## CHAPTER 6 THERMOCHEMISTRY: ENERGY FLOW AND CHEMICAL CHANGE

- 6.1 The sign of the energy transfer is defined from the perspective of the system. Entering the system is positive, and leaving the system is negative.
- 6.2 No, an increase in temperature means that heat has been transferred to the surroundings, which makes q positive.
- 6.3  $\Delta E = q + w = w$ , since q = 0. Thus, the change in work equals the change in internal energy.
- 6.4 The internal energy of the body is the sum of the cellular and molecular activities occurring from skin level inward. The body's internal energy can be increased by adding food, which adds energy to the body through the breaking of bonds in the food. The body's internal energy can also be increased through addition of work and heat, like the rubbing of another person's warm hands on the body's cold hands. The body can lose energy if it performs work, like pushing a lawnmower, and can lose energy by losing heat to a cold room.
- 6.5 a) electric heater b) sound amplifier c) light bulb d) automobile alternator e) battery (voltaic)
- 6.6 The amount of the change in internal energy in the two cases is the same. By the law of energy conservation, the change in energy of the universe is zero. This requires that the change in energy of the system (heater or air conditioner) equals an opposite change in energy of the surroundings (room air). Since both systems consume the same amount of electrical energy, the change in energy of the heater equals that of the air conditioner.

| 6.7 | Heat energy; sound energy $\downarrow$ | (impact)                             |
|-----|----------------------------------------|--------------------------------------|
|     | Kinetic energy $\downarrow$            | (falling text)                       |
|     | Potential energy $\downarrow$          | (raised text)                        |
|     | Mechanical energy $\downarrow$         | (raising of text)                    |
|     | Chemical energy                        | (biological process to move muscles) |

- 6.8 The change in a system's energy is  $\Delta E = q + w$ . If the system receives heat, then its  $q_{\text{final}}$  is greater than  $q_{\text{initial}}$  so q is positive. Since the system performs work, its  $w_{\text{final}} < w_{\text{initial}}$  so w is negative. The change in energy is (+425 J) + (-425 J) = **0** J.
- 6.9  $\Delta E = q + w = -255 \text{ cal} + (-428 \text{ cal}) = -683 \text{ cal}$
- 6.10 A system that releases thermal energy has a negative value for q and a system that has work done on it has a positive value for work. So,  $\Delta E = -675 \text{ J} + (525 \text{ cal x } 4.184 \text{ J/cal}) = 1521.6 = 1.52 \text{ x } 10^3 \text{ J}$

6.11 
$$\Delta E = q + w = (0.615 \text{ kJ}) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) + \left((0.247 \text{ kcal}) \left(\frac{10^3 \text{ cal}}{1 \text{ kcal}}\right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}}\right)\right) = 1648.4 = 1.65 \text{ x } 10^3 \text{ J}$$

6.12 
$$C(s) + O_2(g) \rightarrow CO_2(g) + 3.3 \times 10^{10} \text{ J}$$
  
(1.0 ton)  
a)  $\Delta E(kJ) = (3.3 \times 10^{10} \text{ J}) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) = 3.3 \times 10^7 \text{ kJ}$   
b)  $\Delta E(kcal) = (3.3 \times 10^{10} \text{ J}) \left(\frac{1 \text{ cal}}{4.184 \text{ J}}\right) \left(\frac{1 \text{ kcal}}{10^3 \text{ cal}}\right) = 7.887 \times 10^6 = 7.9 \times 10^6 \text{ kcal}$   
c)  $\Delta E(Btu) = (3.3 \times 10^{10} \text{ J}) \left(\frac{1 \text{ Btu}}{1055 \text{ J}}\right) = 3.12796 \times 10^7 = 3.1 \times 10^7 \text{ Btu}$ 

6.13 
$$CaCO_3(s) + 9.0 \ge 10^6 \text{ kJ} \rightarrow CaO(s) + CO_2(g)$$
  
(5.0 ton)

a) 
$$\Delta E(J) = (9.0 \times 10^{6} \text{ kJ}) \left( \frac{10^{3} \text{ J}}{1 \text{ kJ}} \right) = 9.0 \times 10^{9} \text{ J}$$
  
b)  $\Delta E(\text{cal}) = (9.0 \times 10^{6} \text{ kJ}) \left( \frac{10^{3} \text{ J}}{1 \text{ kJ}} \right) \left( \frac{1 \text{ cal}}{4.184 \text{ J}} \right) = 2.15105 \times 10^{9} = 2.2 \times 10^{9} \text{ cal}$   
c)  $\Delta E(\text{Btu}) = (9.0 \times 10^{6} \text{ kJ}) \left( \frac{10^{3} \text{ J}}{1 \text{ kJ}} \right) \left( \frac{1 \text{ Btu}}{1055 \text{ J}} \right) = 8.5308 \times 10^{6} = 8.5 \times 10^{6} \text{ Btu}$ 

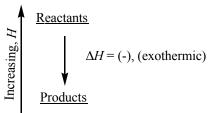
6.14 
$$\Delta E(J) = (4.1 \text{ x } 10^3 \text{ Calorie}) \left(\frac{10^3 \text{ cal}}{1 \text{ Calorie}}\right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}}\right) = 1.7154 \text{ x } 10^7 = 1.7 \text{ x } 10^7 \text{ J}$$
$$\Delta E(J) = (4.1 \text{ x } 10^3 \text{ Calorie}) \left(\frac{10^3 \text{ cal}}{1 \text{ Calorie}}\right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}}\right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) = 1.7154 \text{ x } 10^4 = 1.7 \text{ x } 10^4 \text{ kJ}$$

6.15 Time = 
$$(1.0 \text{ lb})\left(\frac{4.1 \text{ x } 10^3 \text{ Cal}}{1.0 \text{ lb}}\right)\left(\frac{10^3 \text{ cal}}{1 \text{ Cal}}\right)\left(\frac{4.184 \text{ J}}{1 \text{ cal}}\right)\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right)\left(\frac{1}{1850 \text{ kJ}}\right) = 9.2726 = 9.3 \text{ hourse}$$

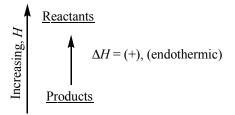
- 6.16 The system does work and thus its internal energy is decreased. This means the sign will be **negative**.
- 6.17 Since many reactions are performed in an open flask, the reaction proceeds at constant pressure. The determination of  $\Delta H$  (constant pressure conditions) requires a measurement of heat only, whereas  $\Delta E$  requires measurement of heat and PV work.
- 6.18 The hot pack is releasing (producing) heat, thus  $\Delta H$  is **negative**, and the process is **exothermic**.
- 6.19 a) **Exothermic**, the system (water) is releasing heat in changing from liquid to solid.
  - b) Endothermic, the system (water) is absorbing heat in changing from liquid to gas.
  - c) Exothermic, the process of digestion breaks down food and releases energy.
  - d) Exothermic, heat is released as a person runs and muscles perform work.
  - e) Endothermic, heat is absorbed as food calories are converted to body tissue.
  - f) Endothermic, the wood being chopped absorbs heat (and work).

g) **Exothermic**, the furnace releases heat from fuel combustion. Alternatively, if the system is defined as the air in the house, the change is endothermic since the air's temperature is increasing by the input of heat energy from the furnace.

- 6.20 The internal energy of a substance is the sum of kinetic  $(E_K)$  and potential  $(E_P)$  terms.  $E_K$  (total) =  $E_K$  (translational) +  $E_K$  (rotational) +  $E_K$  (vibrational)  $E_P = E_P$  (atom) +  $E_P$  (bonds)  $E_P$  (atom) has nuclear, electronic, positional, magnetic, electrical, etc. components.
- 6.21  $\Delta H = \Delta E + P\Delta V \text{ (const P)}$ a)  $\Delta H < \Delta E$ , P $\Delta V$  is negative. b)  $\Delta H = \Delta E$ , a fixed volume means P $\Delta V = 0$ . c)  $\Delta H > \Delta E$ , P $\Delta V$  is positive for the transformation of solid to gas.
- 6.22 An exothermic reaction releases heat, so the reactants have greater  $H(H_{\text{initial}})$  than the products  $(H_{\text{final}})$ .  $\Delta H = H_{\text{final}} - H_{\text{initial}} < 0.$



6.23



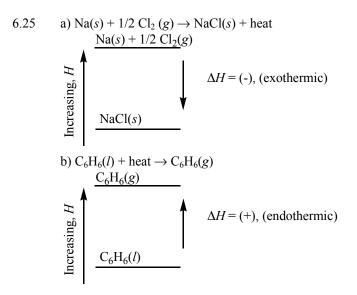
6.24 a) Combustion of methane: 
$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g) + heat$$
  

$$\underbrace{CH_4 + 2 O_2 \text{ (initial)}}_{-}$$

$$\Delta H = (-), \text{ (exothermic)}$$

$$\Delta H = (-), \text{ (exothermic)}$$
b) Freezing of water: H<sub>2</sub>O(*l*)  $\rightarrow$  H<sub>2</sub>O(*s*) + heat H<sub>2</sub>O(*l*) (initial)

H 
$$\hat{B}$$
  
use 20  
H  $2O(s)$  (final)  $\Delta H = (-),$  (exothermic)  
H  $2O(s)$  (final)



a) Combustion of hydrocarbons and related compounds require oxygen (and a heat catalyst) to yield carbon dioxide gas, water vapor, and heat.
 C<sub>2</sub>H<sub>5</sub>OH + 3 O<sub>2</sub> (initial)

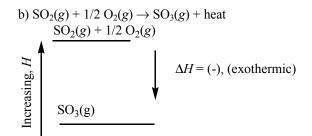
$$\Delta H = (-), \text{ (exothermic)}$$

$$\frac{2 \text{ CO}_2 + 3 \text{ H}_2 \text{ O} \text{ (final)}}{2 \text{ CO}_2 + 3 \text{ H}_2 \text{ O} \text{ (final)}}$$

b) Nitrogen dioxide, NO<sub>2</sub>, forms from N<sub>2</sub> and O<sub>2</sub>.  
N<sub>2</sub>(g) + 2 O<sub>2</sub>(g) + heat 
$$\rightarrow$$
 2 NO<sub>2</sub>(g)  
2 NO<sub>2</sub> (final)  
H shifts  $\Delta H = (+)$ , (endothermic)  
N<sub>2</sub> + 2 O<sub>2</sub> (initial)

6.27 a) 
$$\operatorname{CO}_2(s) + \operatorname{heat} \to \operatorname{CO}_2(g)$$
  

$$\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$



- 6.28 Absolute enthalpy values, like absolute energy values, are unknown.
- 6.29 To determine the specific heat capacity of a substance, you need its mass, the heat added (or lost) and the change in temperature.
- 6.30 Intensive property; it is defined on a per gram basis.
- 6.31 Specific heat capacity is the quantity of heat required to raise one gram of a substance by one kelvin. Heat capacity is also the quantity of heat required for a one kelvin temperature change, but it applies to an object instead of a specified amount of a substance. Thus, specific heat capacity is used when talking about an element or compound while heat capacity is used for a calorimeter or other object.
  a) Use heat capacity because the fixture is a combination of substances.
  b) Use specific heat capacity because the copper wire is a pure substance.
  c) Use specific heat capacity because the water is a pure substance.
- 6.32 In a "coffee cup" calorimeter, reactions occur at constant pressure.  $q_p = \Delta H$ . In a "bomb" calorimeter, reactions occur at constant volume.  $q_v = \Delta E$ .
- 6.33 <u>Plan:</u> The heat required to raise the temperature of water by 80.°C is found by using equation 6.7, or  $q = c \times \max x \Delta T$ . The specific heat capacity,  $c_{water}$ , is found in Table 6.4. Because the Celsius degree is the same size as the kelvin degree,  $\Delta T = 80.°C = 80$ . K.

$$q(J) = (mass) C (\Delta T) = (12.0 g) \left( 4.184 \frac{J}{g \circ C} \right) \left( (100. - 20.) \circ C \right) = 4016.64 = 4.0 x 10^3 J$$

6.34 
$$q(J) = (mass) C (\Delta T) = (0.10 \text{ g}) \left( 2.087 \frac{\text{J}}{\text{g}^{\circ}\text{C}} \right) \left( (-75 - 10.)^{\circ}\text{C} \right) = -17.7 = -18 \text{ J}$$

6.35 
$$q(J) = (mass) C (\Delta T)$$
  
85.0 kJ(10<sup>3</sup> J/kJ) = (295 g) (0.900 J/g°C) (T<sub>f</sub> - 3.00)°C  
 $(T_f - 3.00)°C = \frac{(85.0 \text{ kJ})\left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right)}{(295 \text{ g})\left(\frac{0.900 \text{ J}}{\text{g °C}}\right)} = 320.15°C \text{ (unrounded)}$   
 $T_f = 323°C$ 

6.36 
$$q(J) = (mass) C (\Delta T)$$
  
-688 J = (27.7 g) (2.42J/g°C) (32.5 - T<sub>i</sub>)°C  
(32.5 - T<sub>i</sub>)°C =  $\frac{(-688 J)}{(27.7 g)(\frac{2.42 J}{g°C})}$  = -10.263°C (unrounded)

 $T_i = 42.8^{\circ}C$ 

- 6.37 Since the bolts have the same mass, and one must cool as the other heats, the intuitive answer is  $[(T_1 + T_2)/2] = 77.5^{\circ}C$ .
- 6.38  $\begin{aligned} -q_{\text{lost}} &= q_{\text{gained}} \\ &- 2 \text{ (Mass) } C_{\text{Cu}} (\text{T}_{\text{f}} 105)^{\circ}\text{C} = (\text{Mass}) (\text{C}_{\text{Cu}}) (\text{T}_{\text{f}} 45)^{\circ}\text{C} \\ &- 2 (\text{T}_{\text{f}} 105)^{\circ}\text{C} = (\text{T}_{\text{f}} 45)^{\circ}\text{C} \\ &2 (105^{\circ}\text{C}) 2 \text{ T}_{\text{f}} = \text{T}_{\text{f}} 45^{\circ}\text{C} \\ &210^{\circ}\text{C} + 45^{\circ}\text{C} = \text{T}_{\text{f}} + 2 \text{ T}_{\text{f}} = 3 \text{ T}_{\text{f}} \\ &(255^{\circ}\text{C}) / 3 = \text{T}_{\text{f}} = 85.0^{\circ}\text{C} \end{aligned}$
- 6.39 Use the same procedure in 6.37, but mass is now a factor because the two water samples are not identical. Both volumes are converted to mass using the density (e.g., 85 mL x 1.00 g/mL = 85 g). Convert °C temperatures (22°C, 82°C) to Kelvin temperatures (295 K, 355 K).

 $\begin{aligned} -q_{\text{lost}} &= q_{\text{gained}} \\ - [85 \text{ mL} (1.00 \text{ g/mL})] (4.184 \text{ J/g}^{\circ}\text{C}) (\text{T}_{\text{f}} - 82)^{\circ}\text{C} = [165 \text{ mL} (1.00 \text{ g/mL})] (4.184 \text{ J/g}^{\circ}\text{C}) (\text{T}_{\text{f}} - 22)^{\circ}\text{C} \\ - [85](\text{T}_{\text{f}} - 82) = [165] (\text{T}_{\text{f}} - 22) \\ 6970 - 85 \text{ T}_{\text{f}} = 165 \text{ T}_{\text{f}} - 3630 \\ 6970 + 3630 = 165 \text{ T}_{\text{f}} + 85 \text{ T}_{\text{f}} \\ 10600. = 250. \text{ T}_{\text{f}} \\ \text{T}_{\text{f}} = (10600. / 250.) = 42.4 = 42^{\circ}\text{C} \end{aligned}$ 

- 6.40  $-q_{\text{lost}} = q_{\text{gained}}$  $- [24.4 \text{ mL } (1.00 \text{ g/mL})](4.184 \text{ J/g}^{\circ}\text{C}) (23.5 - 35.0)^{\circ}\text{C} = [\text{mass}](4.184 \text{ J/g}^{\circ}\text{C}) (23.5 - 18.2)^{\circ}\text{C}$ - [24.4](23.5 - 35.0) = [mass](23.5 - 18.2)- [24.4](-11.5) = [mass](5.3)- [24.4](-11.5) / (5.3) = [mass]Mass = -[24.4](-11.5) / (5.3) = 52.943 g (unrounded)52.943 g (mL/1.00 g) = 52.943 = 53 mL
- 6.41 <u>Plan:</u> Heat gained by water plus heat lost by copper tubing must equal zero, so  $q_{water} = -q_{copper}$ . However, some heat will be lost to the insulated container.

Solution:

 $\begin{array}{l} -q_{\text{lost}} = q_{\text{gained}} = q_{\text{water}} + q_{\text{calorimeter}} \\ -(505 \text{ g Cu}) \ (0.387 \text{ J/g}^{\circ}\text{C}) \ (T_{\text{f}} - 99.9)^{\circ}\text{C} = (59.8 \text{ g H}_2\text{O}) \ (4.184 \text{ J/g}^{\circ}\text{C}) \ (T_{\text{f}} - 24.8)^{\circ}\text{C} + (10.0 \text{ J/}^{\circ}\text{C}) \ (T_{\text{f}} - 24.8)^{\circ}\text{C} \\ -(195.435) \ (T_{\text{f}} - 99.9) = (250.2032) \ (T_{\text{f}} - 24.8) + (10.0) \ (T_{\text{f}} - 24.8) \\ 19523.9565 - 195.435 \ T_{\text{f}} = 250.2032 \ T_{\text{f}} - 6205.03936 + 10.0 \ T_{\text{f}} - 248. \\ 19523.9565 + 6205.03936 + 248 = 250.2032 \ T_{\text{f}} + 195.435 \ T_{\text{f}} + 10.0 \ T_{\text{f}} \\ 19523.9565 + 6205.03936 + 248 = 250.2032 \ T_{\text{f}} + 195.435 \ T_{\text{f}} + 10.0 \ T_{\text{f}} \\ 25976.99586 = (455.6382) \ T_{\text{f}} \\ T_{\text{f}} = 25976.99586 / \ (455.6382) = 57.0123 = \textbf{57.0}^{\circ}\text{C} \end{array}$ 

 $\begin{array}{ll} 6.42 & -q_{\text{lost}} = q_{\text{gained}} = q_{\text{water}} + q_{\text{calorimeter}} \\ & -(30.5 \text{ g alloy}) \left( C_{\text{alloy}} \right) (31.1 - 93.0)^{\circ} \text{C} = (50.0 \text{ g H}_2 \text{O}) \left( 4.184 \text{ J/g}^{\circ} \text{C} \right) (31.1 - 22.0)^{\circ} \text{C} + (9.2 \text{ J/}^{\circ} \text{C}) (31.1 - 22.0)^{\circ} \text{C} \\ & -(30.5) \left( C_{\text{alloy}} \right) (31.1 - 93.0) = (50.0) \left( 4.184 \text{ J/g}^{\circ} \text{C} \right) (31.1 - 22.0) + (9.2 \text{ J/}^{\circ} \text{C}) (31.1 - 22.0)^{\circ} \text{C} \\ & -(30.5) \left( C_{\text{alloy}} \right) (-61.9) = (50.0) \left( 4.184 \right) (9.1) + (9.2) \left( 9.1 \right) \\ & 1887.95(C_{\text{alloy}}) = 1903.72 + 83.72 = 1987.44 \\ & (C_{\text{alloy}}) = 1987.44 / 1887.95 = 1.052697 = 1.1 \text{ J/g}^{\circ} \text{C} \end{array}$ 

6.43 Benzoic acid is C<sub>6</sub>H<sub>5</sub>COOH, and will be symbolized as HBz. -  $q_{\text{reaction}} = q_{\text{water}} + q_{\text{calorimeter}}$ - (1.221 g HBz) (1 mol HBz / 122.11 g HBz) (-3227 kJ/mol HBz) (10<sup>3</sup> J/1 kJ) =  $(1.200 \text{ kg}) (10^3 \text{ g}/1 \text{ kg}) (4.184 \text{ J/g}^\circ\text{C})\Delta\text{T} + (1365 \text{ J/}^\circ\text{C})\Delta\text{T}$  $-(1.221)(1/122.11)(-3227)(10^{3}/1) = (1.200)(10^{3}/1)(4.184)\Delta T + (1365)\Delta T$  $-(1.221)(1/122.11)(-3227)(10^{3}/1) = (1.200)(10^{3}/1)(4.184)\Delta T + (1365)\Delta T$  $32267.3573 = 5020.8\Delta T + (1365)\Delta T = (6385.8)\Delta T$  $\Delta T = 32267.3573 / (6385.8) = 5.05298589 = 5.053^{\circ}C$ a) Energy will flow from Cu (at 100.0°C) to Fe (at 0.0°C). 6.44 b) To determine the final temperature, the heat capacity of the calorimeter must be known. c) -  $q_{Cu} = q_{Fe} + q_{calorimeter}$  assume  $q_{calorimeter} = 0$  $-q_{\rm Cu} = q_{\rm Fe} + 0$  $-(20.0 \text{ g Cu}) (0.387 \text{ J/g}^{\circ}\text{C}) (\text{T}_{\text{f}} - 100.0)^{\circ}\text{C} = (30.0 \text{ g Fe}) (0.450 \text{ J/g}^{\circ}\text{C}) (\text{T}_{\text{f}} - 0.0)^{\circ}\text{C} + 0.0$  $-(20.0)(0.387)(T_{\rm f}-100.0) = (30.0)(0.450)(T_{\rm f}-0.0)$  $-(7.74)(T_{\rm f} - 100.0) = (13.5)(T_{\rm f} - 0.0)$ 774 - 7.74  $T_f = 13.5 T_f$  $774 = (13.5 + 7.74) T_f = 21.24 T_f$  $T_f = 774 / 21.24 = 36.44068 = 36.4^{\circ}C$ 6.45 -  $q_{\text{hydrocarbon}} = q_{\text{water}} + q_{\text{calorimeter}}$  $-q_{\text{hydrocarbon}} = (2.500 \text{ L H}_2\text{O}) (1\text{mL}/10^{-3}\text{L}) (1.00\text{g/mL}) (4.184 \text{ J/g}^{\circ}\text{C}) (23.55 - 20.00)^{\circ}\text{C}$ + (403 J/°C) (23.55 - 20.00)°C  $-q_{\text{hydrocarbon}} = (2.500) (1/10^{-3}) (1.00/1) (4.184 \text{ J}) (23.55 - 20.00) + (403 \text{ J}) (23.55 - 20.00)$  $-q_{\text{hydrocarbon}} = (2500.) (4.184 \text{ J}) (3.55) + (403 \text{ J}) (3.55)$  $-q_{\text{hydrocarbon}} = (37133 \text{ J}) + (1430.65 \text{ J}) = 38563.65 \text{ J}$  $q_{\rm hydrocarbon} = -3.856365 \ {\rm x} \ 10^4 \ {\rm J}$  $q_{\text{hydrocarbon}}$  / g = (-3.856365 x 10<sup>4</sup> J) / 1.500 g = -2.57091 x 10<sup>4</sup> = - 2.57 x 10<sup>4</sup> J 6.46 The reaction is:  $2 \text{ KOH}(aq) + H_2 \text{SO}_4(aq) \rightarrow K_2 \text{SO}_4(aq) + 2 H_2 O(l)$ Calculating kJ (25.0 + 25.0) mL (1.00 g/mL)  $(4.184 \text{ J/g}^{\circ}\text{C})$   $(30.17 - 23.50)^{\circ}\text{C}(1 \text{ kJ}/10^{3} \text{ J}) = 1.395364 \text{ kJ}$  (unrounded) (The temperature increased so the heat of reaction is exothermic.) Calculating moles (25.0 mL) (0.500 mol H<sub>2</sub>SO<sub>4</sub> / L) (10<sup>-3</sup> L / 1 mL) = 0.0125 mol H<sub>2</sub>SO<sub>4</sub> (unrounded) (25.0 mL) (1.00 mol KOH / L) (10<sup>-3</sup> L / 1 mL) = 0.0250 mol KOH (unrounded) The moles show that both H<sub>2</sub>SO<sub>4</sub> and KOH are limiting. The enthalpy change could be calculated in any of the following ways:  $\Delta H = -1.395364 \text{ kJ} / 0.0125 \text{ mol } \text{H}_2\text{SO}_4 = -111.62912 = -112 \text{ kJ/mol } \text{H}_2\text{SO}_4$  $\Delta H = -1.395364 \text{ kJ} / 0.0250 \text{ mol KOH} = -55.81456 = -55.8 \text{ kJ/mol KOH}$ (Per mole of  $K_2SO_4$  gives the same value as per mole of  $H_2SO_4$ , and per mole of  $H_2O$  gives the same value as per mole of KOH.) 6.47

- 6.47 Reactants  $\rightarrow$  Products + Energy  $\Delta H_{rxn} = (-)$ Thus, energy is a product.
- 6.48 The reaction has a positive  $\Delta H_{rxn}$ , because this reaction requires the input of energy to break the O O bond: O<sub>2</sub>(g) + energy  $\rightarrow$  2O(g)

6.49 As a substance changes from the gaseous state to the liquid state, energy is released so  $\Delta H$  would be negative for the condensation of 1 mol of water. The value of  $\Delta H$  for the vaporization of 2 mol of water would be twice the value of  $\Delta H$  for the condensation of 1 mol of water vapor but would have an opposite sign (+ $\Delta H$ ).

$$H_2O(g) \rightarrow H_2O(l) + Energy$$

 $\Delta H_{\rm cond} = (-)$ 

It would be opposite in sign to and one-half the value for the vaporization of 2 moles of liquid H<sub>2</sub>O to H<sub>2</sub>O vapor.

6.50 a) This reaction is **exothermic** because  $\Delta H$  is negative.

b) Because  $\Delta H$  is a state function, the total energy required for the reverse reaction, regardless of how the change occurs, is the same magnitude but different sign of the forward reaction. Therefore,  $\Delta H = +20.2 \text{ kJ}$ . c) The  $\Delta H_{\text{rxn}}$  is specific for the reaction as written, meaning that 20.2 kJ is released when 1/8 of a mole of sulfur reacts. In this case, 3.2 moles of sulfur react and we therefore expect that much more energy will be released.

$$\Delta H_{\rm rxn} = (3.2 \text{ mol } S_8) \left( \frac{-20.2 \text{ kJ}}{(1/8) \text{ mol } S_8} \right) = -517.12 = -5.2 \text{ x } 10^2 \text{ kJ}$$

d) The mass of S<sub>8</sub> requires conversion to moles and then a calculation identical to c) can be performed.

$$\Delta H_{\rm rxn} = (20.0 \text{ g } \text{S}_8) \left( \frac{1 \text{ mol } \text{S}_8}{256.56 \text{ g } \text{S}_8} \right) \left( \frac{-20.2 \text{ kJ}}{(1/8) \text{ mol } \text{S}_8} \right) = -12.5974 = -12.6 \text{ kJ}$$

6.51 MgCO<sub>3</sub>(s)  $\rightarrow$  MgO(s) + CO<sub>2</sub>(g)  $\Delta H_{rxn} = 117.3 \text{ kJ}$ a) Absorbed b)  $\Delta H_{rxn}$  (reverse) = -117.3 kJ c)  $\Delta H_{rxn} = (5.35 \text{ mol CO}_2) \left( \frac{-117.3 \text{ kJ}}{1 \text{ mol CO}_2} \right) = -627.555 = -628 \text{ kJ}$ d)  $\Delta H_{rxn} = (35.5 \text{ g CO}_2) \left( \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \right) \left( \frac{-117.3 \text{ kJ}}{1 \text{ mol CO}_2} \right) = -94.618 = -94.6 \text{ kJ}$ 

6.52 a) 
$$1/2 N_2(g) + 1/2 O_2(g) \rightarrow NO(g)$$
  $\Delta H = 90.29 \text{ kJ}$   
b)  $\Delta H_{\text{rxn}} = (1.50 \text{ g NO}) \left(\frac{1 \text{ mol NO}}{30.01 \text{ g NO}}\right) \left(\frac{-90.29 \text{ kJ}}{1 \text{ mol NO}}\right) = -4.5129957 = -4.51 \text{ kJ}$ 

6.53 a) KBr(s) 
$$\rightarrow$$
 K(s) + 1/2 Br<sub>2</sub>(l)  $\Delta H_{rxn} = 394 \text{ kJ}$   
b)  $\Delta H_{rxn} = (10.0 \text{ kg KBr}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol KBr}}{119.00 \text{ g KBr}}\right) \left(\frac{-394 \text{ kJ}}{1 \text{ mol KBr}}\right) = -3.3109 \text{ x } 10^4 \text{ = -3.31 x } 10^4 \text{ kJ}$ 

6.54 For the reaction written, 2 moles of H<sub>2</sub>O<sub>2</sub> release 196.1 kJ of energy upon decomposition.  $2 H_2O_2(l) \rightarrow 2 H_2O(l) + O_2(g) \qquad \Delta H_{rxn} = -196.1 \text{ kJ}$ Heat =  $q = (732 \text{ kg } H_2O_2) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol } H_2O_2}{34.02 \text{ g } H_2O_2}\right) \left(\frac{-196.1 \text{ kJ}}{2 \text{ mol } H_2O_2}\right) = -2.1097 \text{ x } 10^6 = -2.11 \text{ x } 10^6 \text{ kJ}$ 

6.55 For the reaction written, 1 mole of B<sub>2</sub>H<sub>6</sub> releases 755.4 kJ of energy upon reaction.  
B<sub>2</sub>H<sub>6</sub>(g) + 3 Cl<sub>2</sub>(g) 
$$\rightarrow$$
 2 BCl<sub>3</sub>(g) + 6 HCl(g)  $\Delta H_{rxn} = -755.4$  kJ  
Heat =  $q = \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol } B_2H_6}{27.67 \text{ g } B_2H_6}\right) \left(\frac{-755.4 \text{ kJ}}{1 \text{ mol } B_2H_6}\right) = -2.73003 \text{ x } 10^4 = -2.7330 \text{ x } 10^4 \text{ kJ/kg}$ 

6.56 
$$4 \operatorname{Fe}(s) + 3 \operatorname{O}_{2}(g) \rightarrow 2 \operatorname{Fe}_{2}\operatorname{O}_{3}(s)$$
  $\Delta H_{\operatorname{rxn}} = -1.65 \times 10^{3} \operatorname{kJ}$   
a) Heat =  $q = (0.100 \operatorname{kg} \operatorname{Fe}) \left(\frac{10^{3} \operatorname{g}}{1 \operatorname{kg}}\right) \left(\frac{1 \operatorname{mol} \operatorname{Fe}}{55.85 \operatorname{g} \operatorname{Fe}}\right) \left(\frac{-1.65 \times 10^{3} \operatorname{kJ}}{4 \operatorname{mol} \operatorname{Fe}}\right) = -738.585 = -739 \operatorname{kJ}$   
b) Mass Fe<sub>2</sub>O<sub>3</sub> =  $(-4.93 \times 10^{3} \operatorname{kJ}) \left(\frac{2 \operatorname{mol} \operatorname{Fe}_{2}\operatorname{O}_{3}}{-1.65 \times 10^{3} \operatorname{kJ}}\right) \left(\frac{159.70 \operatorname{g} \operatorname{Fe}_{2}\operatorname{O}_{3}}{1 \operatorname{mol} \operatorname{Fe}_{2}\operatorname{O}_{3}}\right) = 954.328 = 954 \operatorname{g} \operatorname{Fe}_{2}\operatorname{O}_{3}$ 

6.57 
$$2 \operatorname{HgO}(s) \rightarrow 2 \operatorname{Hg}(l) + O_2(g)$$
  $\Delta H_{rxn} = 181.6 \text{ kJ}$   
a) Heat =  $q = (555 \text{ g HgO}) \left( \frac{1 \text{ mol HgO}}{216.6 \text{ g HgO}} \right) \left( \frac{181.6 \text{ kJ}}{2 \text{ mol Hg}} \right) = 232.659 = 233 \text{ kJ}$   
b) Mass Hg =  $(275 \text{ kJ}) \left( \frac{2 \text{ mol Hg}}{181.6 \text{ kJ}} \right) \left( \frac{200.6 \text{ g Hg}}{1 \text{ mol Hg}} \right) = 607.544 = 608 \text{ g Hg}$ 

6.58 a) 
$$C_2H_4(g) + 3 O_2(g) \rightarrow 2 CO_2(g) + 2 H_2O(l)$$
  
b) Mass  $C_2H_4 = (-70.0 \text{ kJ}) \left(\frac{1 \text{ mol } C_2H_4}{-1411 \text{ kJ}}\right) \left(\frac{28.04 \text{ g } C_2H_4}{1 \text{ mol } C_2H_4}\right) = 1.39107 = 1.39 \text{ g } C_2H_4$ 

6.59 a) 
$$C_{12}H_{22}O_{11}(s) + 12 O_2(g) \rightarrow 12 CO_2(g) + 11 H_2O(l) \Delta H_{rxn} = -5.64 \text{ x } 10^3 \text{ kJ}$$
  
b)  $Heat = q = \left(\frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.30 \text{ g } C_{12}H_{22}O_{11}}\right) \left(\frac{-5.64 \text{ x } 10^3 \text{ kJ}}{1 \text{ mol } C_{12}H_{22}O_{11}}\right) = -16.47677 = -16.5 \text{ kJ/g}$ 

- 6.60 Hess's Law:  $\Delta H_{rxn}$  is independent of the number of steps or the path of the reaction.
- 6.61 Hess's Law provides a useful way of calculating energy changes for reactions which are difficult or impossible to measure directly.
- 6.62 Two chemical equations can be written based on the description given:

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \qquad \Delta H_1 \qquad (1)$$
  

$$CO(g) + 1/2 O_2(g) \rightarrow CO_2(g) \qquad \qquad \Delta H_2 \qquad (2)$$

The second reaction can be reversed, its  $\Delta H$  sign changed, and appropriate coefficients can be multiplied to one or both of the equations to allow addition of the two reactions. In this case, no coefficients are necessary because the CO<sub>2</sub> cancels.

$$\begin{array}{cc} C(s) + O_2(g) \rightarrow \overrightarrow{CO_2(g)} & \Delta H_1 \\ \hline CO_2(g) \rightarrow CO(g) + 1/2 & O_2(g) & -\Delta H_2 \\ Total & C(s) + 1/2 & O_2(g) \rightarrow CO(g) & \Delta H_{rxn} = \Delta H_1 + (-\Delta H_2) \end{array}$$

How are the  $\Delta H$ 's for each reaction determined? The reverse of equation (2) was used in Sample Problem 6.7, with  $\Delta H_2 = -283.0$  kJ. The  $\Delta H_1$  can be found by using the heats of formation in Appendix B:  $\Delta H_1 = \Delta H_f(CO_2) = -393.5$  kJ/mol - (0 + 0) = -393.5 kJ/mol. Assume one mole for equation (1) and  $\Delta H_{rxn} = \Delta H_1 - \Delta H_2 = -393.5$  kJ - (-283.0 kJ) = **-110.5** kJ.

6.63 To obtain the overall reaction, add the first reaction to the reverse of the second.

| $Ca(s) + 1/2 O_2(g) \rightarrow CaO(s)$                                                                                                                                                                                                                                                      | $\Delta H = -635.1 \text{ kJ}$                                                                                                               |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$                                                                                                                                                                                                                                                     | $\Delta H = -178.3 \text{ kJ}$                                                                                                               |
| $Ca(s) + 1/2 O_2(g) + CO_2(g) \rightarrow CaCO_3(s)$                                                                                                                                                                                                                                         | $\Delta H = -813.4 \text{ kJ}$                                                                                                               |
| 6.64 $2 \operatorname{NOCl}(g) \rightarrow 2 \operatorname{NO}(g) + \operatorname{Cl}_2(g)$ $2 \operatorname{NO}(g) \rightarrow \operatorname{N}_2(g) + \operatorname{O}_2(g)$ $2 \operatorname{NOCl}(g) \rightarrow \operatorname{N}_2(g) + \operatorname{O}_2(g) + \operatorname{Cl}_2(g)$ | $\Delta H = -2(-38.6 \text{ kJ})$<br>$\Delta H = -2(90.3 \text{ kJ})$<br>$\Delta H = 77.2 \text{ kJ} - 180.6 \text{ kJ} = -103.4 \text{ kJ}$ |

6.65 Vaporization is the change in state from a liquid to a gas. The two equations describing these chemical reactions can be combined to yield the equation for vaporization.

|      | $\begin{aligned} \mathrm{H_2O}(l) &\rightarrow \mathrm{H_2}(g) + 1/2 \ \mathrm{O_2}(g) \\ \mathrm{H_2}(g) + 1/2 \ \mathrm{O_2}(g) &\rightarrow \mathrm{H_2O}(g) \\ \mathrm{H_2O}(l) &\rightarrow \mathrm{H_2O}(g) \end{aligned}$ | $\Delta H = +285.8 \text{ kJ}$<br>$\Delta H = -241.8 \text{ kJ}$<br>$\Delta H_{\text{vap}} = 44.0 \text{ kJ}$ |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| 6.66 | $C(s) + 1/4 S_8(s) \rightarrow CS_2(l)$<br>$CS_2(l) \rightarrow CS_2(g)$<br>$C(s) + 1/4 S_8(s) \rightarrow CS_2(g)$                                                                                                              | $\Delta H = +89.7 \text{ kJ}$<br>$\Delta H = +27.7 \text{ kJ}$<br>$\Delta H = +117.4 \text{ kJ}$              |

6.67 Equation 3 is:  $N_2(g) + 2 O_2(g) \rightarrow 2 NO_2(g)$   $\Delta H_{rxn} = +66.4 \text{ kJ}$ In Figure P6.67, A represents reaction 1 with a larger amount of energy absorbed, B represents reaction 2 with a smaller amount of energy released and C represents reaction 3 as the sum of A and B.

| 6.68 | 1) $P_4(s) + 6 \operatorname{Cl}_2(g) \rightarrow 4 \operatorname{PCl}_3(g)$  | $\Delta H_1$           | = <b>-</b> 1148 kJ        |
|------|-------------------------------------------------------------------------------|------------------------|---------------------------|
|      | 2) 4 $PCl_3(g) + 4 Cl_2(g) \rightarrow 4 PCl_5(g)$                            | $\Delta H_2$           | = -460 kJ                 |
|      | 3) $P_4(s) + 10 \operatorname{Cl}_2(g) \rightarrow 4 \operatorname{PCl}_5(g)$ | $\Delta H_{\rm overa}$ | <sub>all</sub> = -1608 kJ |
|      | Equation (1) = B, equation (2) = C, equation (3) = A                          |                        |                           |
|      |                                                                               |                        |                           |
| 6.69 | $C(diamond) + O_2(g) \rightarrow CO_2(g)$                                     | $\Delta H =$           | -395.4 kJ                 |
|      | $CO_2(g) \rightarrow C(graphite) + O_2(g)$                                    | $\Delta H =$           | -(-393.5 kJ)              |
|      | $C(diamond) \rightarrow C(graphite)$                                          | $\Delta H =$           | - 1.9 kJ                  |

- 6.70 The standard heat of reaction,  $\Delta H_{ran}^{\circ}$ , is the enthalpy change for any reaction where all substances are in their standard states. The standard heat of formation,  $\Delta H_{f}^{\circ}$ , is the enthalpy change that accompanies the formation of one mole of a compound in its standard state from elements in their standard states. Standard state is 1 atm for gases, 1 *M* for solutes, and pure state for liquids and solids. Standard state does not include a specific temperature, but a temperature must be specified in a table of standard values.
- 6.71 The standard heat of reaction is the sum of the standard heats of formation of the products minus the sum of the standard heats of formation of the reactants multiplied by their respective stoichiometric coefficients.  $\Delta H_{\rm rxn} = \Sigma m \Delta H_{\ell}^{\circ} \text{ (products)} - \Sigma n \Delta H_{\ell}^{\circ} \text{ (reactants)}$
- 6.72 a) 1/2 Cl<sub>2</sub>(g) + Na(s) → NaCl(s) The element chlorine occurs as Cl<sub>2</sub>, not Cl.
  b) H<sub>2</sub>(g) + 1/2 O<sub>2</sub>(g) → H<sub>2</sub>O(l) The element hydrogen exists as H<sub>2</sub>, not H, and the formation of water is written with water as the product in the liquid state.
  c) No changes
- 6.73 a)  $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$ b)  $Na(s) + 1/2 H_2(g) + C(graphite) + 3/2 O_2(g) \rightarrow NaHCO_3(s)$ c)  $C(graphite) + 2 Cl_2(g) \rightarrow CCl_4(l)$ d)  $1/2 H_2(g) + 1/2 N_2(g) + 3/2 O_2(g) \rightarrow HNO_3(l)$
- 6.74 a)  $1/2 H_2(g) + 1/2 I_2(s) \rightarrow HI(g)$ b)  $Si(s) + 2 F_2(g) \rightarrow SiF_4(g)$ c)  $3/2 O_2(g) \rightarrow O_3(g)$ d)  $3 Ca(s) + 1/2 P_4(s) + 4 O_2(g) \rightarrow Ca_3(PO_4)_2(s)$
- 6.75 The enthalpy change of a reaction is the sum of the  $\Delta H_{\rm f}$  of the products minus the sum of the  $\Delta H_{\rm f}$  of the reactants. Since the  $\Delta H_{\rm f}$  values (Appendix B) are reported as energy per one mole, use the appropriate coefficient to reflect the higher number of moles.

 $\Delta H_{ran}^{o} = \sum [\Delta H_{f}^{o} \text{ (products)}] - \sum [\Delta H_{f}^{o} \text{ (reactants)}]$ 

a) 
$$\Delta H_{ss}^{*} = 2 \Delta H_{7}^{*} [SO_{5}(g)] + 2 \Delta H_{7}^{*} [H_{3}(g)] - 2 \Delta H_{7}^{*} [H_{3}(g)] - 3 \Delta H_{7}^{*} [O_{5}(g)]$$
  
= 2 mol(-296.8 kJ/mol) + 2 mol(-241.826 kJ/mol) - 2 mol(-20.2 kJ/mol) - 3(0.0)  
= -103.6 kJ  
b) The balanced equation is  $CH_{4}(g) + 4 Cl_{2}(g) \rightarrow CCl_{4}(f) + 4 HCl(g)$   
 $\Delta H_{ss}^{*} = 1 mol(\Delta H_{7}^{*}, SiF_{4}(g)) + 2 mol(\Delta H_{7}^{*}, H_{3}O(f)) - 1 mol(-74.87 kJ/mol) - 4 mol(0)
= -433 kJ
6.76 a)  $\Delta H_{ss}^{*} = 1 mol(\Delta H_{7}^{*}, SiF_{4}(g)) + 2 mol(\Delta H_{7}^{*}, H_{3}O(f)) - 1 mol(\Delta H_{7}^{*}, SiO_{5}(s)) - 4 mol(\Delta H_{7}^{*}, HF(g))
= 1 mol(-1614.9 kJ)
b) 2 C_{2}H_{6}(g) + 7 O_{2}(g) \rightarrow 4 CO_{2}(g) + 6 H_{2}O(g)
 $\Delta H_{ss}^{*} = 4 mol(\Delta H_{7}^{*}, CO_{2}(g)) + 6 mol(\Delta H_{7}^{*}, H_{5}O(g)) - 2 mol(\Delta H_{7}^{*}, C_{2}H_{6}(g)) - 7 mol(\Delta H_{7}^{*}, O_{2}(g))
= 4 mol(\Delta H_{7}^{*}, CO_{2}(g)) + 6 mol(-241.826 kJ) - 2 mol(-284.667 kJ) - 7 mol(\Delta H_{7}^{*}, O_{2}(g))
= 4 mol(-393.5 kJ) + 6 mol(-241.826 kJ) - 2 mol(-284.667 kJ) - 7 mol(0)
= -2885.6 kJ (or -1427.8 kJ for reaction of 1 mol of C_{2}H_{0})
= 2 mol(\Delta H_{7}^{*}, CUO(s)) - 1 mol(-4H_{7}^{*}, Cu_{2}(s)) - 1/2 mol(\Delta H_{7}^{*}, O_{2}(g))
-146.0 kJ = 2 mol(\Delta H_{7}^{*}, CuO(s)) + 1 mol(-168.6 kJ)
 $\Delta H_{ss}^{*} = -146.0 kJ$   
 $\Delta H_{ss}^{*} = 2 mol(\Delta H_{7}^{*}, CuO(s)) + 1 mol(-168.6 kJ)$   
 $\Delta H_{ss}^{*} = -126.0 kJ - 2 mol(\Delta H_{7}^{*}, CuO(s)) + 1 mol(-4H_{8}^{*}, H_{2}O(g)) - 1/2 mol(0)$   
 $-146.0 kJ = 2 mol(\Delta H_{7}^{*}, CuO(s)) + 1 mol(-241.826 kJ/mol) - 1 mol(\Delta H_{7}^{*}, C_{2}H_{2}(g)) - 5/2 mol(\Delta H_{7}^{*}, O_{2}(g))$   
 $-1255.8 kJ = 2 mol(\Delta H_{7}^{*}, CuO(s)) + 1 mol(\Delta H_{7}^{*}, H_{2}O(g)) - 1 mol(\Delta H_{7}^{*}, C_{2}H_{2}(g)) - 5/2 mol(0.0)$   
 $-1255.8 kJ = 2 mol(\Delta H_{7}^{*}, O_{2}(g)) + 1 mol(\Delta H_{7}^{*}, H_{2}O(g)) - 1 mol(\Delta H_{7}^{*}, C_{2}H_{2}(g)) - 5/2 mol(0.0)$   
 $-1255.8 kJ = 2 mol(\Delta H_{7}^{*}, O_{2}(g)) + 1 mol(\Delta H_{7}^{*}, H_{2}O(g)) + 1 mol(\Delta H_{7}^{*}, C_{2}H_{2}(g)) - 5/2 mol(0.0)$   
 $-1255.8 kJ = 2 mol(\Delta H_{7}^{*}, O_{2}(g)) + 1 mol(\Delta H_{7}^{*}, C_{2}H_{2}(g))$   
 $\Delta H_{7}^{*} = 6 mol(\Delta H_{7}^{*}, O_{2}(g)) + 1 mol$$$$ 

$$\Delta H_{f}^{\circ}$$
, C<sub>3</sub>H<sub>5</sub>(NO<sub>3</sub>)<sub>3</sub>(*l*) =  $\frac{-15760 \text{ kJ}}{-4 \text{ mol}}$  = **3940 kJ/mol**

6.80 2 PbSO<sub>4</sub>(s) + 2 H<sub>2</sub>O(l)  $\rightarrow$  Pb(s) + PbO<sub>2</sub>(s) + 2 H<sub>2</sub>SO<sub>4</sub>(l) a)  $\Delta H_{ran}^{\circ} = 1 \mod (\Delta H_{f}^{\circ}, Pb(s)) + 1 \mod (\Delta H_{f}^{\circ}, PbO_{2}(s)) + 2 \mod (\Delta H_{f}^{\circ}, H_{2}SO_{4}(l)) - 2 \mod (\Delta H_{f}^{\circ}, PbSO_{4}(s))$ 

$$-2 \operatorname{mol} \left( \Delta H_{f}^{\circ}, \operatorname{H}_{2} O(l) \right)$$
  
= 1 mol  $\left( 0 \frac{\mathrm{kJ}}{\mathrm{mol}} \right) + 1 \operatorname{mol} \left( -276.6 \frac{\mathrm{kJ}}{\mathrm{mol}} \right) + 2 \operatorname{mol} \left( -813.989 \frac{\mathrm{kJ}}{\mathrm{mol}} \right) - 2 \operatorname{mol} \left( -918.39 \frac{\mathrm{kJ}}{\mathrm{mol}} \right) - 2 \operatorname{mol} \left( -285.840 \frac{\mathrm{kJ}}{\mathrm{mol}} \right)$   
= 503.9 kJ

b) Reverse the first equation (changing the sign of  $\Delta H_{rxn}^{o}$ ) and multiply the coefficients (and  $\Delta H_{rxn}^{o}$ ) of the second reaction by 2.

$$\begin{array}{ll} 2 \ \mathrm{PbSO}_4(s) \rightarrow \mathrm{Pb}(s) + \mathrm{PbO}_2(s) + 2 \ \mathrm{SO}_3(g) & \Delta H^\circ = -(-768 \ \mathrm{kJ}) \\ 2 \ \mathrm{SO}_3(g) + 2 \ \mathrm{H}_2\mathrm{O}(l) \rightarrow 2 \ \mathrm{H}_2\mathrm{SO}_4(l) & \Delta H^\circ = 2(-132 \ \mathrm{kJ}) \\ \mathrm{Reaction:} \ 2 \ \mathrm{PbSO}_4(s) + 2 \ \mathrm{H}_2\mathrm{O}(l) \rightarrow \mathrm{Pb}(s) + \mathrm{PbO}_2(s) + 2 \ \mathrm{H}_2\mathrm{SO}_4(l) & \Delta H^\circ_{ran} = 504 \ \mathrm{kJ} \end{array}$$

6.81 a) 
$$C_{18}H_{36}O_2(s) + 26 O_2(g) \rightarrow 18 CO_2(g) + 18 H_2O(g)$$
  
b)  $\Delta H^{\circ}_{comb} = 18 mol (\Delta H^{\circ}_{f} CO_2(g)) + 18 mol (\Delta H^{\circ}_{f} H_2O(g)) - 1 mol (\Delta H^{\circ}_{f} C_{18}H_{36}O_2(s)) - 26 mol (\Delta H^{\circ}_{f} O_2(g))$   
= 18 mol (-393.5 kJ/mol) + 18 mol (-241.826 kJ/mol) - 1 mol (-948 kJ/mol) - 26 mol (0 kJ/mol)  
= -10,488 kJ  
c)  $q(kJ) = (1.00 \text{ g } C_{18}H_{36}O_2) \left(\frac{1 \text{ mol } C_{18}H_{36}O_2}{284.47 C_{18}H_{36}O_2}\right) \left(\frac{-10,488 \text{ kJ}}{1 \text{ mol } C_{18}H_{36}O_2}\right)$   
= -36.9 kJ  
 $q(kcal) = (-36.9 \text{ kJ}) \left(\frac{1 \text{ kcal}}{4.184 \text{ kJ}}\right) = -8.81 \text{ kcal}$ 

d) q(kcal) = 8.81 kcal/g x 11.0 g = 96.9 kcalThe calculated calorie content is consistent with the package information.

6.82 a) 
$$H_2SO_4(l) \rightarrow H_2SO_4(aq)$$

 $\Delta H_{rsn}^{\circ} = 1 \mod (\Delta H_{f}^{\circ}, H_{2}SO_{4}(aq)) - 1 \mod (\Delta H_{f}^{\circ}, H_{2}SO_{4}(l))$ = 1 mol (-907.51 kJ/mol) - 1 mol (-813.989 kJ/mol) = -93.52 kJ

b) q = (mass) (specific heat) ( $\Delta T$ )

93.52 kJ x 10<sup>3</sup> J/kJ = [1000. mL x 1.060 g/mL] x 
$$\frac{3.50 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}}$$
 x (T<sub>f</sub> - 25.0°C)  
9.352 x 10<sup>4</sup> J = 1060. g x  $\frac{3.50 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}}$  x (T<sub>f</sub> - 25.0°C)  
9.352 x 10<sup>4</sup> J = (T<sub>f</sub>) 3710 J/°C - 9.28 x 10<sup>4</sup> J  
T<sub>f</sub> = **50.2°C**

c) Adding the acid to a large amount of water releases the heat to a large mass of solution and thus, the potential temperature rise is minimized due to the large heat capacity of the larger volume.

6.83 a) A first read of this problem suggests there is insufficient information to solve the problem. Upon more careful reading, you find that the question asks volumes for each mole of helium.

$$T = 273 + 15 = 288 \text{ K} \text{ or } T = 273 + 30 = 303 \text{ K}$$
$$V_{15} / n = RT / P = \frac{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(288 \text{ K})}{(1.00 \text{ atm})} = 23.6448 = 23.6 \text{ L/mol}$$
$$V_{30} / n = RT / P = \frac{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(303 \text{ K})}{(1.00 \text{ atm})} = 24.8763 = 24.9 \text{ L/mol}$$

b) Internal energy is the sum of the potential and kinetic energies of each He atom in the system (the balloon). The energy of one mole of helium atoms can be described as a function of temperature, E = 3/2 nRT, where n = 1 mole. Therefore, the internal energy at 15°C and 30°C can be calculated. The inside back cover lists values of R with different units.

 $E = 3/2 \text{ nRT} = (3/2) (1.00 \text{ mol}) (8.314 \text{ J/mol} \cdot \text{K}) (303 - 288)\text{K} = 187.065 = 187 \text{ J}$ 

c) When the balloon expands as temperature rises, the balloon performs PV work. However, the problem specifies that pressure remains constant, so work done <u>on</u> the surroundings by the balloon is defined by equation 6.4:  $w = -P\Delta V$ . When pressure and volume are multiplied together, the unit is L•atm. Since we would like to express work in Joules, we can create a conversion factor between L•atm and J by comparing two gas constants.

$$w = -P\Delta V = -(1.00 \text{ atm})((24.8763 - 23.6448)L) \left[ \left( \frac{101325 \text{ Pa}}{1 \text{ atm}} \right) \left( \frac{\text{kg/ms}^2}{\text{Pa}} \right) \left( \frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right) \right] \left( \frac{1 \text{ J}}{\text{kg} \cdot \text{m}^2/\text{s}^2} \right)$$

= -124. /8 = -1.2 x 10<sup>2</sup> J d)  $q_{\rm P} = \Delta E + {\rm P}\Delta V = (187.065 \text{ J}) + (124.78 \text{ J}) = 311.845 = 3.1 x 10<sup>2</sup> J$  $e) <math>\Delta H = q_{\rm P} = 310 \text{ J}.$ 

f) When a process occurs at constant pressure, the change in heat energy of the system can be described by a state function called enthalpy. The change in enthalpy equals the heat (q) lost at constant pressure:  $\Delta H = \Delta E + P\Delta V = \Delta E - w = (q + w) - w = q_p$ 

## 6.84 a) Respiration:

 $C_{6}H_{12}O_{6}(s) + 6 O_{2}(g) \rightarrow 6 CO_{2}(g) + 6 H_{2}O(l)$   $\Delta H_{rxn} = [6 \mod \Delta H_{f}(CO_{2}) + 6 \mod \Delta H_{f}(H_{2}O)] - [1 \mod \Delta H_{f}(C_{6}H_{12}O_{6}) + 6 \mod \Delta H_{f}(O_{2})]$   $\Delta H_{rxn} = [6(-393.5 \text{ kJ}) + 6(-285.840 \text{ kJ})] - [-1237.3 \text{ kJ} + 6(0.0 \text{ kJ})] = -2838.74 = -2838.7 \text{ kJ}$ Fermentation:  $C_{6}H_{12}O_{6}(s) \rightarrow 2 CO_{2}(g) + 2 CH_{3}CH_{2}OH(l)$   $\Delta H_{rxn} = [2 \mod \Delta H_{f}(CO_{2}) + 2 \mod \Delta H_{f}(CH_{3}CH_{2}OH)] - [1 \mod \Delta H_{f}(C_{6}H_{12}O_{6})]$   $\Delta H_{rxn} = [2(-393.5 \text{ kJ}) + 2(-235.1 \text{ kJ})] - [-1237.3 \text{ kJ}] = -19.9 \text{ kJ}$ b) Combustion of ethanol:  $CH_{3}CH_{2}OH(l) + 3 O_{2}(g) \rightarrow 2 CO_{2}(g) + 3 H_{2}O(l)$   $\Delta H_{rxn} = [2 \mod \Delta H_{f}(CO_{2}) + 3 \mod \Delta H_{f}(H_{2}O)] - [1 \mod \Delta H_{f}(CH_{3}CH_{2}OH) + 3 \mod \Delta H_{f}(O_{2})]$   $\Delta H_{rxn} = [2(-393.5 \text{ kJ}) + 3(-285.840 \text{ kJ})] - [-235.1 \text{ kJ} + 6(0.0 \text{ kJ})] = -1409.42 = -1409.4 \text{ kJ}$ Heats of combustion / mol C: Sugar: (-2838.74 \text{ kJ/mol sugar}) / (6 \mod C/mol sugar) = -473.12333 = -473.12 \text{ kJ/mol C}

Ethanol: (-1409.42 kJ/mol ethanol) / (2 mol C/mol ethanol) = -704.71 kJ/mol C Ethanol has a higher value.

## 6.85 a) Reactions:

1)  $C_{21}H_{44}(s) + 32 O_2(g) \rightarrow 21 CO_2(g) + 22 H_2O(g)$ 2)  $C_{21}H_{44}(s) + 43/2 O_2(g) \rightarrow 21 CO(g) + 22 H_2O(g)$ 3)  $C_{21}H_{44}(s) + 11 O_2(g) \rightarrow 21 C(s) + 22 H_2O(g)$ Heats of combustion: 1)  $\Delta H_{rxn} = [21 \mod \Delta H_f(CO_2) + 22 \mod \Delta H_f(H_2O)] - [1 \mod \Delta H_f(C_{21}H_{44}) + 32 \mod \Delta H_f(O_2)]$   $\Delta H_{rxn} = [21(-393.5 \text{ kJ}) + 22(-241.826 \text{ kJ})] - [-476.3 \text{ kJ} + 32(0.0 \text{ kJ})] = -13107.372 = -13107.4 \text{ kJ}$ 2)  $\Delta H_{rxn} = [21 \mod \Delta H_f(CO) + 22 \mod \Delta H_f(H_2O)] - [1 \mod \Delta H_f(C_{21}H_{44}) + 43/2 \mod \Delta H_f(O_2)]$   $\Delta H_{rxn} = [21(-110.5 \text{ kJ}) + 22(-241.826 \text{ kJ})] - [-476.3 \text{ kJ} + 43/2(0.0 \text{ kJ})] = -7164.372 = -7164.4 \text{ kJ}$ 3)  $\Delta H_{rxn} = [21 \mod \Delta H_f(C) + 22 \mod \Delta H_f(H_2O)] - [1 \mod \Delta H_f(C_{21}H_{44}) + 11 \mod \Delta H_f(O_2)]$   $\Delta H_{rxn} = [21(0.0 \text{ kJ}) + 22(-241.826 \text{ kJ})] - [-476.3 \text{ kJ} + 11(0.0 \text{ kJ})] = -4843.872 = -4843.9 \text{ kJ}$ b)  $q = (854 \text{ g} C_{21}H_{44}) \left(\frac{1 \mod C_{21}H_{44}}{296.56 \text{ g} C_{21}H_{44}}\right) \left(\frac{-13107.372 \text{ kJ}}{1 \mod C_{21}H_{44}}\right) = -37745.1 = -3.77 \text{ x } 10^4 \text{ kJ}$  c) The moles of  $C_{21}H_{44}$  need to be calculated one time for multiple usage. It must be assumed that the remaining 90.00% of the candle undergoes complete combustion.

Moles  $C_{21}H_{44} = (854 \text{ g } C_{21}H_{44}) (1 \text{ mol } C_{21}H_{44} / 296.56 \text{ g } C_{21}H_{44}) = 2.879687 \text{ mol (unrounded)}$  q = [(90.00%/100%) (-13107.4 kJ/mol) + (5.00%/100%) (-7164.4 kJ/mol) $+ (5.00\%/100\%) (-4843.9 \text{ kJ/mol})](2.879687 \text{ mol}) = -35699.696 = -3.57 \text{ x } 10^4 \text{ kJ}$ 

6.86 a) From the information given, the reaction is written as follows:

 $SiO_2(s) + 3 C(s) \rightarrow SiC(s) + 2 CO(g) \Delta H^o_{rxn} = 624.7 \text{ kJ/mol SiC}$  (sign is positive because reaction is endothermic) Use Hess's Law and Appendix B to solve for  $[\Delta H^o_f SiC(s)]$ .

 $\Delta H_{rxm}^{o} = [\Delta H_{f}^{o} \operatorname{SiC}(s)] + 2 [\Delta H_{f}^{o} \operatorname{CO}(g)] - [\Delta H_{f}^{o} \operatorname{SiO}_{2}(s)] - 3 [\Delta H_{f}^{o} \operatorname{C}(s)]$   $624.7 \text{ kJ/mol} = [\Delta H_{f}^{o} \operatorname{SiC}(s)] + 2(-110.5 \text{ kJ/mol}) - (-910.0 \text{ kJ/mol}) - 0$   $624.7 \text{ kJ/mol} = [\Delta H_{f}^{o} \operatorname{SiC}(s)] + 689.9 \text{ kJ/mol}$  $[\Delta H_{f}^{o} \operatorname{SiC}(s)] = -65.2 \text{ kJ/mol}$ 

b) The problem states that 624.7 kJ is absorbed *per mole* of SiC formed. Convert kJ/mol to kJ/kg using the molar mass of SiC (40.10 g/mol).

kJ / kg SiC = 
$$\left(\frac{624.7 \text{ kJ}}{1 \text{ mol SiC}}\right) \left(\frac{1 \text{ mol SiC}}{40.10 \text{ g SiC}}\right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) = 15578.55 = 1.558 \text{ x } 10^4 \text{ kJ/kg SiC}$$

6.87

| a)     | $\operatorname{Fe_2O_3}(s) + 3 \operatorname{CO}(g) \rightarrow 2 \operatorname{Fe}(s) + 3 \operatorname{CO}_2(g)$          | $\Delta H_{rxn}^{o} = ?$                         |
|--------|-----------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------|
| b)     | $Fe_2O_3(s) + 1/3 CO(g) \rightarrow 2/3 Fe_3O_4(s) + 1/3 CO_2(g)$                                                           | $\Delta H^{\circ} = 1/3 \; (-48.5 \; \text{kJ})$ |
|        | $2 \operatorname{FeO}(s) + 2 \operatorname{CO}(g) \rightarrow 2 \operatorname{Fe}(s) + 2 \operatorname{CO}_2(g)$            | $\Delta H^{\circ} = -2(-11.0 \text{ kJ})$        |
|        | $2/3 \operatorname{Fe_3O_4}(s) + 2/3 \operatorname{CO}(g) \rightarrow 2 \operatorname{FeO}(s) + 2/3 \operatorname{CO_2}(g)$ | $\Delta H^{\circ} = 2/3 \ (22 \text{ kJ})$       |
| Total: | $\operatorname{Fe_2O_3(s)} + 3 \operatorname{CO}(g) \rightarrow 2 \operatorname{Fe}(s) + 3 \operatorname{CO}_2(g)$          | $\Delta H_{rxn}^{o} = 21 \text{ kJ}$             |

6.88 a) Heat = 
$$(20.4 \text{ gal})\left(\frac{4 \text{ qt}}{1 \text{ gal}}\right)\left(\frac{1 \text{ L}}{1.057 \text{ qt}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{0.702 \text{ g}}{\text{mL}}\right)\left(\frac{1 \text{ mol } C_8 H_{18}}{114.22 \text{ g}}\right)\left(\frac{-5.45 \text{ x } 10^3 \text{ kJ}}{1 \text{ mol } C_8 H_{18}}\right)$$

 $= -2.585869657 \times 10^6 = -2.59 \times 10^6 \text{ kJ}$ 

b) Miles =  $(2.585869657 \times 10^6 \text{ kJ}) (1 \text{ h} / 5.5 \times 10^4 \text{ kJ}) (65 \text{ mi} / \text{ h}) (1 \text{ km} / 0.62 \text{ mi}) = 4929.1 = 4.9 \times 10^3 \text{ km}$ c) Only a small percentage of the chemical energy in the fuel is converted to work to move the car; most of the chemical energy is lost as waste heat flowing into the surroundings.

- 6.89  $C_{6}H_{12}O_{6}(s) + C_{6}H_{12}O_{6}(s) \rightarrow C_{12}H_{22}O_{11}(s) + H_{2}O(l)$   $\Delta H_{rsm}^{o} = 1 \text{ mol sucrose } (-2226 \text{ kJ/mol}) + 1 \text{ mol } H_{2}O(-285.840 \text{ kJ/mol}) - [1 \text{ mol glucose } (-1273 \text{ kJ/mol})$ + 1 mol fructose (-1266 kJ/mol)] = 27 kJ/mol sucrose
- 6.90 The  $\Delta H_{ran}^{\circ}$ , which in this case is  $\Delta H_{comb}^{\circ}$ , is the combination of the heats of formation of the reactants and products. We can write a chemical equation that shows the combustion of oleic acid, assuming that the combustion is complete and yields only  $CO_2(g)$  and  $H_2O(g)$ :

 $C_{18}H_{34}O_{2}(s) + 53/2 O_{2}(g) \rightarrow 18 CO_{2}(g) + 17 H_{2}O(g)$   $\Delta H^{\circ}_{\text{comb}} = 18 \Delta H^{\circ}_{f} [CO_{2}(g)] + 17 \Delta H^{\circ}_{f} [H_{2}O(g)] - [\Delta H^{\circ}_{f} [C_{18}H_{34}O_{2}(s)] + 53/2 \Delta H^{\circ}_{f} [O_{2}(g)]]$   $- 1.11 \text{ x } 10^{4} \text{ kJ} = 18 \text{ mol}(-393.5 \text{ kJ/mol}) + 17 \text{ mol}(-241.826 \text{ kJ/mol}) - (1 \text{ mol}) \Delta H^{\circ}_{f} [C_{18}H_{34}O_{2}(s)] - 53/2 (0)$   $(1 \text{ mol}) \Delta H^{\circ}_{f} [C_{18}H_{34}O_{2}(s)] = 1.11 \text{ x } 10^{4} \text{ kJ} - 7.083 \text{ x } 10^{3} \text{ kJ} - 4.111 \text{ x } 10^{3} \text{ kJ}$  $\Delta H^{\circ}_{f} [C_{18}H_{34}O_{2}(s)] = -94 \text{ kJ/mol}$   $\begin{array}{ll} 6.91 & \operatorname{ClF}(g) + \operatorname{F}_2(g) \to \operatorname{ClF}_3(l) & \Delta H^\circ_{rm} = ? \\ & \operatorname{ClF}(g) + 1/2 \operatorname{O}_2(g) \to 1/2 \operatorname{Cl}_2\operatorname{O}(g) + 1/2 \operatorname{OF}_2(g) & \Delta H^\circ = 1/2(167.5 \text{ kJ}) \\ & \operatorname{F}_2(g) + 1/2 \operatorname{O}_2(g) \to \operatorname{OF}_2(g) & \Delta H^\circ = 1/2(-43.5 \text{ kJ}) \\ & 1/2 \operatorname{Cl}_2\operatorname{O}(g) + 3/2 \operatorname{OF}_2(g) \to \operatorname{ClF}_3(l) + \operatorname{O}_2(g) & \Delta H^\circ = -1/2(394.1 \text{ kJ}) \\ & \operatorname{ClF}(g) + \operatorname{F}_2(g) \to \operatorname{ClF}_3(l) & \Delta H^\circ_{rm} = -135.1 \text{ kJ} \end{array}$ 

$$\begin{array}{l} 6.92 \quad \text{a) } AgNO_{3}(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_{3}(aq) \\ \text{Moles } AgNO_{3} = (50.0 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{5.0 \text{ g } AgNO_{3}}{1 \text{ L}} \right) \left( \frac{1 \text{ mol } AgNO_{3}}{169.9 \text{ g } AgNO_{3}} \right) \\ \quad = 1.47145 \text{ x } 10^{-3} \text{ mol } AgNO_{5} (unrounded) \\ \text{Moles } NaI = (50.0 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{5.0 \text{ g } NaI}{1 \text{ L}} \right) \left( \frac{1 \text{ mol } NaI}{149.9 \text{ g } NaI} \right) \\ \quad = 1.667785 \text{ x } 10^{-3} \text{ mol } NaI (unrounded) \\ \text{The } AgNO_{3} \text{ is limiting, and will be used to finish the problem:} \\ \text{Grams } AgI = (1.47145 \text{ x } 10^{-3} \text{ mol } AgNO_{5}) (1 \text{ mol } AgI / 1 \text{ mol } AgNO_{3}) (234.8 \text{ g } AgI / 1 \text{ mol } AgI) \\ \quad = 0.345496 = 0.35 \text{ g } \text{ AgI} \\ \text{b) } Ag^{2}(aq) + \Gamma(aq) \rightarrow AgI(s) \\ \Delta H^{2}_{am} = 1 \text{ mol } (AH^{2}_{\gamma}, AgI(s)) - 1 \text{ mol } (\Delta H^{2}_{\gamma}, Ag^{2}(aq)) - 1 \text{ mol } (\Delta H^{2}_{\gamma}, \Gamma(aq)) \\ \quad = 1 \text{ mol } (A2238 \text{ J/mol}) - 1 \text{ mol } (105.9 \text{ kJ/mol}) - 1 \text{ mol } (55.94 \text{ kJ/mol}) \\ \quad = -112.3 \text{ kJ} \\ \text{c) } \Delta H^{a}_{am} = \text{Cm}\Delta T \\ \Delta T = \Delta H^{a}_{am} / \text{ Cm} = \frac{\left[ \left( \frac{112.3 \text{ kJ}}{1 \text{ mol } AgI} \right) \left( \frac{1 \text{ mol } AgI}{1 \text{ mol } AgIO_{3}} \right) \left( (1.47145 \text{ x } 10^{-3} \text{ mol } AgNO_{3}) \right) \right] \\ \quad = 0.39494 = 0.39 \text{ K} \\ 6.93 \qquad a) \left( \frac{1 \text{ cal}}{g^{\circ} \text{ C}} \right) \left( \frac{45.36 \text{ g}}{1 \text{ lb}} \right) \left( \frac{10^{\circ} \text{ C}}{1.8^{\circ} \text{ F}} \right) \left( \frac{1054.368 \text{ J}}{1 \text{ ten}} \right) = 1.054.368 \text{ mol } -1.1 \text{ x } 10^{8} \text{ J} \text{ Bu} \\ \text{b) } E = (1.00 \text{ term}) \left( \frac{100,000 \text{ Btu}}{1 \text{ term}} \right) \left( \frac{1054.368 \text{ J}}{10^{3}} \right) = 1.054.368 \text{ x } 10^{8} \text{ = 1.1 x } 10^{8} \text{ J} \text{ C} 2(g)) \\ \Delta H^{a}_{am} = 1 \text{ mol } (AH^{2}_{\gamma} \text{ C}_{2}(g) + 2 \text{ Or}_{2}(g) \text{ Or}_{2}(g) + 2 \text{ Or}_{2}(G) \text{ Or}_{2}(g) + 2 \text{ Or}_{2}(G) + 2 \text{ Or}_{2}(g) +$$

e) Cost = 
$$(308 \text{ gal}) \left(\frac{3.78 \text{ L}}{1 \text{ gal}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) \left(\frac{1.0 \text{ g}}{\text{mL}}\right) \left(\frac{4.184 \text{ J}}{\text{g}^{\circ}\text{C}}\right) ((40.0 - 15.0)^{\circ}\text{C}) \left(\frac{1 \text{ therm}}{1.054368 \text{ x } 10^{8} \text{ J}}\right) \left(\frac{\$0.46}{1 \text{ therm}}\right) = 0.5313 = \$ 0.53$$

6.94 a) Mass = 
$$(5,600 \text{ EJ})\left(\frac{10^{18} \text{ J}}{1 \text{ EJ}}\right)\left(\frac{1 \text{ kJ}}{10^{3} \text{ J}}\right)\left(\frac{1 \text{ mol } \text{CH}_{4}}{802 \text{ kJ}}\right)\left(\frac{16.04 \text{ g } \text{CH}_{4}}{1 \text{ mol } \text{CH}_{4}}\right)\left(\frac{1 \text{ kg}}{10^{3} \text{ g}}\right) = 1.12 \text{ x } 10^{14} \text{ kg } \text{CH}_{4}$$
  
b) Years =  $(5,600 \text{ EJ})\left(\frac{1 \text{ year}}{4.0 \text{ x } 10^{2} \text{ EJ}}\right) = 14 \text{ years}$   
c) Moles CH<sub>4</sub> =  $(1.00 \text{ qt})\left(\frac{1 \text{ L}}{1.057 \text{ qt}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1.00 \text{ g}}{\text{mL}}\right)\left(\frac{4.184 \text{ J}}{\text{g}^{\circ}\text{C}}\right)\left((100.0 - 20.0)^{\circ}\text{C}\right)\left(\frac{1 \text{ kJ}}{10^{3} \text{ J}}\right)\left(\frac{1 \text{ mol } \text{CH}_{4}}{802 \text{ kJ}}\right)$   
= 0.394850 mol CH<sub>4</sub> (unrounded)  
Volume =  $(0.394850 \text{ mol } \text{CH}_{4})\left(\frac{16.04 \text{ g } \text{CH}_{4}}{1 \text{ mol } \text{CH}_{4}}\right)\left(\frac{1 \text{ L}}{0.72 \text{ g } \text{CH}_{4}}\right)\left(\frac{10^{-3} \text{ m}^{3}}{1 \text{ L}}\right)\left(\frac{35.3 \text{ ft}^{3}}{1 \text{ m}^{3}}\right)$   
= 0.310512 = **0.31 ft^{3}**  
d) Volume =  $(2 \text{ x } 10^{13} \text{ J})\left(\frac{1 \text{ kJ}}{10^{3} \text{ J}}\right)\left(\frac{1 \text{ mol } \text{CH}_{4}}{802 \text{ kJ}}\right)\left(\frac{16.04 \text{ g } \text{CH}_{4}}{1 \text{ mol } \text{CH}_{4}}\right)\left(\frac{1 \text{ L}}{0.72 \text{ g } \text{CH}_{4}}\right)\left(\frac{10^{-3} \text{ m}^{3}}{1 \text{ L}}\right)\left(\frac{35.3 \text{ ft}^{3}}{1 \text{ m}^{3}}\right)$   
= 1.9611 x 10^{7} = **2 x 10^{7} \text{ ft}^{3}**

6.95 Chemical equations can be written that describe the three processes. Assume one mole of each substance of interest so that units are expressed as kJ.

$$C(\text{graphite}) + 2 \text{ H}_{2}(g) \rightarrow C\text{H}_{4}(g) \qquad \Delta H_{f}^{\circ} = \Delta H_{rxn}^{\circ} = -74.9 \text{ kJ}$$
(1)  

$$C\text{H}_{4}(g) \rightarrow C(g) + 4 \text{ H}(g) \qquad \Delta H^{\circ}_{\text{atom}} = \Delta H_{rxn}^{\circ} = 1660 \text{ kJ}$$
(2)  

$$H_{2}(g) \rightarrow 2 \text{ H}(g) \qquad \Delta H^{\circ}_{\text{atom}} = \Delta H_{rxn}^{\circ} = 432 \text{ kJ}$$
(3)

The third equation is reversed and its coefficients are multiplied by 2 to add the three equations.

$$C(\text{graphite}) + \frac{2 H_2(g)}{2 H_2(g)} \rightarrow CH_4(g) \qquad \Delta H^\circ_{rxn} = -74.9 \text{ kJ}$$

$$CH_4(g) \rightarrow C(g) + 4 H(g) \qquad \Delta H^\circ_{rxn} = 1660 \text{ kJ}$$

$$4 H(g) \rightarrow 2 H_2(g) \qquad \Delta H^\circ_{rxn} = -864 \text{ kJ}$$

$$C(\text{graphite}) \rightarrow C(g) \qquad \Delta H^\circ_{rxn} = \Delta H^\circ_{\text{atom}} = 721.1 = 721 \text{ kJ per one mol C(graphite)}$$

- 6.96 **Exothermic**, the argon atoms in the chamber after the reaction are moving with greater kinetic energy, indicating an increase in temperature.
- 6.97 a) No heat is transferred; work is done on the system.
  - b) No work is done; heat is transferred out of the system.
  - c) Heat is transferred out of the system; work is done on the system.
  - d) Heat is transferred into the system; no work is done.
  - e) Heat is transferred into the system; no work is done.
- 6.98 According to Chemical Connections, sodium sulfate decahydrate will transfer 354 kJ/mol.

Heat = 
$$(500.0 \text{ kg } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}{322.21 \text{ g } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}\right) \left(\frac{-354 \text{ kJ}}{1 \text{ mol } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}\right)$$
  
= -5.4933 x 10<sup>5</sup> = -5.49 x 10<sup>5</sup> kJ

6.99 Write balanced chemical equations for the combustion reactions and use the standard heats of formation to determine the energy released.

 $C_6H_6(g) + 7/2 O_2(g) \rightarrow 6 CO_2(g) + 3 H_2O(g)$ 

 $\Delta H_{rm}^{o} = [6 \text{ mol } (\Delta H_{f}^{o} \text{ CO}_{2}(g)) + 3 \text{ mol } (\Delta H_{f}^{o} \text{ H}_{2}\text{O}(g)) - 1 \text{ mol } (\Delta H_{f}^{o} \text{ C}_{6}\text{H}_{6}(g)) - 7/2 \text{ mol } (\Delta H_{f}^{o} \text{ O}_{2}(g))](1 \text{ mol } \text{ C}_{6}\text{H}_{6}/6 \text{ mol } \text{ CH})$  $\Delta H_{rm}^{o}$ 

= 
$$[6 \text{ mol} (-393.5 \text{ kJ/mol}) + 3 \text{ mol} (-241.826 \text{ kJ/mol}) - 1 \text{ mol} (82.9 \text{kJ/mol}) - 7/2 \text{ mol} (0.0)] (1 \text{ mol} C_6 H_6/6 \text{ mol} CH)$$
  
=  $-528.2297 = -528.2 \text{ kJ/mol} CH$ 

$$\begin{split} & C_{2}H_{2}(g) + 5/2 \ O_{2}(g) \to 2 \ CO_{2}(g) + H_{2}O(g) \\ & \Delta H_{am}^{\circ} = \\ & [2 \ \mathrm{mol}(\Delta H_{f}^{\circ} \ \mathrm{CO}_{2}(g)) + 1 \ \mathrm{mol}(\Delta H_{f}^{\circ} \ \mathrm{H}_{2}O(g)) - 1 \ \mathrm{mol}(\Delta H_{f}^{\circ} \ \mathrm{C}_{2}H_{2}(g)) - 5/2 \ \mathrm{mol}(\Delta H_{f}^{\circ} \ \mathrm{O}_{2}(g))](1 \ \mathrm{mol} \ \mathrm{C}_{6}H_{6}/2 \ \mathrm{mol} \ \mathrm{CH}) \\ & \Delta H_{cm}^{\circ} = [2 \ \mathrm{mol}(-393.5 \ \mathrm{kJ/mol}) + 1 \ \mathrm{mol}(-241.826 \ \mathrm{kJ/mol}) \\ & - 1 \ \mathrm{mol}(227 \mathrm{kJ/mol}) - 5/2 \ \mathrm{mol}(0.0)] (1 \ \mathrm{mol} \ \mathrm{C}_{6}H_{6}/2 \ \mathrm{mol} \ \mathrm{CH}) \\ & = -627.913 = -628 \ \mathrm{kJ} \ / \ \mathrm{mol} \ \mathrm{CH} \\ & \text{Thus, acetylene releases more energy per \ \mathrm{CH} \ \mathrm{than} \ \mathrm{does \ benzene.} \end{split}$$
6.100 a) 2 C\_{12}H\_{26}(l) + 37 \ \mathrm{O}\_{2}(g) \rightarrow 24 \ \mathrm{CO}\_{2}(g) + 26 \ \mathrm{H}\_{2}O(g) \\ & b) \ \Delta H\_{cm}^{\circ} = 24 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{CO}\_{2}(g)) + 26 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{H}\_{2}O(g)) - 2 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{C}\_{12}H\_{26}(g)) - 37 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{O}\_{2}(g)) \\ & -1.50 \ \mathrm{x} \ 10^{4} \mathrm{kJ} = 24 \ \mathrm{mol}(-393.5 \ \mathrm{kJ/mol}) + 26 \ \mathrm{mol}(-241.826 \ \mathrm{kJ/mol}) - 2 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{C}\_{12}H\_{26}(g)) - 37 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{C}\_{12}H\_{26}(g)) \\ & -1.50 \ \mathrm{x} \ 10^{4} \mathrm{kJ} = -9444.0 \ \mathrm{kJ} + -6287.476 \ \mathrm{kJ} - 2 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{C}\_{12}H\_{26}(g)) - 0.0 \ \mathrm{kJ} \\ & -1.50 \ \mathrm{x} \ 10^{4} \mathrm{kJ} = -15731.476 \ \mathrm{kJ} - 2 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{C}\_{12}H\_{26}(g)) \\ & -1.50 \ \mathrm{x} \ 10^{4} \mathrm{kJ} = -15731.476 \ \mathrm{kJ} - 2 \ \mathrm{mol}(\Delta H\_{f}^{\circ} \ \mathrm{C}\_{12}H\_{26}(g)) \\ & \Delta H\_{f}^{\circ} \ \mathrm{C}\_{12}H\_{26}(g) = -365.738 = -4 \ \mathrm{x} \ 10^{2} \ \mathrm{kJ} \ \mathrm{mol} \\ \ \mathrm{The \ heat \ of \ combustion \ value \ given \ in \ the \ problem \ limits \ the \ significant \ figures \ to \ hundreds \ of \ \mathrm{kilojoules.} \\ & \mathrm{c}) \ E = (0.50 \ \mathrm{gal}) \left( \frac{4 \ \mathrm{qt}}{1 \ \mathrm{gal}} \right) \left( \frac{1 \ \mathrm{mL}}{10^{-7} \ \mathrm{qt}} \right) \left( \frac{0.749 \ \mathrm{g} \ \mathrm{C}\_{12}H\_{26}}{\mathrm{mL}} \right) \left( \frac{1 \ \mathrm{mol} \ \mathrm{C}\_{12}H\_{26}}{\mathrm{mol} \ \mathrm{mol} \ \mathrm{C}\_{12}H\_{26}} \right) \left( \frac{-1.50 \ \mathrm{x} \ 10^{4} \ \mathrm{kJ}}{2 \ \mathrm{mol} \ \mathrm{C}\_{12}H\_{26}} \right) \\ & = -6.2403 \ \mathrm{x} \ 10^{4} \ \mathrm{sJ} = 6.2 \ \mathrm{x} \ 10^{4} \ \mathrm{kJ} \ \mathrm{sJ} = 0.0105

6.101 The values for the heats of reaction are either given in the problem or in the Chemical Connections.

a) 1) 
$$C(coal) + H_2O(g) \rightarrow CO(g) + H_2(g)$$
  $\Delta H^o_{rxn} = 129.7 \text{ kJ}$   
2)  $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$   $\Delta H^o_{rxn} = -41 \text{ kJ}$   
3)  $CO(g) + 3 H_2(g) \rightarrow CH_4(g) + H_2O(g)$   $\Delta H^o_{rxn} = -206 \text{ kJ}$   
Equation 1) must be multiplied by 2, then the reactions sum to:

 $2 \operatorname{C}(\operatorname{coal}) + 2 \operatorname{H}_2\operatorname{O}(g) \to \operatorname{CH}_4(g) + \operatorname{CO}_2(g)$ b) The total may be determined by doubling the value for equation 1) and adding to the other two values.  $\Delta H_{ran}^{o} = 2(129.7 \text{ kJ}) + (-41 \text{ kJ}) + (-206 \text{ kJ}) = 12.4 = 12 \text{ kJ}$ 

c) Calculating the heat of combustion of CH<sub>4</sub>:

$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g)$$

$$\Delta H^{\circ}_{\text{comb}} = 1 \mod \left( \Delta H^{\circ}_{f} \operatorname{CO}_{2}(g) \right) + 2 \mod \left( \Delta H^{\circ}_{f} \operatorname{H}_{2} \operatorname{O}(g) \right) - 1 \mod \left( \Delta H^{\circ}_{f} \operatorname{CH}_{4}(g) \right) - 2 \mod \left( \Delta H^{\circ}_{f} \operatorname{O}_{2}(g) \right)$$

$$\Delta H^{\circ}_{\text{comb}} = 1 \mod (-395.5 \text{ kJ/mol}) + 2 \mod (-241.826 \text{ kJ/mol}) - 1 \mod (-74.87 \text{kJ/mol}) - 2 \mod (0.0 \text{ kJ/mol}) = -804.282 \text{ kJ/mol} \text{ CH}_4 \text{ (unrounded)}$$

Total heat for gasification of 1.00 kg coal:

$$\Delta H^{\circ} = (1.00 \text{ kg Coal}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol Coal}}{12.00 \text{ g Coal}}\right) \left(\frac{12.4 \text{ kJ}}{2 \text{ mol Coal}}\right) = 516.667 \text{ kJ (unrounded)}$$

Total heat from burning the methane formed from 1.00 kg of coal:

$$\Delta H^{\circ} = (1.00 \text{ kg Coal}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol Coal}}{12.00 \text{ g Coal}}\right) \left(\frac{1 \text{ mol CH}_4}{2 \text{ mol Coal}}\right) \left(\frac{-804.282 \text{ kJ}}{1 \text{ mol CH}_4}\right)$$

= -33511.75 kJ (unrounded)

Total heat = 516.667 kJ -33511.75 kJ = 32995.083 = **3.30 x 10<sup>4</sup> kJ** 

| 6.102 |       | $PCl_3(g) \rightarrow 1/4 P_4(s) + 3/2 Cl_2(g)$                               | $\Delta H = -1/4(-1280 \text{ kJ})$                                       |
|-------|-------|-------------------------------------------------------------------------------|---------------------------------------------------------------------------|
|       |       | $1/4 P_4(s) + 5/2 \operatorname{Cl}_2(g) \rightarrow \operatorname{PCl}_5(g)$ | $\Delta H = 1/4(-1774 \text{ kJ})$                                        |
| Т     | otal: | $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$                                     | $\Delta H = 320 \text{ kJ} - 443.5 \text{ kJ} = -123.5 = -124 \text{ kJ}$ |

6.103 Combustion reactions can be written and  $\Delta H_{ran}^o$  can be calculated for each hydrocarbon.

I)  $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g)$   $\Delta H_{ran}^o = (-393.5) + 2 (-241.826) - (-74.87) - 2 (0.0) = -802.282 = -802.3 \text{ kJ per mol } CH_4(g)$ II)  $C_2H_4(g) + 3 O_2(g) \rightarrow 2 CO_2(g) + 2 H_2O(g)$   $\Delta H_{ran}^o = 2 (-393.5) + 2 (-241.826) - (52.47) - 3 (0.0) = -1323.122 = -1323.1 \text{ kJ per mol } C_2H_4(g)$ III)  $C_2H_6(g) + 7/2 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(g)$   $\Delta H_{ran}^o = 2 (-393.5) + 3 (-241.826) - (-84.667) - 7/2 (0.0) = -1427.811 = -1427.8 \text{ kJ per mol } C_2H_6(g)$ a) A negative enthalpy change denotes an exothermic reaction, so the combustion of  $C_2H_6(g)$  yields the most heat, followed by  $C_2H_4(g)$  and  $CH_4(g)$ ; III > II > I.

b) Use molecular weights to convert kJ/mol to kJ/g.

I) 
$$\left(\frac{-802.282 \text{ kJ}}{1 \text{ mol } \text{CH}_4}\right) \left(\frac{1 \text{ mol } \text{CH}_4}{16.04 \text{ g } \text{CH}_4}\right) = -50.01758 = -50.02 \text{ kJ/g } \text{CH}_4$$
  
II)  $\left(\frac{-1323.122 \text{ kJ}}{1 \text{ mol } \text{C}_2\text{H}_4}\right) \left(\frac{1 \text{ mol } \text{C}_2\text{H}_4}{28.05 \text{ g } \text{C}_2\text{H}_4}\right) = -47.1701 = -47.17 \text{ kJ/g } \text{C}_2\text{H}_4$   
III)  $\left(\frac{-1427.811 \text{ kJ}}{1 \text{ mol } \text{C}_2\text{H}_6}\right) \left(\frac{1 \text{ mol } \text{C}_2\text{H}_6}{30.07 \text{ g } \text{C}_2\text{H}_6}\right) = -47.4829 = -47.48 \text{ kJ/g } \text{C}_2\text{H}_4$ 

On a per mass basis, CH<sub>4</sub> yields more heat followed by  $C_2H_6(g)$  and  $C_2H_4(g)$ ; I > III > II.

6.104 a) 
$$E = (2 \text{ oz}) \left(\frac{28.4 \text{ g}}{1.00 \text{ oz}}\right) \left(\frac{4.0 \text{ Cal}}{1.0 \text{ g}}\right) \left(\frac{1 \text{ kcal}}{1 \text{ Cal}}\right) \left(\frac{4.184 \text{ kJ}}{1 \text{ kcal}}\right) = 950.60 = 1 \text{ x } 10^3 \text{ kJ}$$
  
b)  $E = \text{mgh}$   
 $h = E / \text{mg} = \frac{(950.60 \text{ kJ})}{(58 \text{ kg})(9.8 \text{ m/s}^2)} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}}\right) = 1672.41 = 2 \text{ x } 10^3 \text{ m}$ 

c) Energy is also converted to heat.

6.105 a) The heat of reaction is calculated from the heats of formation found in Appendix B. The  $\Delta H_f^{\circ}$ 's for all of the species, except SiCl<sub>4</sub>, are found in Appendix B. Use reaction 3, with its given  $\Delta H_{ran}^{\circ}$ , to find  $\Delta H_f^{\circ}$  [SiCl<sub>4</sub>(g)].  $\Delta H_{ran}^{\circ} = \Delta H_f^{\circ}$  [SiO<sub>2</sub>(s)] + 4  $\Delta H_f^{\circ}$  [HCl(g)] - [ $\Delta H_f^{\circ}$  [SiCl<sub>4</sub>(g)] + 2  $\Delta H_f^{\circ}$  [H<sub>2</sub>O(g)]]

$$-139.5 \text{ kJ} = (-910.9 \text{ kJ}) + 4(-92.31 \text{ kJ}) - \Delta H_{f}^{\circ} [\text{SiCl}_{4}(g)] - 2(-241.826 \text{ kJ})$$

 $\Delta H_f^o$  [SiCl<sub>4</sub>(g)] = -656.988 kJ/mol (unrounded)

The heats of reaction for the first two steps can now be calculated.  $\Delta H^{\circ}_{rxn1} = \Delta H^{\circ}_{f} [SiCl_{4}(g)] - \Delta H^{\circ}_{f} [Si(s)] + 2 \Delta H^{\circ}_{f} [Cl_{2}(g)]$   $\Delta H^{\circ}_{rxn1} = -656.988 \text{ kJ} - 0 - 2(0) = -656.988 = -657.0 \text{ kJ}$   $\Delta H^{\circ}_{rxn2} = \Delta H^{\circ}_{f} [SiCl_{4}(g)] + 2 \Delta H^{\circ}_{f} [CO(g)] - \Delta H^{\circ}_{f} [SiO_{2}(g)] - 2 \Delta H^{\circ}_{f} [C(gr)] - 2 \Delta H^{\circ}_{f} [Cl_{2}(g)]$   $\Delta H^{\circ}_{rxn2} = -656.988 \text{ kJ} + 2(-110.5 \text{ kJ}) - (-910.9 \text{ kJ}) - 2(0) - 2(0) = 32.912 = 32.9 \text{ kJ}$ b) Adding reactions 2 and 3 yield: 2 C(gr) + 2 Cl\_{2}(g) + 2 H\_{2}O(g) \rightarrow 2 CO(g) + 4 HCl(g)  $\Delta H^{\circ}_{rxn2+3} = 32.912 \text{ kJ} + (-139.5 \text{ kJ}) = -106.588 = -106.6 \text{ kJ}$ Confirm this result by calculating  $\Delta H^{\circ}_{rxn}$  using Appendix B values.  $\Delta H^{\circ}_{rxn2+3} = 2 \Delta H^{\circ}_{f} [CO(g)] + 4 \Delta H^{\circ}_{f} [HCl(g)] - 2 \Delta H^{\circ}_{f} [C(gr)] - 2 \Delta H^{\circ}_{f} [Cl_{2}(g)] - 2 \Delta H^{\circ}_{f} [H_{2}O(g)]$   $\Delta H^{\circ}_{rxn2+3} = 2(-110.5 \text{ kJ}) + 4(-92.31 \text{ kJ}) - 2(0) - 2(0) - 2(-241.826 \text{ kJ}) = -106.588 = -106.6 \text{ kJ}$ 

6.106 This is a Hess's Law problem with the following equations given:  
1) N<sub>3</sub>(g) + 3 H<sub>3</sub>(g) → 2 NH<sub>4</sub>(g) ΔH<sup>\*</sup><sub>cm</sub> = -91.8 kJ  
2) N<sub>4</sub>(g) + 4 H<sub>3</sub>(g) + Cl<sub>3</sub>(g) → 2 NH<sub>4</sub>(g) ΔH<sup>\*</sup><sub>cm</sub> = -91.8 kJ  
2) N<sub>4</sub>(g) + 4 H<sub>3</sub>(g) + Cl<sub>3</sub>(g) → 2 NH<sub>4</sub>(g) ΔH<sup>\*</sup><sub>cm</sub> = -76.8 kJ  
3) NH<sub>3</sub>(g) + HCl<sub>3</sub>(g) → NH<sub>4</sub>(ls) ΔH<sup>\*</sup><sub>cm</sub> = -76.8 kJ  
3) NH<sub>3</sub>(g) + HCl<sub>3</sub>(g) + NH<sub>4</sub>(ls) ΔH<sup>\*</sup><sub>cm</sub> = 172 (91.8 kJ)  
2) 1/2 N<sub>5</sub>(g) + 2 H<sub>3</sub>(g) + 12 Cl<sub>3</sub>(g) → NH<sub>4</sub>(ls) ΔH<sup>\*</sup><sub>cm</sub> = 172 (91.8 kJ)  
2) 1/2 N<sub>5</sub>(g) + 2 H<sub>3</sub>(g) + 12 Cl<sub>3</sub>(g) → NH<sub>4</sub>(ls) ΔH<sup>\*</sup><sub>cm</sub> = 172.2 (628.8 kJ)  
3) NH<sub>4</sub>(Cl<sub>3</sub>) → NH<sub>3</sub>(g) + HCl<sub>3</sub>(g) ΔH<sup>\*</sup><sub>cm</sub> = 172.2 kJ  
The new equations and enthalpy changes add to:  
1/2 H<sub>3</sub>(g) + 1/2 Cl<sub>3</sub>(g) → HCl<sub>3</sub>(g) ΔH<sup>\*</sup><sub>cm</sub> = 172.2 kJ  
6.107 a) -q<sub>rec</sub> = q<sub>setes</sub> + q<sub>caterimeter</sub>  
-q<sub>rec</sub> = 
$$\left(50.0 \text{ nL} \left(\frac{104}{1 \text{ nL}}\right) \left(\frac{200 \text{ mol}}{L} \left(\frac{-57.32 \text{ kJ}}{\text{ mol}}\right) = 5.732 \text{ kJ}$$
 (unrounded)  
q<sub>setes</sub> =  $\left[100.0 \text{ nL} \left(\frac{104 \text{ g}}{1 \text{ mL}}\right) \left(\frac{3.93 \frac{1}{g^{*}\text{ C}}}{L} \right) ((30.4 - 16.9)^{\circ}\text{C} \left(\frac{1 \text{ kJ}}{10^{1} \text{ J}}\right) = 5.51772 \text{ kJ}$  (unrounded)  
q<sub>setesminet</sub> - q<sub>setes</sub> = q<sub>caterimeter</sub>  
-q<sub>rec</sub> =  $\left[100.0 \text{ mL} \left(\frac{104 \text{ g}}{1 \text{ mL}}\right) \left(\frac{1.00 \text{ mol} \text{ HCl}}{1 \text{ mL}}\right) = 0.100 \text{ mol HCl}$   
b) Mole HCl =  $(100.0 \text{ mL} \left(\frac{10^{1}{1 \text{ mL}}}{1 \text{ mL}}\right) \left(\frac{1.00 \text{ mol} \text{ HCl}}{1 \text{ mOl} \text{ mOl}}\right) = 0.02000 \text{ mol Zn}$   
Zn is the limiting reactant:  
-  $\frac{q_{rec}}{q_{setesminet}} q_{setesminet}$   
=  $\left[100.0 \text{ mL} \left(\frac{100^{1}{2} \text{ L}}{1 \text{ mL}}\right) + 1.3078 \text{ g} \right] \left(\frac{3.95 \frac{1}{g^{\circ}\text{C}}}{g^{\circ}\text{C}}\right) ((24.1 - 16.8)^{\circ}\text{C} \left(\frac{1 \text{ kJ}}{10^{3}}\right) + \left(0.01587 \frac{\text{ kJ}}{2}\right) ((24.1 - 16.8)^{\circ}\text{C} \right) - 3.0803 \text{ kJ} (unrounded)$   
 $AH^*_{rec} = (3.0803 \text{ kJ}) / (0.02000 \text{ mol Zn}) = -154.0 = -15 \text{ x 10^{2} \text{ kJ/mol}$   
() Zn(s) + 2 HCl(aq) → ZnCl<sub>3</sub>(aq) + H<sub>4</sub>(g) → 1 \text{ mol} (0.0 \text{ kJ/mol}) + 1 \text{ mol} (0.0 \text{ kJ/mol}) + 2 \text{ mol} (-1.652 \text{ x 10^{2} \text{ kJ/mol})  
 $AH^*_{rec} = 1 \text{ mol} (-4.122 \text{ x 10^{2} \text{ kJ/mol}) + 1 \text{ mol} (0.0 \text{ kJ/mol}) + 2 \text{ mol} (-1.652 \text{ x 10^{2} \text{ kJ/mol})$   

6.109 Only reaction 3 contains  $N_2O_4(g)$ , and only reaction 1 contains  $N_2O_3(g)$ , so we can use those reactions as a starting point.  $N_2O_5$  appears in both reactions 2 and 5, but note the physical states present: solid and gas. As a rough start, adding reactions 1, 3, and 5 yield the desired reactants and products, with some undesired intermediates:

| (Reverse 1) | $N_2O_3(g)$                | $\rightarrow \mathrm{NO}(g) + \mathrm{NO}_2(g)$ | $\Delta H^{\circ}_{rxn1} = 39.8 \text{ kJ}$       |
|-------------|----------------------------|-------------------------------------------------|---------------------------------------------------|
| (Twice 3)   | $4 \operatorname{NO}_2(g)$ | $\rightarrow 2 \text{ N}_2\text{O}_4(g)$        | $\Delta H^{\circ}_{\rm rxn3} = -114.4 \text{ kJ}$ |
| (Reverse 5) | $N_2O_5(s)$                | $\rightarrow N_2O_5(g)$                         | $\Delta H^{\circ}_{rxn5} = 54.1 \text{ kJ}$       |

To cancel out the  $N_2O_5(g)$  intermediate, reverse equation 2. This also cancels out some of the undesired  $NO_2(g)$  but adds NO(g) and  $O_2(g)$ . Finally, add equation 4 to remove those intermediates:

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|---------------------------------------|-----------------------------------|---------------------------------------------------------------------------------------------------|---------------------------------------------------|
| (Reverse 1)                           | $N_2O_3(g)$                       | $\rightarrow \frac{\mathrm{NO}(g)}{\mathrm{NO}_2(g)} + \frac{\mathrm{NO}_2(g)}{\mathrm{NO}_2(g)}$ | $\Delta H^{\circ}_{rxn1} = 39.8 \text{ kJ}$       |
| (Twice 3)                             | 4 NO <sub>2</sub> (g)             | $\rightarrow 2 \text{ N}_2\text{O}_4(g)$                                                          | $\Delta H^{\circ}_{\rm rxn3} = -114.4 \text{ kJ}$ |
| (Reverse 5)                           | $N_2O_5(s)$                       | $\rightarrow N_2 \Theta_5(g)$                                                                     | $\Delta H^{\circ}_{\rm rxn5} = 54.1 \text{ kJ}$   |
| (Reverse 2)                           | $N_2O_5(g)$                       | $\rightarrow \mathrm{NO}(g) + \mathrm{NO}_2(g) + \mathrm{O}_2(g)$                                 | $\Delta H^{\circ}_{\rm rxn2} = 112.5 \text{ kJ}$  |
| (4)                                   | <del>2 NO(g)</del> + <del>C</del> | $\Theta_2(g) \rightarrow 2 \operatorname{NO}_2(g)$                                                | $\Delta H^{\circ}_{\rm rxn4} = -114.2 \text{ kJ}$ |
| Total:                                | $N_2O_3(g) + N_2$                 | $_{2}O_{5}(s) \rightarrow 2 N_{2}O_{4}(g)$                                                        | $\Delta H_{rxn}^{o} = -22.2 \text{ kJ}$           |
|                                       |                                   |                                                                                                   |                                                   |

6.110 a) 
$$\Delta H_{rsn}^{\circ} = \Delta H_{f}^{\circ} [N_{2}H_{4}(aq)] + \Delta H_{f}^{\circ} [NaCl(aq)] + \Delta H_{f}^{\circ} [H_{2}O(l)] - 2\Delta H_{f}^{\circ} [NH_{3}(aq)] - \Delta H_{f}^{\circ} [NaOCl(aq)]$$
  
Note that the Appendix B value for N<sub>2</sub>H<sub>4</sub> is for the liquid state, so this term must be calculated. In addition, Appendix B does not list a value for NaCl(aq), so this term must be broken down into

 $\Delta H_{f}^{\circ}$  [Na<sup>+</sup>(*aq*)] and  $\Delta H_{f}^{\circ}$  [Cl<sup>-</sup>(*aq*)].

$$-151 \text{ kJ} = \Delta H_f^{\circ} [\text{N}_2\text{H}_4(aq)] + (-239.66 \text{ kJ}) + (-167.46 \text{ kJ}) + (-285.840 \text{ kJ}) - 2(-80.83 \text{ kJ}) - (-346 \text{ kJ})$$

 $\Delta H_{f}^{\circ}$  [N<sub>2</sub>H<sub>4</sub>(*aq*)] = 34.3 = **34 kJ/mol** 

b) Determine the moles of O<sub>2</sub> present, and then multiply by the  $\Delta H_{rxn}^{o}$  for the first reaction. Moles of O<sub>2</sub> = (5.00 x 10<sup>3</sup> L) (2.50 x 10<sup>-4</sup> mol/L) = 1.25 mol O<sub>2</sub>  $\Delta H_{rxn}^{o} = \Delta H_{f}^{o} [N_{2}(g)] + 2 \Delta H_{f}^{o} [H_{2}O(l)] - \Delta H_{f}^{o} [N_{2}H_{4}(aq)] - \Delta H_{f}^{o} [O_{2}(g)]$   $\Delta H_{rxn}^{o} = 0 + 2(-285.840 \text{ kJ}) - (34.3 \text{ kJ}) - 0 = -605.98 \text{ kJ /mol O}_{2}$  (unrounded) Heat = (-605.98 kJ /mol O<sub>2</sub>) (1.25 mol O<sub>2</sub>) = -757.475 = -757 kJ

6.111 
$$\operatorname{CO}(g) + 2 \operatorname{H}_2(g) \rightarrow \operatorname{CH}_3\operatorname{OH}(l)$$

 $\Delta H_{ran}^{o} = 1 \mod \left( \Delta H_{f}^{o} \operatorname{CH}_{3} \operatorname{OH}(l) \right) - 1 \mod \left( \Delta H_{f}^{o} \operatorname{CO}(g) \right) - 2 \mod \left( \Delta H_{f}^{o} \operatorname{H}_{2}(g) \right)$  $\Delta H_{ran}^{o} = 1 \mod \left( -238.6 \text{ kJ/mol} \right) - 1 \mod \left( -110.5 \text{ kJ mol} \right) - 2 \mod \left( 0.0 \text{ kJ/mol} \right)$ = -128.1 kJFind the limiting reactant:

$$Moles CO = PV / RT = \frac{(112 \text{ kPa})(15.0 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \left((273 + 85)\text{K}\right)} \left(\frac{1 \text{ atm}}{101.325 \text{ kPa}}\right)$$
  
= 0.56411 mol CO (unrounded)  
$$Moles H_2 = PV / RT = \frac{(744 \text{ torr})(18.5 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \left((273 + 75)\text{K}\right)} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right)$$

 $= 0.633882 \text{ mol } H_2 \text{ (unrounded)}$ 

H<sub>2</sub> is limiting

$$\Delta E = (0.633882 \text{ mol } \text{H}_2) \left( \frac{-128.1 \text{ kJ}}{2 \text{ mol } \text{H}_2} \right) = -40.6001 = -40.6 \text{ kJ}$$

6.112 a) The balanced chemical equation for this reaction is  $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g)$ 

Instead of burning one mole of methane,  $(25.0 \text{ g CH}_4) \left( \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \right) = 1.5586 \text{ mol CH}_4$  (unrounded) of methane are burned. Therefore, 1.5586 mol of CO<sub>2</sub> and 3.1172 mol of H<sub>2</sub>O form upon combustion of 25.0 g of methane.

are burned. Therefore, 1.5586 mol of CO<sub>2</sub> and 3.1172 mol of H<sub>2</sub>O form upon combustion of 25.0 g of methane.  $\Delta H_{ron}^{o} = 1.5586 \text{ mol } (-393.5 \text{ kJ/mol}) + 3.1172 \text{ mol } (-241.826 \text{ kJ/mol}) - 1.5586 \text{ mol } (-74.87 \text{ kJ/mol})$  $\Delta H_{ron}^{o} = -1250.4 = -1.25 \text{ x } 10^3 \text{ kJ}$  b) The heat released by the reaction is "stored" in the gaseous molecules by virtue of their specific heat capacities, c, using the equation  $\Delta H = \text{mc}\Delta T$ . The problem specifies heat capacities on a molar basis, so we modify the equation to use moles, instead of mass.

The gases that remain at the end of the reaction are  $CO_2$  and  $H_2O$ . All of the methane and oxygen molecules were consumed. However, the oxygen was added as a component of air, which is 78% N<sub>2</sub> and 21% O<sub>2</sub>, and there is leftover N<sub>2</sub>.

Moles of  $CO_2(g) = 1.5586$  mol Moles of  $H_2O(g) = 3.1172$  mol

Mole fraction  $N_2 = (79\% / 100\%) = 0.79$ 

Mole fraction  $O_2 = (21\% / 100\%) = 0.21$ 

Moles of  $N_2(g) = (3.1172 \text{ mol } O_2 \text{ used}) (0.79 \text{ mol } N_2 / 0.21 \text{ mol } O_2) = 11.7266 \text{ mol } N_2 \text{ (unrounded)}$ 

1250.4 kJ ( $10^3$  J/ kJ) = 1.5586 mol CO<sub>2</sub> (57.2 J / mol°C) (T<sub>f</sub> - 0.0)°C

+ 3.1172 mol H<sub>2</sub>O (36.0 J / mol°C) (T<sub>f</sub> - 0.0)°C

+ 11.7266 mol N<sub>2</sub> (30.5 J / mol $^{\circ}$ C) (T<sub>f</sub> - 0.0) $^{\circ}$ C

 $1.2504 \times 10^{6} \text{ J} = ((89.1519 + 112.2192 + 357.6613) \text{ J} /^{\circ}\text{C})\text{T}_{\text{f}} = (559.0324 \text{ J} /^{\circ}\text{C})\text{T}_{\text{f}}$ 

 $T_f = (1.2504 \text{ x } 10^6 \text{ J}) / (559.0324 \text{ J } /^{\circ}\text{C}) = 2236.72 = 2.24 \text{ x } 10^{3\circ}\text{C}$