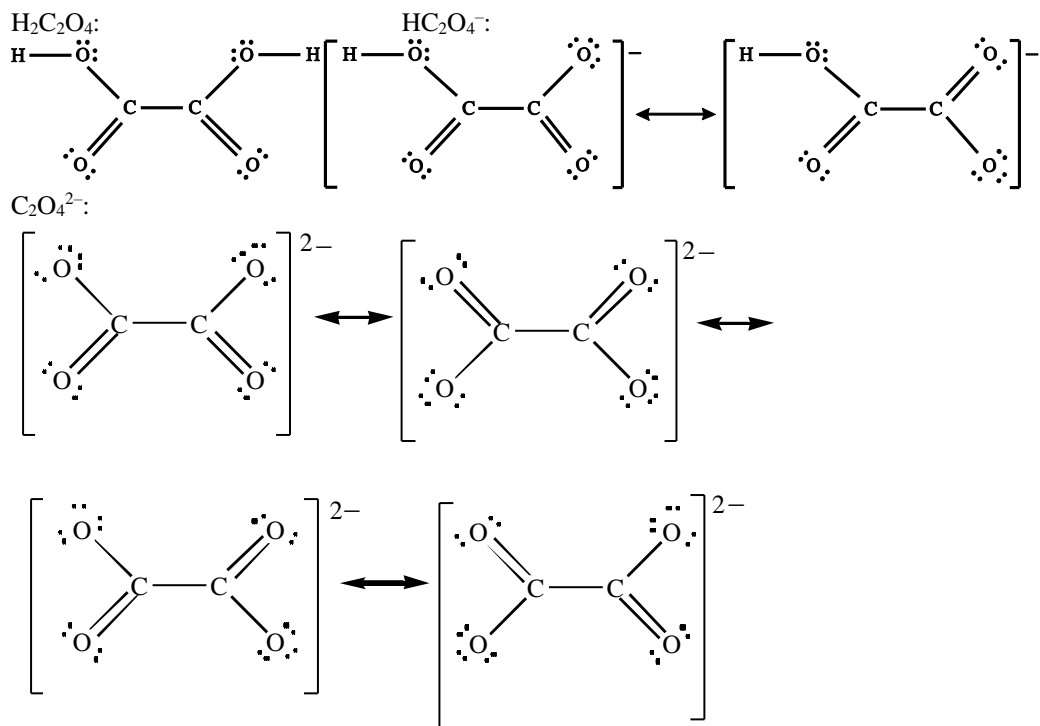
$$\begin{aligned} \Delta_r H^\circ &= \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ \\ &= 2648 \text{ kJ/mol} + (-3466 \text{ kJ/mol}) \\ &= -818 \text{ kJ/mol} \quad \text{Per mole of O}_2 \\ &= -818 \text{ kJ/mol} / 2 \\ &= \mathbf{-409 \text{ kJ/mol O}_2} \end{aligned}$$



$$\begin{aligned} 4 \times \text{S-H} &= (4)(347 \text{ kJ/mol}) = 1388 \text{ kJ/mol} \\ 3 \times \text{O=O} &= (3)(498 \text{ kJ/mol}) = 1494 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} 4 \times \text{S=O} &= (4)(-552 \text{ kJ/mol}) = -2208 \text{ kJ/mol} \\ 4 \times \text{O-H} &= (4)(-467 \text{ kJ/mol}) = -1868 \text{ kJ/mol} \end{aligned}$$

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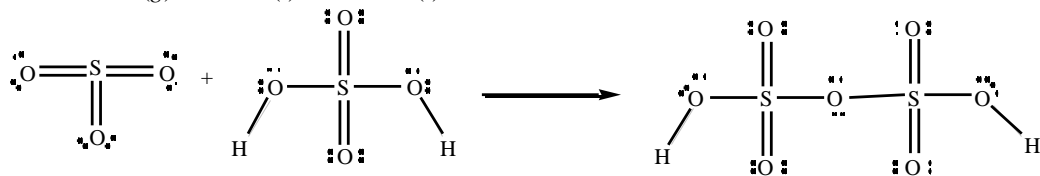
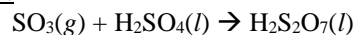
In  $\text{H}_2\text{C}_2\text{O}_4$ , there are two shorter  $\text{C}=\text{O}$  bonds and two longer, weaker  $\text{C}—\text{O}$  bonds.

In  $\text{HC}_2\text{O}_4^-$ , the  $\text{C}—\text{O}$  bonds on the side retaining the H remain as one long  $\text{C}—\text{O}$  bond and one shorter, stronger  $\text{C}=\text{O}$  bond. The  $\text{C}—\text{O}$  bonds on the other side of the molecule have resonance forms with an average bond order of 1.5, so they are intermediate in length and strength.

In  $\text{C}_2\text{O}_4^{2-}$ , all the carbon to oxygen bonds are resonating and have an average bond order of 1.5.

8.135 Plan: Draw the Lewis structures. Calculate the heat of reaction using the bond energies in Table 8.2.

Solution:



Reactant bonds broken:

$$5 \times \text{S}=\text{O} = (5)(552 \text{ kJ/mol}) = 2760 \text{ kJ/mol}$$

$$2 \times \text{S}-\text{O} = (2)(265 \text{ kJ/mol}) = 530 \text{ kJ/mol}$$

$$2 \times \text{O}-\text{H} = (2)(467 \text{ kJ/mol}) = 934 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds broken}} H^\circ = 4224 \text{ kJ/mol}$$

Product bonds formed:

$$4 \times \text{S}=\text{O} = (4)(-552 \text{ kJ/mol}) = -2208 \text{ kJ/mol}$$

$$4 \times \text{S}-\text{O} = (4)(-265 \text{ kJ/mol}) = -1060 \text{ kJ/mol}$$

$$2 \times \text{O}-\text{H} = (2)(-467 \text{ kJ/mol}) = -934 \text{ kJ/mol}$$

$$\Sigma \Delta_{\text{bonds formed}} H^\circ = -4202 \text{ kJ/mol}$$

$$\Delta_r H^\circ = \Sigma \Delta_{\text{bonds broken}} H^\circ + \Sigma \Delta_{\text{bonds formed}} H^\circ = 4224 \text{ kJ/mol} + (-4202 \text{ kJ/mol}) = \mathbf{22 \text{ kJ/mol}}$$