CHAPTER 6 THERMOCHEMISTRY: ENERGY FLOW AND CHEMICAL CHANGE

END-OF-CHAPTER PROBLEMS

- 8.1 No, an increase in temperature means that heat has been transferred to the surroundings, which makes q negative.
- 6.2 $\Delta E = q + w = w$, since q = 0. Thus, the change in work equals the change in internal energy.
- 6.3 a) electric heater b) sound amplifier c) light bulb d) automobile alternator e) battery (voltaic cell)
- 6.4 Heat energy; sound energy

 Kinetic energy

 Potential energy

 Mechanical energy

 Chemical energy

 (impact)

 (falling text)

 (raised text)

 (raising of text)

 Chemical energy

 (biological process to move muscles)
- 6.5 Plan: The change in a system's energy is $\Delta E = q + w$. If the system receives heat, then its q_{final} is greater than q_{initial} so q is positive. Since the system performs work, its $w_{\text{final}} < w_{\text{initial}}$ so w is negative. Solution:

$$\frac{\Box}{\Delta E = q + w}$$

$$\Delta E = (+425 \text{ J}) + (-425 \text{ J}) = \mathbf{0} \text{ J}$$

- 6.6 q + w = -255 cal + (-428 cal) = -683 cal
- 6.7 <u>Plan:</u> Convert 6.6x10¹⁰ J to the other units using conversion factors. <u>Solution:</u>

$$C(s) + O_2(g) \rightarrow CO_2(g) + 6.6x10^{10} J$$

(2.0 tons)

a)
$$\Delta E (kJ) = (6.6 \text{ x } 10^{10} \text{ J}) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = 6.6 \text{ x} 10^7 \text{ kJ}$$

b)
$$\Delta E \text{ (kcal)} = (6.6 \text{ x } 10^{10} \text{ J}) \left(\frac{1 \text{ cal}}{4.184 \text{ J}}\right) \left(\frac{1 \text{ kcal}}{10^3 \text{ cal}}\right) = 1.577 \text{x} 10^7 = \mathbf{1.6 x} \mathbf{10}^7 \text{ kcal}$$

c)
$$\Delta E$$
 (Btu) = $(6.6 \text{ x } 10^{10} \text{ J}) \left(\frac{1 \text{ Btu}}{1055 \text{ J}} \right) = 6.256 \text{x} 10^7 = \textbf{6.3x} \textbf{10}^7 \text{ Btu}$

6.8 $CaCO_3(s) + 9.0x10^6 \text{ kJ} \rightarrow CaO(s) + CO_2(g)$ (5.0 tons)

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)
$$\Delta E$$
 (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)
$$\Delta E \text{ (Btu)} = (9.0 \times 10^6 \text{ kJ}) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) \left(\frac{1 \text{ Btu}}{1055 \text{ J}} \right) = 8.5308 \times 10^6 = 8.5 \times 10^6 \text{ Btu}$$

6.9
$$\Delta E (J) = (4.1 \times 10^{3} \text{ Calorie}) \left(\frac{10^{3} \text{ cal}}{1 \text{ Calorie}} \right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}} \right) = 1.7154 \times 10^{7} = \mathbf{1.7 \times 10^{7} J}$$
$$\Delta E (kJ) = (4.1 \times 10^{3} \text{ Calorie}) \left(\frac{10^{3} \text{ cal}}{1 \text{ Calorie}} \right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}} \right) \left(\frac{1 \text{ kJ}}{10^{3} \text{ J}} \right) = 1.7154 \times 10^{4} = \mathbf{1.7 \times 10^{4} kJ}$$

- 6.10 <u>Plan:</u> An exothermic process releases heat and an endothermic process absorbs heat. Solution:
 - 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.
- 6.11 Absolute enthalpy values, like absolute energy values, are unknown.
- 6.12 Plan: An exothermic reaction releases heat, so the reactants have greater $H(H_{\text{initial}})$ than the products (H_{final}) . $\Delta H = H_{\text{final}} H_{\text{initial}} < 0$. Solution:

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

6.13

Products
$$\Delta H = (+), \text{ (endothermic)}$$
Reactants

6.14 Plan: Combustion of hydrocarbons and related compounds require oxygen (and a heat catalyst) to yield carbon dioxide gas, water vapor, and heat. Combustion reactions are exothermic. The freezing of liquid water is an exothermic process as heat is removed from the water in the conversion from liquid to solid. An exothermic reaction or process releases heat, so the reactants have greater $H(H_{\text{initial}})$ than the products H_{final} .

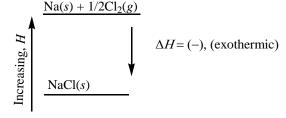
a) Combustion of ethane:
$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g) + \text{heat}$$

 $2C_2H_6 + 7O_2 \text{ (initial)}$

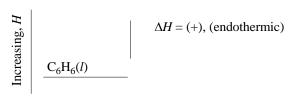
$$\begin{array}{c|c} H & \Delta H = (-), \text{ (exothermic)} \\ & \Delta H = (-), \text{ (ex$$

b) Freezing of water: $H_2O(l) \rightarrow H_2O(s) + \text{heat}$ $H_2O(l)$ (initial)

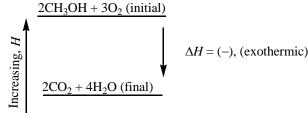
6.15 a) $Na(s) + 1/2Cl_2(g) \rightarrow NaCl(s) + heat$



b) $C_6H_6(l) + \text{heat} \rightarrow C_6H_6(g)$ $C_6H_6(g)$



- 6.16 Plan: Combustion of hydrocarbons and related compounds require oxygen (and a heat catalyst) to yield carbon dioxide gas, water vapor, and heat. Combustion reactions are exothermic. An exothermic reaction releases heat, so the reactants have greater $H(H_{\text{initial}})$ than the products (H_{final}) . If heat is absorbed, the reaction is endothermic and the products have greater $H(H_{\text{final}})$ than the reactants (H_{initial}) . Solution:
 - a) $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g) + heat$



b) Nitrogen dioxide, NO₂, forms from N₂ and O₂.

$$1/2N_2(g) + O_2(g) + \text{heat} \rightarrow NO_2(g)$$

$$\Delta H = (+)$$
, (endothermic)

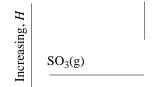
6.17 a) $CO_2(s) + heat \rightarrow CO_2(g)$ $CO_2(g)$

Hucreasing,
$$H$$
 $CO_2(s)$

 $\Delta H = (+)$, (endothermic)

b)
$$SO_2(g) + 1/2O_2(g) \rightarrow SO_3(g) + heat$$

 $SO_2(g) + 1/2O_2(g)$



 $\Delta H = (-)$, (exothermic)

- 6.18 Plan: Recall that $q_{\rm sys}$ is positive if heat is absorbed by the system (endothermic) and negative if heat is released by the system (exothermic). Since $\Delta E = q + w$, the work must be considered in addition to $q_{\rm sys}$ to find $\Delta E_{\rm sys}$. Solution:
 - a) This is a phase change from the solid phase to the gas phase. Heat is absorbed by the system so q_{sys} is **positive** (+).
 - b) The system is expanding in volume as more moles of gas exist after the phase change than were present before the phase change. So the system has done work of expansion and w is negative. $\Delta E_{\rm sys} = q + w$. Since q is positive and w is negative, the sign of $\Delta E_{\rm sys}$ cannot be predicted. It will be positive if q > w and negative if q < w.
 - c) $\Delta E_{\text{univ}} = \mathbf{0}$. If the system loses energy, the surroundings gain an equal amount of energy. The sum of the energy of the system and the energy of the surroundings remains constant.
- 6.19 a) There is a volume decrease; $V_{\text{final}} < V_{\text{initial}}$ so ΔV is negative. Since $w_{\text{sys}} = -P\Delta V$, w is **positive**, +.
 - b) ΔH_{sys} is as heat has been removed from the system to liquefy the gas.
 - c) $\Delta E_{\rm sys} = q + w$. Since q is negative and w is positive, the sign of $\Delta E_{\rm sys}$ and $\Delta E_{\rm surr}$ cannot be predicted. $\Delta E_{\rm sys}$ will be positive and $\Delta E_{\rm surr}$ will be negative if w > q and $\Delta E_{\rm sys}$ will be negative and $\Delta E_{\rm surr}$ will be positive if w < q.
- 6.20 To determine the specific heat capacity of a substance, you need its mass, the heat added (or lost), and the change in temperature.
- 6.21 Specific heat capacity is an **intensive property**; it is defined on a per gram basis. The specific heat capacity of a particular substance has the same value, regardless of the amount of substance present.

6.22 Plan: The heat required to raise the temperature of water is found by using the equation q = c x mass x ΔT . The specific heat capacity, c_{water} , is found in Table 6.2. Because the Celsius degree is the same size as the Kelvin degree, $\Delta T = 100^{\circ}\text{C} - 25^{\circ}\text{C} = 75^{\circ}\text{C} = 75^{\circ}\text{K}$. Solution:

$$q(J) = c \times \text{mass } \times \Delta T = \left(4.184 \frac{J}{g \cdot K}\right) (22.0 \text{ g}) (75 \text{ K}) = 6903.6 = 6.9 \times 10^3 \text{ J}$$

6.23
$$q(J) = c \times \text{mass } \times \Delta T = \left(2.087 \frac{J}{g \cdot K}\right) (0.10 \text{ g}) ((-75 - 10.) \text{ K}) = -17.7395 = -18 \text{ J}$$

6.24 Plan: Use the relationship q = c x mass x ΔT . We know the heat (change kJ to J), the specific heat capacity, and the mass, so ΔT can be calculated. Once ΔT is known, that value is added to the initial temperature to find the final temperature.

Solution:

$$q(J) = c \text{ x mass x } \Delta T$$
 $T_{\text{initial}} = 13.00^{\circ}\text{C}$ $T_{\text{final}} = ?$ mass = 295 g $c = 0.900 \text{ J/g} \cdot \text{K}$ $q = (75.0 \text{ kJ}) \left(\frac{10^{3} \text{ J}}{1 \text{ kJ}}\right) = 7.50 \text{x} 10^{4} \text{ J}$

$$7.50 \times 10^4 \text{ J} = (0.900 \text{ J/g} \cdot \text{K})(295 \text{ g})(\Delta T)$$

$$\Delta T = \frac{\left(7.50 \text{x} 10^4 \text{ J}\right)}{\left(295 \text{ g}\right) \left(\frac{0.900 \text{ J}}{\text{g} \cdot \text{K}}\right)}$$

 $\Delta T = 282.4859 \text{ K} = 282.4859^{\circ}\text{C}$ (Because the Celsius degree is the same size as the Kelvin degree, ΔT is the same in either temperature unit.)

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

$$T_{\text{final}} = \Delta T + T_{\text{initial}}$$

$$T_{\text{final}} = 282.4859^{\circ}\text{C} + 13.00^{\circ}\text{C} = 295.49 = 295^{\circ}\text{C}$$

6.25
$$q(J) = c \times \max X \Delta T$$

$$-688 \text{ J} = (2.42 \text{ J/g} \cdot \text{K})(27.7 \text{ g})(\Delta T)$$

$$(\Delta T) = \frac{\left(-688 \text{ J}\right)}{\left(27.7 \text{ g}\right) \left(\frac{2.42 \text{ J}}{\text{g} \cdot \text{K}}\right)} = -10.26345 \text{ K} = -10.26345^{\circ}\text{C}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

 $T_{\text{initial}} = T_{\text{final}} - \Delta T$
 $T_{\text{initial}} = 32.5^{\circ}\text{C} - (-10.26345^{\circ}\text{C}) = 42.76345 = 42.8^{\circ}\text{C}$

6.26 <u>Plan:</u> Since the bolts have the same mass and same specific heat capacity, and one must cool as the other heats (the heat lost by the "hot" bolt equals the heat gained by the "cold" bolt), the final temperature is an average of the two initial temperatures.

Solution:

$$\left\lceil \frac{\left(T_1 + T_2\right)}{2} \right\rceil = \left\lceil \frac{\left(100.^{\circ}\text{C} + 55^{\circ}\text{C}\right)}{2} \right\rceil = 77.5^{\circ}\text{C}$$

6.27
$$-q_{\text{lost}} = q_{\text{gained}}$$

$$-2(\text{mass})(c_{\text{Cu}})(T_{\text{final}} - 105)^{\circ}\text{C} = (\text{mass})(c_{\text{Cu}})(T_{\text{final}} - 45)^{\circ}\text{C}$$

$$-2(T_{\text{final}} - 105)^{\circ}\text{C} = (T_{\text{final}} - 45)^{\circ}\text{C}$$

$$2(105^{\circ}\text{C}) - 2T_{\text{final}} = T_{\text{final}} - 45^{\circ}\text{C}$$

$$210^{\circ}\text{C} + 45^{\circ}\text{C} = T_{\text{final}} + 2T_{\text{final}} = 3T_{\text{final}}$$

$$(255^{\circ}\text{C})/3 = T_{\text{final}} = 85.0^{\circ}\text{C}$$

6.28 Plan: The heat lost by the water originally at 85°C is gained by the water that is originally at 26°C. Therefore $-q_{\text{lost}} = q_{\text{gained}}$. Both volumes are converted to mass using the density. Solution:

Mass (g) of 75 mL =
$$(75 \text{ mL}) \left(\frac{1.00 \text{ g}}{1 \text{ mL}}\right) = 75 \text{ g}$$
 Mass (g) of 155 mL = $(155 \text{ mL}) \left(\frac{1.00 \text{ g}}{1 \text{ mL}}\right) = 155 \text{ g}$ $-q_{\text{lost}} = q_{\text{gained}}$ $c \times \text{mass} \times \Delta T (85^{\circ}\text{C water}) = c \times \text{mass} \times \Delta T (26^{\circ}\text{C water})$

$$-(4.184 \text{ J/g}^{\circ}\text{C})(75 \text{ g})(T_{\text{final}} - 85)^{\circ}\text{C} = (4.184 \text{ J/g}^{\circ}\text{C})(155 \text{ g})(T_{\text{final}} - 26)^{\circ}\text{C}$$

− $(75 \text{ g})(T_{\text{final}} - 85)^{\circ}\text{C} = (155 \text{ g})(T_{\text{final}} - 26)^{\circ}\text{C}$

$$6375 - 75T_{\text{final}} = 155T_{\text{final}} - 4030$$

 $6375 + 4030 = 155T_{\text{final}} + 75T_{\text{final}}$

$$10405 = 230.T_{\text{final}}$$

 $T_{\text{final}} = (10405/230.) = 45.24 = 45^{\circ}\text{C}$

6.29
$$-q_{\text{lost}} = q_{\text{gained}}$$

$$- [24.4 \text{ mL}(1.00 \text{ g/mL})](4.184 \text{ J/g°C})(23.5 - 35.0)^{\circ}\text{C} = (\text{mass})(4.184 \text{ J/g°C})(23.5 - 18.2)^{\circ}\text{C}$$

$$- (24.4)(23.5 - 35.0) = (\text{mass})(23.5 - 18.2)$$

$$- (24.4)(-11.5) = (\text{mass})(5.3)$$

$$280.6 = (\text{mass})(5.3)$$

52.943 g = mass
Volume (mL) =
$$(52.943 \text{ g}) \left(\frac{1 \text{ mL}}{1.00 \text{ g}} \right) = 52.943 =$$
53 mL

6.30 Benzoic acid is C₆H₅COOH, and will be symbolized as HBz.

$$-q_{
m reaction} = q_{
m water} + q_{
m calorimeter}$$

$$-q_{\text{reaction}} = -\left(1.221 \text{ g HBz}\right) \left(\frac{1 \text{ mol HBz}}{122.12 \text{ g HBz}}\right) \left(\frac{-3227 \text{ kJ}}{1 \text{ mol HBz}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) = 3.226472 \text{x} 10^4 \text{ J}$$

$$q_{\text{water}} = c \text{ x mass x } \Delta T = 4.184 \text{ J/g}^{\circ}\text{C x } 1200 \text{ g x } \Delta T$$

$$q_{\text{calorimeter}} = C \times \Delta T = 1365 \text{ J/°C} \times \Delta T$$

$$-q_{\text{reaction}} = q_{\text{water}} + q_{\text{calorimeter}}$$

$$3.226472 \times 10^4 \text{ J} = 4.184 \text{ J/g}^{\circ}\text{C} \times 1200 \text{ g} \times \Delta T + 1365 \text{ J/}^{\circ}\text{C} \times \Delta T$$

$$3.226472 \times 10^4 \text{ J} = 5020.8(\Delta T) + 1365(\Delta T)$$

$$3.226472 \times 10^4 \text{ J} = 6385.8 (\Delta T)$$

$$\Delta T = 3.226472 \times 10^4 / 6385.8 = 5.052573 = 5.053^{\circ} \text{C}$$

- 6.31 a) Energy will flow from Cu (at 100.0°C) to Fe (at 0.0°C).
 - b) To determine the final temperature, the heat capacity of the calorimeter must be known.

c) –
$$q_{\text{Cu}} = q_{\text{Fe}} + q_{\text{calorimeter}}$$
 assume $q_{\text{calorimeter}} = 0$.

$$-q_{\mathrm{Cu}} = q_{\mathrm{Fe}} + 0$$

$$-(20.0 \text{ g Cu})(0.387 \text{ J/g}^{\circ}\text{C})(T_{\text{final}} - 100.0)^{\circ}\text{C} = (30.0 \text{ g Fe})(0.450 \text{ J/g}^{\circ}\text{C})(T_{\text{final}} - 0.0)^{\circ}\text{C} + 0.0 \text{ J}$$

$$-(20.0 \text{ g})(0.387 \text{ J/g}^{\circ}\text{C})(T_{\text{final}} - 100.0^{\circ}\text{C}) = (30.0 \text{ g})(0.450 \text{ J/g}^{\circ}\text{C})(T_{\text{final}} - 0.0^{\circ}\text{C})$$

$$-(7.74)(T_{\text{final}} - 100.0) = (13.5)(T_{\text{final}} - 0.0)$$

$$774 - 7.74 T_{\text{final}} = 13.5 T_{\text{final}}$$

$$774 = (13.5 + 7.74) T_{\text{final}} = 21.24 T_{\text{final}}$$

$$T_{\text{final}} = 774/21.24 = 36.44068 = 36.4^{\circ}\text{C}$$

6.32 The reaction is: $2\text{KOH}(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{K}_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l)$ $q \text{ (kJ)} = (25.0 + 25.0) \text{ mL}(1.00 \text{ g/mL})(4.184 \text{ J/g}^{\circ}\text{C})(30.17 - 23.50)^{\circ}\text{C}(1 \text{ kJ/10}^3 \text{ J}) = 1.395364 \text{ kJ}$ (The temperature increased so the heat of reaction is exothermic.) Amount (moles) of $\text{H}_2\text{SO}_4 = (25.0 \text{ mL})(0.500 \text{ mol H}_2\text{SO}_4/\text{L})(10^{-3} \text{ L/1 mL}) = 0.0125 \text{ mol H}_2\text{SO}_4$ Amount (moles) of KOH = $(25.0 \text{ mL})(1.00 \text{ mol KOH/L})(10^{-3} \text{ L/1 mL}) = 0.0250 \text{ mol KOH}$ The moles show that both H_2SO_4 and KOH are limiting.

The enthalpy change could be calculated in any of the following ways:

 $\Delta H = -1.395364 \text{ kJ}/0.0125 \text{ mol H}_2\text{SO}_4 = -111.62912 = -112 \text{ kJ/mol H}_2\text{SO}_4$

 $\Delta H = -1.395364 \text{ kJ/}0.0250 \text{ mol KOH} = -55.81456 = -55.8 \text{ kJ/mol KOH}$

(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.)

6.33 Plan: Recall that ΔH is positive for an endothermic reaction in which heat is absorbed, while ΔH is negative for an

exothermic reaction in which heat is released.

Solution:

The reaction has a **positive** ΔH_{rxn} , because this reaction requires the input of energy to break the oxygen-oxygen bond in O_2 :

$$O_2(g) + \text{energy} \rightarrow 2O(g)$$

6.34 Plan: Recall that ΔH is positive for an endothermic reaction in which heat is absorbed, while ΔH is negative for an

exothermic reaction in which heat is released.

Solution:

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

$$H_2O(g) \rightarrow H_2O(l) + Energy$$
 $2H_2O(l) + Energy \rightarrow 2H_2O(g)$ $\Delta H_{\text{condensation}} = (-)$ $\Delta H_{\text{vaporization}} = (+)2[\Delta H_{\text{condensation}}]$

The enthalpy for 1 mole of water condensing would be opposite in sign to and one-half the value for the conversion of 2 moles of liquid H_2O to H_2O vapor.

- 6.35 Plan: Recall that ΔH is positive for an endothermic reaction in which heat is absorbed, while ΔH is negative for an exothermic reaction in which heat is released. The $\Delta H_{\rm rxn}$ is specific for the reaction as written, meaning that 20.2 kJ is released when one-eighth of a mole of sulfur reacts. Use the ratio between moles of sulfur and ΔH to convert between amount of sulfur and heat released. Solution:
 - a) This reaction is **exothermic** because ΔH is negative.
 - b) Because ΔH 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)
$$\Delta H_{\text{rxn}} = (2.6 \text{ mol } S_8) \left(\frac{-20.2 \text{ kJ}}{(1/8) \text{ mol } S_8} \right) = -420.16 = -4.2 \text{x} \cdot 10^2 \text{ kJ}$$

d) The mass of S₈ requires conversion to moles and then a calculation identical to part c) can be performed.

$$\Delta H_{\text{rxn}} = (25.0 \text{ g S}_8) \left(\frac{1 \text{ mol S}_8}{256.56 \text{ g S}_8} \right) \left(\frac{-20.2 \text{ kJ}}{(1/8) \text{ mol S}_8} \right) = -15.7468 = -15.7 \text{ kJ}$$

6.36
$$\operatorname{MgCO}_3(s) \to \operatorname{MgO}(s) + \operatorname{CO}_2(g)$$

$$\Delta H_{\rm rxn} = 117.3 \text{ kJ}$$

- a) Absorbed
- b) $\Delta H_{\rm rxn}$ (reverse) = -117.3 kJ

c)
$$\Delta H_{\text{rxn}} = (5.35 \text{ mol CO}_2) \left(\frac{-117.3 \text{ kJ}}{1 \text{ mol CO}_2} \right) = -627.555 = -628 \text{ kJ}$$

d)
$$\Delta H_{\text{rxn}} = (35.5 \text{ g CO}_2) \left(\frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \right) \left(\frac{-117.3 \text{ kJ}}{1 \text{ mol CO}_2} \right) = -94.618 = -94.6 \text{ kJ}$$

6.37 Plan: A thermochemical equation is a balanced equation that includes the heat of reaction. Since heat is absorbed in this reaction, ΔH will be positive. Convert the mass of NO to moles and use the ratio between NO and ΔH to find the heat involved for this amount of NO. Solution:

a)
$$1/2N_2(g) + 1/2O_2(g) \rightarrow NO(g)$$
 $\Delta H = 90.29 \text{ kJ}$
b) $\Delta H_{\text{rxn}} = (3.50 \text{ g NO}) \left(\frac{1 \text{ mol NO}}{30.01 \text{ g NO}}\right) \left(\frac{-90.29 \text{ kJ}}{1 \text{ mol NO}}\right) = -10.5303 = -10.5 \text{ kJ}$

6.38 a)
$$KBr(s) \rightarrow K(s) + 1/2Br_2(l)$$
 $\Delta H_{rxn} = 394 \text{ kJ}$
b) $\Delta H_{rxn} = \left(10.0 \text{ kg KBr}\right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol KBr}}{119.00 \text{ g KBr}}\right) \left(\frac{-394 \text{ kJ}}{1 \text{ mol KBr}}\right) = -3.3109 \text{x} 10^4 = -3.31 \text{x} 10^4 \text{ kJ}$

6.39 Plan: For the reaction written, 2 moles of H_2O_2 release 196.1 kJ of energy upon decomposition. Use this ratio to convert between the given amount of reactant and the amount of heat released. The amount of H_2O_2 must be converted from kg to g to moles. Solution:

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g) \qquad \Delta H_{\text{rxn}} = -196.1 \text{ kJ}$$

$$\text{Heat (kJ)} = q = \left(652 \text{ kg } \text{H}_2\text{O}_2\right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol } \text{H}_2\text{O}_2}{34.02 \text{ g } \text{H}_2\text{O}_2}\right) \left(\frac{-196.1 \text{ kJ}}{2 \text{ mol } \text{H}_2\text{O}_2}\right) = -1.87915 \times 10^6 = -1.88 \times 10^6 \text{ kJ}$$

For the reaction written, 1 mole of B_2H_6 releases 755.4 kJ of energy upon reaction.

$$\begin{aligned} \mathbf{B}_2\mathbf{H}_6(g) + 6\mathbf{Cl}_2(g) &\to 2\mathbf{B}\mathbf{Cl}_3(g) + 6\mathbf{H}\mathbf{Cl}(g) \\ \text{Heat (kJ)} &= q = \left(1 \text{ kg}\right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol } \mathbf{B}_2\mathbf{H}_6}{27.67 \text{ g } \mathbf{B}_2\mathbf{H}_6}\right) \left(\frac{-755.4 \text{ kJ}}{1 \text{ mol } \mathbf{B}_2\mathbf{H}_6}\right) = -2.73003 \text{x} \\ 10^4 &= -2.730 \text{x} \\ 10^4 \text{ kJ/kg} \end{aligned}$$

- 6.41 <u>Plan:</u> A thermochemical equation is a balanced equation that includes the heat of reaction. Heat is released in this reaction so ΔH is negative. Use the ratio between ΔH and moles of C_2H_4 to find the amount of C_2H_4 that must react to produce the given quantity of heat. Solution:
 - a) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$ $\Delta H_{\text{rxn}} = -1411 \text{ kJ}$ b) Mass (g) of $C_2H_4 = \left(-70.0 \text{ kJ}\right) \left(\frac{1 \text{ mol } C_2H_4}{-1411 \text{ kJ}}\right) \left(\frac{28.05 \text{ g } C_2H_4}{1 \text{ mol } C_2H_4}\right) = 1.39157 = \mathbf{1.39} \text{ g } \mathbf{C_2H_4}$
- 6.42 a) $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(g)\Delta H_{rxn} = -5.64x10^3 \text{ kJ}$ b) Heat (kJ) = $q = \left(1 \text{ g } C_{12}H_{22}O_{11}\right) \left(\frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.30 \text{ g } C_{12}H_{22}O_{11}}\right) \left(\frac{-5.64x10^3 \text{ kJ}}{1 \text{ mol } C_{12}H_{22}O_{11}}\right) = -16.47677 = -16.5 \text{ kJ/g}$
- 6.43 Hess's law: ΔH_{rxn} is independent of the number of steps or the path of the reaction.
- 6.44 <u>Plan:</u> To obtain the overall reaction, add the first reaction to the reverse of the second. When the second reaction is reversed, the sign of its enthalpy change is reversed from positive to negative.

 <u>Solution:</u>

$$\begin{array}{ll} \operatorname{Ca}(s) + 1/2\operatorname{O}_2(g) \to \operatorname{CaO}(s) & \Delta H = -635.1 \text{ kJ} \\ \overline{\operatorname{CaO}(s)} + \operatorname{CO}_2(g) \to \operatorname{CaCO}_3(s) & \Delta H = -178.3 \text{ kJ (reaction is reversed)} \\ \overline{\operatorname{Ca}(s)} + 1/2\operatorname{O}_2(g) + \operatorname{CO}_2(g) \to \operatorname{CaCO}_3(s) & \Delta H = -813.4 \text{ kJ} \end{array}$$

$$\begin{array}{lll} 6.45 & 2 \text{NOCl}(g) \to \frac{2 \text{NO}(g)}{2} + \text{Cl}_2(g) & \Delta H = -2(-38.6 \text{ kJ}) \\ & \frac{2 \text{NO}(g)}{2} \to \text{N}_2(g) + \text{O}_2(g) & \Delta H = -2(90.3 \text{ kJ}) \\ & 2 \text{NOCl}(g) \to \text{N}_2(g) + \text{O}_2(g) + \text{Cl}_2(g) & \Delta H = 77.2 \text{ kJ} + (-180.6 \text{ kJ}) = -103.4 \text{ kJ} \end{array}$$

6.46 Plan: Add the two equations, canceling substances that appear on both sides of the arrow. When matching the equations with the arrows in the Figure, remember that a positive ΔH corresponds to an arrow pointing up while a negative ΔH corresponds to an arrow pointing down.

- 1) $\Delta H = 180.6 \text{ kJ}$ $N_2(g) + O_2(g) \rightarrow 2NO(g)$ 2)
 - $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H = -114.2 \text{ kJ}$
- $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ $\Delta H_{\rm rxn} = +66.4 \text{ kJ}$ 3)

In Figure P6.46, 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.

- 6.47 1) $P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(g)$ $\Delta H_1 = -1148 \text{ kJ}$ 2) $4PCl_3(g) + 4Cl_2(g) \rightarrow 4PCl_5(g)$ $\Delta H_2 = -460 \text{ kJ}$
 - 3) $P_4(s) + 10Cl_2(g) \rightarrow 4PCl_5(g)$ $\Delta H_{\text{overall}}$ = -1608 kJEquation 1) = B, equation 2) = C, equation 3) = A

6.48 C (diamond) +
$$\Theta_2(g) \rightarrow C\Theta_2(g)$$
 $\Delta H = -395.4 \text{ kJ}$

$$\frac{C\Theta_2(g) \rightarrow C(\text{graphite}) + \Theta_2(g)}{C(\text{diamond}) \rightarrow C(\text{graphite})}$$

$$\Delta H = -(-393.5 \text{ kJ})$$

$$\Delta H = -1.9 \text{ kJ}$$

- 6.49 The standard heat of reaction, ΔH_{rxn}° , is the enthalpy change for any reaction where all substances are in their standard states. The standard heat of formation, $\Delta H_{\rm f}^{\circ}$, 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 the most stable form for liquids and solids. Standard state does not include a specific temperature, but a temperature must be specified in a table of standard values.
- <u>Plan:</u> ΔH_f° is for the reaction that shows the formation of <u>one</u> mole of compound from its elements in their 6.50 standard states.

Solution:

- a) $1/2Cl_2(g) + Na(s) \rightarrow NaCl(s)$ The element chlorine occurs as Cl_2 , not Cl.
- b) $H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$ The element hydrogen exists as H_2 , not H, and the formation of water is written with water as the product.
- c) No changes
- 6.51 Plan: Formation equations show the formation of one mole of compound from its elements. The elements must be in their most stable states ($\Delta H_{\rm f}^{\circ} = 0$).

Solution:

- a) $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$
- b) $Na(s) + 1/2H_2(g) + C(graphite) + 3/2O_2(g) \rightarrow NaHCO_3(s)$
- c) C(graphite) + $2Cl_2(g) \rightarrow CCl_4(l)$
- d) $1/2H_2(g) + 1/2N_2(g) + 3/2O_2(g) \rightarrow HNO_3(l)$
- 6.52 a) $1/2H_2(g) + 1/2I_2(s) \rightarrow HI(g)$
 - b) $Si(s) + 2F_2(g) \rightarrow SiF_4(g)$
 - c) $3/2O_2(g) \to O_3(g)$
 - d) $3Ca(s) + 1/2P_4(s) + 4O_2(g) \rightarrow Ca_3(PO_4)_2(s)$
- 6.53 Plan: The enthalpy change of a reaction is the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants. Since the $\Delta H_{\rm f}^{\rm c}$ values (Appendix B) are reported as energy per one mole, use the appropriate stoichiometric coefficient to reflect the higher number of moles.

$$\begin{split} \Delta H_{\text{rxn}}^{\circ} &= \sum m \, \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \, \Delta H_{\text{f}}^{\circ}(\text{reactants}) \\ \text{a)} \quad \Delta H_{\text{rxn}}^{\circ} &= \{2 \, \Delta H_{\text{f}}^{\circ}[\text{SO}_2(g)] + 2 \, \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(g)]\} - \{2 \, \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{S}(g)] + 3 \, \Delta H_{\text{f}}^{\circ}[\text{O}_2(g)]\} \\ &= [(2 \, \text{mol})(-296.8 \, \text{kJ/mol}) + (2 \, \text{mol})(-241.826 \, \text{kJ/mol})] - [(2 \, \text{mol})(-20.2 \, \text{kJ/mol}) + (3 \, \text{mol})(0.0 \, \text{kJ/mol})] \\ &= -\textbf{1036.9 \, kJ} \\ \text{b)} \text{ The balanced equation is } \text{CH}_4(g) + 4 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + 4 \text{HCl}(g) \\ \Delta H_{\text{rxn}}^{\circ} &= \{1 \, \Delta H_{\text{f}}^{\circ}[\text{CCl}_4(l)] + 4 \, \Delta H_{\text{f}}^{\circ}[\text{HCl}(g)]\} - \{1 \, \Delta H_{\text{f}}^{\circ}[\text{CH}_4(g)] + 4 \, \Delta H_{\text{f}}^{\circ}[\text{Cl}_2(g)]\} \\ \Delta H_{\text{rxn}}^{\circ} &= [(1 \, \text{mol})(-139 \, \text{kJ/mol}) + (4 \, \text{mol})(-92.31 \, \text{kJ/mol})] - [(1 \, \text{mol})(-74.87 \, \text{kJ/mol}) + (4 \, \text{mol})(0 \, \text{kJ/mol})] \\ &= -\textbf{433 \, kJ} \\ 6.54 \quad \Delta H_{\text{rxn}}^{\circ} &= \sum m \, \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \, \Delta H_{\text{f}}^{\circ}(\text{reactants}) \\ \text{a)} \quad \Delta H_{\text{rxn}}^{\circ} &= \{1 \, \Delta H_{\text{f}}^{\circ}[\text{SiF}_4(g)] + 2 \, \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(l)]\} - \{1 \, \Delta H_{\text{f}}^{\circ}[\text{SiO}_2(s)] + 4 \, \Delta H_{\text{f}}^{\circ}[\text{HF}(g)]\} \\ &= [(1 \, \text{mol})(-1614.9 \, \text{kJ/mol}) + (2 \, \text{mol})(-285.840 \, \text{kJ/mol})] \\ &= -\textbf{184 \, kJ} \\ \text{b)} \quad 2\text{C}_2 H_6(g) + 7\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(g) \\ \Delta H_{\text{rxn}}^{\circ} &= \{4 \, \Delta H_{\text{f}}^{\circ}[\text{CO}_2(g)] + 6 \, \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(g)]\} - \{2 \, \Delta H_{\text{f}}^{\circ}[\text{C}_2\text{H}_6(g)] + 7 \, \Delta H_{\text{f}}^{\circ}[\text{O}_2(g)]\} \\ &= [(4 \, \text{mol})(-393.5 \, \text{kJ/mol}) + (6 \, \text{mol})(-241.826 \, \text{kJ/mol})] - [(2 \, \text{mol})(-84.667 \, \text{kJ/mol}) + (7 \, \text{mol})(0 \, \text{kJ/mol})] \\ &= -\textbf{2855.6 \, kJ} \text{ (or } -1427.8 \, \text{kJ for reaction of } 1 \, \text{mol of } \text{C}_2\text{H}_6) \\ \end{pmatrix}$$

6.55 Plan: The enthalpy change of a reaction is the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants. Since the $\Delta H_{\rm f}^{\circ}$ values (Appendix B) are reported as energy per one mole, use the appropriate stoichiometric coefficient to reflect the higher number of moles. In this case, $\Delta H_{\rm rxn}^{\circ}$ is known and $\Delta H_{\rm f}^{\circ}$ of CuO must be calculated.

Solution:

 $\Delta H_{\rm rxn}^{\circ} = \sum_{i} m \Delta H_{\rm f(products)}^{\circ} - \sum_{i} n \Delta H_{\rm f(reactants)}^{\circ}$

$$Cu_{2}O(s) + 1/2O_{2}(g) \rightarrow 2CuO(s) \qquad \Delta H_{rxn}^{\circ} = -146.0 \text{ kJ}$$

$$\Delta H_{rxn}^{\circ} = \left\{ 2 \Delta H_{f}^{\circ} \left[CuO(s) \right] \right\} - \left\{ 1 \Delta H_{f}^{\circ} \left[Cu_{2}O(s) \right] + 1/2 \Delta H_{f}^{\circ} \left[O_{2}(g) \right] \right\}$$

$$-146.0 \text{ kJ} = \left\{ (2 \text{ mol}) \Delta H_{f}^{\circ} \left[CuO(s) \right] \right\} - \left\{ (1 \text{ mol})(-168.6 \text{ kJ/mol}) + (1/2 \text{ mol})(0 \text{ kJ/mol}) \right\}$$

$$-146.0 \text{ kJ} = 2 \text{ mol} \Delta H_{f}^{\circ} \left[CuO(s) \right] + 168.6 \text{ kJ}$$

$$\Delta H_{f}^{\circ} \left[CuO(s) \right] = -\frac{314.6 \text{ kJ}}{2 \text{ mol}} = -157.3 \text{ kJ/mol}$$

$$6.56 \qquad \Delta H_{rxn}^{\circ} = \sum_{m} \Delta H_{f}^{\circ} \left[\text{roducts} \right] - \sum_{m} \Delta H_{f}^{\circ} \left[\text{reactants} \right]$$

$$C_{2}H_{2}(g) + 5/2O_{2}(g) \rightarrow 2CO_{2}(g) + H_{2}O(g) \qquad \Delta H_{rxn}^{\circ} = -1255.8 \text{ kJ}$$

$$\Delta H_{rxn}^{\circ} = \left\{ 2 \Delta H_{f}^{\circ} \left[CO_{2}(g) \right] + 1 \Delta H_{f}^{\circ} \left[H_{2}O(g) \right] \right\} - \left\{ 1 \Delta H_{f}^{\circ} \left[C_{2}H_{2}(g) \right] + 5/2 \Delta H_{f}^{\circ} \left[O_{2}(g) \right] \right\}$$

$$-1255.8 \text{ kJ} = \left\{ (2 \text{ mol})(-393.5 \text{ kJ/mol}) + (1 \text{ mol})(-241.826 \text{ kJ/mol}) \right\}$$

$$-\left\{ (1 \text{ mol}) \Delta H_{f}^{\circ} \left[C_{2}H_{2}(g) \right] + (5/2 \text{ mol})(0.0 \text{ kJ/mol}) \right\}$$

$$-1255.8 \text{ kJ} = -787.0 \text{ kJ} - 241.8 \text{ kJ} - (1 \text{ mol}) \Delta H_{f}^{\circ} \left[C_{2}H_{2}(g) \right]$$

$$\Delta H_{f}^{\circ} \left[C_{2}H_{2}(g) \right] = \frac{-227.0 \text{ kJ}}{-1 \text{ mol}} = 227.0 \text{ kJ/mol}$$

6.57 a)
$$4C_3H_5(NO_3)_3(l) \rightarrow 6N_2(g) + 10H_2O(g) + 12CO_2(g) + O_2(g)$$

b) $\Delta H_{\rm rxn}^{\circ} = \{6\Delta H_{\rm f}^{\circ} [N_2(g)] + 10\Delta H_{\rm f}^{\circ} [H_2O(g)] + 12\Delta H_{\rm f}^{\circ} [CO_2(g)] + 1\Delta H_{\rm f}^{\circ} [O_2(g)]\} - \{4\Delta H_{\rm f}^{\circ} [C_3H_5(NO_3)_3(l)]\}$
 $-2.29 \times 10^4 \text{ kJ} = \{(6 \text{ mol})(0 \text{ kJ/mol}) + (10 \text{ mol})(-241.826 \text{ kJmol}) + (12 \text{ mol})(-393.5 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJmol})\}$
 $-\{(4 \text{ mol})\Delta H_{\rm f}^{\circ} [C_3H_5(NO_3)_3(l)]\}$
 $-2.29 \times 10^4 \text{ kJ} = -2418 \text{ kJ} - 4722 \text{ kJ} - (4 \text{ mol})\Delta H_{\rm f}^{\circ} [C_3H_5(NO_3)_3(l)]$
 $\Delta H_{\rm f}^{\circ} [C_3H_5(NO_3)_3(l)] = \frac{-15760 \text{ kJ}}{-4 \text{ mol}} = 3940 \text{ kJ/mol}$

6.58 Plan: The enthalpy change of a reaction is the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants. Since the $\Delta H_{\rm f}^{\circ}$ values (Appendix B) are reported as energy per one mole, use the appropriate stoichiometric coefficient to reflect the higher number of moles. Hess's law can also be used to calculate the enthalpy of reaction. In part b), rearrange equations 1) and 2) to give the equation wanted. Reverse the first equation (changing the sign of $\Delta H_{\rm rxn}^{\circ}$) and multiply the coefficients (and $\Delta H_{\rm rxn}^{\circ}$) of the second reaction by 2.

Solution:

$$\begin{split} 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) &\to \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(l) \\ \Delta H_{\text{rxn}}^{\circ} &= \sum_{} m \Delta H_{\text{f (products)}}^{\circ} - \sum_{} n \Delta H_{\text{f (reactants)}}^{\circ} \\ \text{a)} \quad \Delta H_{\text{rxn}}^{\circ} &= \{1 \Delta H_{\text{f}}^{\circ} \left[\text{Pb}(s)\right] + 1 \Delta H_{\text{f}}^{\circ} \left[\text{PbO}_2(s)\right] + 2 \Delta H_{\text{f}}^{\circ} \left[\text{H}_2\text{SO}_4(l)\right] \} \\ &\qquad \qquad - \{2 \Delta H_{\text{f}}^{\circ} \left[\text{PbSO}_4(s)\right] + 2 \Delta H_{\text{f}}^{\circ} \left[\text{H}_2\text{O}(l)\right] \} \\ &= \left[(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(-276.6 \text{ kJmol}) + (2 \text{ mol})(-813.989 \text{ kJ/mol})\right] \\ &\qquad \qquad - \left[(2 \text{ mol})(-918.39 \text{ kJ/mol}) + (2 \text{ mol})(-285.840 \text{ kJ/mol})\right] \end{split}$$

b) Use Hess's law:

$$PbSO_4(s) \rightarrow Pb(s) + PbO_2(s) + \frac{2SO_3(g)}{2SO_3(g)} \qquad \Delta H_{rxn}^{\circ} = -(-768 \text{ kJ}) \text{ Equation has been reversed.}$$

$$\frac{2SO_3(g)}{2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(l)} \qquad \Delta H_{rxn}^{\circ} = 2(-132 \text{ kJ})$$

$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(l) \qquad \Delta H_{rxn}^{\circ} = \mathbf{504 kJ}$$

6.59 <u>Plan:</u> The enthalpy change of a reaction is the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants. Since the $\Delta H_{\rm f}^{\circ}$ values (Appendix B) are reported as energy per one mole, use the appropriate stoichiometric coefficient to reflect the higher number of moles. Convert the mass of stearic acid to moles and use the ratio between stearic acid and $\Delta H_{\rm rxn}^{\circ}$ to find the heat involved for this amount of acid. For part d), use the kcal/g of fat relationship calculated in part c) to convert 11.0 g of fat to total kcal and compare to the 100. Cal amount.

a)
$$C_{18}H_{36}O_{2}(s) + 26O_{2}(g) \rightarrow 18CO_{2}(g) + 18H_{2}O(g)$$

b) $\Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f (products)}}^{\circ} - \sum n \Delta H_{\text{f (reactants)}}^{\circ}$
 $\Delta H_{\text{rxn}}^{\circ} = \{18 \Delta H_{\text{f}}^{\circ} [\text{CO}_{2}(g)] + 18 \Delta H_{\text{f}}^{\circ} [\text{H}_{2}O(g)]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{C}_{18}H_{36}O_{2}(s)] + 26 \Delta H_{\text{f}}^{\circ} [\text{O}_{2}(g)]\}$
 $= [(18 \text{ mol})(-393.5 \text{ kJ/mol}) + (18 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-948 \text{ kJ/mol}) + (26 \text{ mol})(0 \text{ kJ/mol})]$
 $= -10,487.868 = -10,488 \text{ kJ}$
c) $q \text{ (kJ)} = (1.00 \text{ g C}_{18}H_{36}O_{2}) \left(\frac{1 \text{ mol C}_{18}H_{36}O_{2}}{284.47 \text{ C}_{18}H_{36}O_{2}}\right) \left(\frac{-10,487.868 \text{ kJ}}{1 \text{ mol C}_{18}H_{36}O_{2}}\right) = -36.8681 \text{ kJ}$
 $q \text{ (kcal)} = (-36.8681 \text{ kJ}) \left(\frac{1 \text{ kcal}}{4.184 \text{ kJ}}\right) = -8.811688 = -8.81 \text{ kcal}$

d)
$$q$$
 (kcal) = $(11.0 \text{ g fat}) \left[\frac{-8.811688 \text{ kcal}}{1.0 \text{ g fat}} \right] = 96.9286 = 96.9 \text{ kcal}$

Since 1 kcal = 1 Cal, 96.9 kcal = 96.9 Cal. The calculated calorie content is consistent with the package information.

6.60 Plan: Use the ideal gas law, PV = nRT, to calculate the volume of one mole of helium at each temperature. Then use the given equation for ΔE to find the change in internal energy. The equation for work, $w = -P\Delta V$, is needed for part c), and $q_P = \Delta E + P\Delta V$ is used for part d). For part e), recall that $\Delta H = q_P$.

a)
$$PV = nRT$$
 or $V = \frac{nRT}{P}$

$$T = 273 + 15 = 288 \text{ K} \quad \text{and} \quad T = 273 + 30 = 303 \text{ K}$$
Initial volume (L) = $V = \frac{nRT}{P} = \frac{\left(0.0821 \frac{\text{L•atm}}{\text{mol•K}}\right) \left(288 \text{ K}\right)}{\left(1.00 \text{ atm}\right)} = 23.6448 = 23.6 \text{ L/mol}$
Final volume (L) = $V = \frac{nRT}{P} = \frac{\left(0.0821 \frac{\text{L•atm}}{\text{mol•K}}\right) \left(303 \text{ K}\right)}{\left(1.00 \text{ atm}\right)} = 24.8763 = 24.9 \text{ L/mol}$

Final volume (L) =
$$V = \frac{nRT}{P} = \frac{\left(0.0821 \frac{\text{L•atm}}{\text{mol • K}}\right) \left(303 \text{ K}\right)}{\left(1.00 \text{ atm}\right)} = 24.8763 = 24.9 \text{ L/mol}$$

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 = 3/2nRT, 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.

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

c) When the balloon expands as temperature rises, the balloon performs PV work. However, the problem specifies that pressure remains constant, so work done on the surroundings by the balloon is defined by the equation: $w = -P\Delta V$. When pressure and volume are multiplied together, the unit is L•atm, so a conversion factor is needed to convert work in units of L•atm to joules.

$$w = -P\Delta V = -(1.00 \text{ atm})((24.8763 - 23.6448) \text{ L})(\frac{101.3 \text{ J}}{1 \text{ L*atm}}) = -124.75 = -1.2 \times 10^2 \text{ J}$$

d)
$$q_P = \Delta E + P\Delta V = (187.065 \text{ J}) + (124.75 \text{ J}) = 311.815 = 3.1 \text{x} 10^2 \text{ J}$$

- e) $\Delta H = q_P =$ **310 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: $\Delta H = \Delta E + P\Delta V =$ $\Delta E - w = (q + w) - w = q_P$
- 6.61 a) Respiration:

Fermentation:

$$C_6H_{12}O_6(s) \rightarrow 2CO_2(g) + 2CH_3CH_2OH(l)$$

$$\Delta H_{\rm rxn}^{\circ} = \{2 \Delta H_{\rm f}^{\circ} [{\rm CO}_{2}(g)] + 2 \Delta H_{\rm f}^{\circ} [{\rm CH}_{3}{\rm CH}_{2}{\rm OH}(l)]\} - [1 \Delta H_{\rm f}^{\circ} [{\rm C}_{6}{\rm H}_{12}{\rm O}_{6}(s)]\}$$

$$= [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-277.63 \text{ kJ/mol})] - [(1 \text{ mol})(-1273.3 \text{ kJ/mol})] = -68.96 = -69.0 \text{ kJ}$$
b) Combustion of ethanol:

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

$$\Delta H_{\text{rxn}}^{\circ} = \{2 \Delta H_{\text{f}}^{\circ} [\text{CO}_{2}(g)] + 3 \Delta H_{\text{f}}^{\circ} [\text{H}_{2}\text{O}(g)]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{CH}_{3}\text{CH}_{2}\text{OH}(l)] + 3 \Delta H_{\text{f}}^{\circ} [\text{O}_{2}(g)]\}$$

 $\Delta H_{\text{rxn}}^{\circ} = [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (3 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-277.63 \text{ kJ/mol}) + (3 \text{ mol})(0.0 \text{ kJ/mol})]$ = -1234.848 = - **1234.8 kJ**

Heats of combustion/mol C:

Sugar:
$$\left(\frac{-2538.656 \text{ kJ}}{1 \text{ mol } C_6 H_{12} O_6}\right) \left(\frac{1 \text{ mol } C_6 H_{12} O_6}{6 \text{ mol } C}\right) = -423.1093 = -423.11 \text{ kJ/mol } C$$

Ethanol:
$$\left(\frac{-1234.848 \text{ kJ}}{1 \text{ mol CH}_3\text{CH}_2\text{OH}}\right) \left(\frac{1 \text{ mol CH}_3\text{CH}_2\text{OH}}{2 \text{ mol C}}\right) = -617.424 = -617.42 \text{ kJ/mol C}$$

Ethanol has a higher value

6.62 a)
$$3N_2O_5(g) + 3NO(g) \rightarrow 9NO_2(g)$$

$$\Delta H_{\text{rxn}}^{\circ} = \{9 \Delta H_{\text{f}}^{\circ} [\text{NO}_2(g)]\} - \{3 \Delta H_{\text{f}}^{\circ} [\text{N}_2O_5(g)] + 3 \Delta H_{\text{f}}^{\circ} [\text{NO}(g)]\}$$

$$= [(9 \text{ mol})(33.2 \text{ kJ/mol})] - [(3 \text{ mol})(11 \text{ kJ/mol}) + (3 \text{ mol})(90.29 \text{ kJ/mol})]$$

$$= -5.07 = -5 \text{ kJ}$$

b) (9 molecules product)
$$\left(\frac{1.50 \times 10^{-2} \text{ mol}}{1 \text{ molecule product}}\right) \left(\frac{-5.07 \text{ kJ}}{9 \text{ moles product}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) = -76.05 = -76.0 \text{ J}$$

6.63 a)
$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$
 $\Delta H^{\circ}_{rXn} = ?$
b) $Fe_2O_3(s) + 1/3CO(g) \rightarrow \frac{2/3Fe_3O_4(s)}{2} + 1/3CO_2(g)$ $\Delta H^{\circ} = 1/3 (-48.5 \text{ kJ}) = -16.2 \text{ kJ}$ $\frac{2FeO(s)}{2} + 2CO(g) \rightarrow 2Fe(s) + 2CO_2(g)$ $\Delta H^{\circ} = -2(-11.0 \text{ kJ}) = 22.0 \text{ kJ}$ $\frac{2/3Fe_3O_4(s)}{2} + \frac{2/3CO(g)}{2} \rightarrow \frac{2FeO(s)}{2} + \frac{2/3CO_2(g)}{2} = \frac{\Delta H^{\circ} = 2/3 (22 \text{ kJ})}{2} = 14.7 \text{ kJ}$

Total:
$$\operatorname{Fe_2O_3}(s) + 3\operatorname{CO}(g) \rightarrow 2\operatorname{Fe}(s) + 3\operatorname{CO_2}(g)$$
 $\Delta H_{\operatorname{rxn}}^{\circ} =$ 21 kJ

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

$$= -2.585869657 \text{ x } 10^6 \text{ kJ}$$
b) Miles = $\left(-2.585869657 \text{ x } 10^6 \text{ kJ}\right) \left(\frac{1 \text{ h}}{-5.5 \text{ x } 10^4 \text{ kJ}}\right) \left(\frac{65 \text{ mi}}{1 \text{ h}}\right) \left(\frac{1 \text{ km}}{0.62 \text{ mi}}\right) = 4929.1 = \textbf{4.9 x } \textbf{10}^3 \text{ km}$

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.

6.65 $q = c \times \text{mass} \times \Delta T$

In this situation, all of the samples have the same mass, 50. g, so mass is not a variable.

All also have the same q value, 450. J. So, 450. J α (c x ΔT). c, specific heat capacity, and ΔT are inversely proportional. The higher the ΔT , the lower the value of specific heat capacity:

 ΔT : B > D > C > A

Specific heat capacity: $\mathbf{B} < \mathbf{D} < \mathbf{C} < \mathbf{A}$

6.66
$$C_6H_{12}O_6(s) + C_6H_{12}O_6(s) \rightarrow C_{12}H_{22}O_{11}(s) + H_2O(l)$$

 $\Delta H_{rxn}^{\circ} = [(1 \text{ mol sucrose})(-2226 \text{ kJ/mol}) + (1 \text{ mol } H_2O)(-285.840 \text{ kJ/mol})] - [(1 \text{ mol glucose})(-1273 \text{ kJ/mol}) + (1 \text{ mol fructose})(-1266 \text{ kJ/mol})] = 27 \text{ kJ/mol sucrose}$

6.67
$$\text{ClF}(g) + \frac{1}{2}\text{O}_{2}(g) \rightarrow \frac{1}{2}\text{Cl}_{2}\text{O}(g) + \frac{1}{2}\text{OF}_{2}(g)$$
 $\Delta H_{\text{rxn}}^{\circ} = \frac{1}{2}(167.5 \text{ kJ}) = 83.75 \text{ kJ}$

$$F_{2}(g) + \frac{1}{2}\text{O}_{2}(g) \rightarrow \text{OF}_{2}(g)$$
 $\Delta H_{\text{rxn}}^{\circ} = \frac{1}{2}(-43.5 \text{ kJ}) = -21.75 \text{ kJ}$

$$\frac{1}{2}\text{ClF}_{2}\text{O}(g) + \frac{3}{2}\text{OF}_{2}(g) \rightarrow \text{ClF}_{3}(l) + \Theta_{2}(g) \qquad \Delta H_{\text{rxn}}^{\circ} = -\frac{1}{2}(394.1 \text{ kJ}) = -197.05 \text{ kJ}$$

$$\overline{\text{ClF}}(g) + F_{2}(g) \rightarrow \text{ClF}_{3}(l) \qquad \Delta H_{\text{rxn}}^{\circ} = -\frac{135.1 \text{ kJ}}{2}$$

6.68 a)
$$AgNO_3(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_3(aq)$$

Moles of AgNO₃ =
$$(50.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{5.0 \text{ g AgNO}_3}{1 \text{ L}} \right) \left(\frac{1 \text{ mol AgNO}_3}{169.9 \text{ g AgNO}_3} \right)$$

Moles of NaI =
$$(50.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{5.0 \text{ g NaI}}{1 \text{ L}} \right) \left(\frac{1 \text{ mol NaI}}{149.9 \text{ g NaI}} \right)$$

$$= 1.6677785 x 10^{-3} mol NaI$$

The AgNO₃ is limiting, and will be used to finish the problem:

$$Mass~(g)~of~AgI = \Big(1.47145 x 10^{-3}~mol~AgNO_3\Big) \Bigg(\frac{1~mol~AgI}{1~mol~AgNO_3}\Bigg) \left(\frac{234.8~g~AgI}{1~mol~AgNO_3}\right) \Bigg(\frac{234.8~g~AgI}{1~mol~AgI}\Bigg)$$

$$= 0.345496 = 0.35 \text{ g AgI}$$

b)
$$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$$

$$\Delta H_{\text{rxn}}^{\circ} = \{1 \Delta H_{\text{f}}^{\circ} [\text{AgI}(s)]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{Ag}^{+}(aq)] + 1 \Delta H_{\text{f}}^{\circ} [\text{I}^{-}(aq)]\}$$

$$= [(1 \text{ mol})(-62.38 \text{ kJ/mol})] - [(1 \text{ mol})(105.9 \text{ kJ/mol}) + (1 \text{ mol})(-55.94 \text{ kJ/mol})]$$

$$= -112.3 \text{ kJ}$$

c)
$$\Delta H_{\text{rxn}}^{\circ} = q = c \text{ x mass x } \Delta T$$

$$\Delta T = \Delta H_{\text{rxn}}^{\circ} / c \text{ x mass} = \frac{\left[\left(\frac{112.3 \text{ kJ}}{\text{mol AgI}} \right) \left(\frac{1 \text{ mol AgI}}{1 \text{ mol AgNO}_3} \right) \left(1.47145 \text{ x} 10^{-3} \text{ mol AgNO}_3 \right) \right]}{\left(\frac{4.184 \text{ J}}{\text{g} \cdot \text{K}} \right) \left[\left(50.0 + 50.0 \right) \text{mL} \left(\frac{1.00 \text{ g}}{\text{mL}} \right) \right]} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right)$$

$$= 0.39494 = 0.39 \text{ K}$$

6.69 a) Mass (kg) of =
$$(5600 \text{ EJ}) \left(\frac{10^{18} \text{ J}}{1 \text{ EJ}}\right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) \left(\frac{1 \text{ mol CH}_4}{802 \text{ kJ}}\right) \left(\frac{16.04 \text{ g CH}_4}{1 \text{ mol CH}_4}\right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) = \mathbf{1.12x10^{14} \text{ kg CH}_4}$$

b) Years =
$$(5600 \text{ EJ}) \left(\frac{1 \text{ yr}}{4.0 \text{x} 10^2 \text{ EJ}} \right) = 14 \text{ yr}$$

c) Moles of
$$CH_4 = (1.00 \text{ qt}) \left(\frac{1 \text{ L}}{1.057 \text{ qt}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) \left(\frac{1.00 \text{ g}}{\text{mL}}\right) \left(\frac{4.184 \text{ J}}{\text{g}^{\circ}\text{C}}\right) \left((100.0 - 25.0)^{\circ}\text{C}\right) \left(\frac{1 \text{ kJ}}{10^{3} \text{ J}}\right) \left(\frac{1 \text{ mol } \text{CH}_4}{802 \text{ kJ}}\right) = 0.370172 \text{ mol } \text{CH}_4$$

$$Volume~(ft^3)~of~CH_4 = \left(0.370172~mol~CH_4\right) \left(\frac{16.04~g~CH_4}{1~mol~CH_4}\right) \left(\frac{1~L}{0.72~g~CH_4}\right) \left(\frac{10^{-3}~m^3}{1~L}\right) \left(\frac{35.3~ft^3}{1~m^3}\right)$$

$$= 0.291105 = 0.29 \text{ ft}^3$$

d) Volume =
$$\left(2x10^{13} \text{ J}\right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) \left(\frac{1 \text{ mol CH}_4}{802 \text{ kJ}}\right) \left(\frac{16.04 \text{ g CH}_4}{1 \text{ mol CH}_4}\right) \left(\frac{1 \text{ L}}{0.72 \text{ g CH}_4}\right) \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}}\right) \left(\frac{35.3 \text{ ft}^3}{1 \text{ m}^3}\right)$$

= $1.9611x10^7 = 2x10^7 \text{ ft}^3$

6.70 <u>Plan:</u> 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. To obtain the overall reaction, reverse the third reaction and multiply its coefficients by two and add to the first two reactions. When the third reaction is reversed, the sign of its enthalpy change is reversed from positive to negative.

Solution:

(1) C(graphite) +
$$2H_2(g) \rightarrow CH_4(g)$$
 $\Delta H_f^{\circ} = \Delta H_{rxn}^{\circ} = -74.9 \text{ kJ}$

(2)
$$CH_4(g) \rightarrow C(g) + 4H(g)$$
 $\Delta H_{atom}^{\circ} = \Delta H_{rxn}^{\circ} = 1660 \text{ kJ}$

(3)
$$H_2(g) \rightarrow 2H(g)$$
 $\Delta H_{\text{atom}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} = 432 \text{ kJ}$

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

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

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

$$\frac{4H(g) \rightarrow 2H_{2}(g)}{C(\text{graphite}) \rightarrow C(g)} \qquad \Delta H_{\text{rxn}}^{\circ} = -2(432 \text{ kJ}) = -864 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{atom}}^{\circ} = 721.1 = 721 \text{ kJ} \text{ per one mol C(graphite)}$$

- 6.71 The reaction is **exothermic**. The argon atoms in the chamber after the reaction are moving with greater kinetic energy, indicating an increase in temperature.
- 6.72 <u>Plan:</u> Write balanced chemical equations for the combustion reactions and use the standard heats of formation to determine the energy released.

Solution:

$$C_{6}H_{6}(g) + 15/2O_{2}(g) \rightarrow 6CO_{2}(g) + 3H_{2}O(g)$$

$$\Delta H_{rxn}^{\circ} = \{6 \Delta H_{f}^{\circ} [CO_{2}(g)] + 3 \Delta H_{f}^{\circ} [H_{2}O(g)]\} - \{1 \Delta H_{f}^{\circ} [C_{6}H_{6}(g)] + 15/2 \Delta H_{f}^{\circ} [O_{2}(g)]\}$$

$$\Delta H_{rxn}^{\circ} = [(6 \text{ mol})(-393.5 \text{ kJ/mol}) + (3 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(82.9 \text{ kJ/mol}) + (15/2 \text{ mol})(0.0 \text{ kJ/mol})]$$

$$= -3169.378$$

$$\Delta H_{\text{rxn}}^{\circ}$$
 per mole of CH = $\left(\frac{-3169.378 \text{ kJ}}{\text{mol C}_{6} \text{H}_{6}}\right) \left(\frac{1 \text{ mol C}_{6} \text{H}_{6}}{6 \text{ mol CH}}\right) = -528.2297 = -528.2 \text{ kJ/mol CH}$

$$C_2H_2(g) + 5/2O_2(g) \rightarrow 2CO_2(g) + H_2O(g)$$

$$\Delta H_{\rm rxn}^{\circ} = \{2 \, \Delta H_{\rm f}^{\circ} \, [{\rm CO}_2(g)] + 1 [\, \Delta H_{\rm f}^{\circ} \, [{\rm H}_2{\rm O}(g)]\} \\ - \{1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm O}_2(g)]\} \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm O}_2(g)]\} \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + 5/2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] + (1 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}_2{\rm H}_2(g)] \\ + (1$$

$$\Delta H_{rxn}^{\circ} = [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (1 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(227 \text{ kJ/mol}) + (5/2 \text{ mol})(0.0 \text{ kJ/mol})] = -1255.826 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^{\circ}$$
 per mole of CH = $\left(\frac{-1255.826 \text{ kJ}}{\text{mol C}_2\text{H}_2}\right) \left(\frac{1 \text{ mol C}_2\text{H}_2}{2 \text{ mol CH}}\right) = -627.913 = -628 \text{ kJ/mol CH}$

Thus, acetylene releases more energy per CH than benzene does.

6.73
$$\begin{aligned} & \text{H}_2\text{SO}_4(aq) \ + \ 2\text{NaOH}(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) \ + \ 2\text{H}_2\text{O}(l) \\ & 2\text{H}^+(aq) \ + \ 2\text{OH}^-(aq) \rightarrow \ 2\text{H}_2\text{O}(l) \\ & \Delta H_{\text{rxn}}^\circ = \{2\ \Delta H_{\text{f}}^\circ \ [\text{H}_2\text{O}(l)]\} - \{2\ \Delta H_{\text{f}}^\circ \ [\text{H}^+(aq)] \ + \ 2\ \Delta H_{\text{f}}^\circ \ [\text{OH}^-(aq)]\} \\ & = [(2\ \text{mol})(-285.84\ \text{kJ/mol})] - [(2\ \text{mol})(0\ \text{kJ/mol}) \ + \ (2\ \text{mol})(-229.94\ \text{kJ/mol})] \\ & = -111.8\ \text{kJ} \end{aligned}$$

1 mole of H₂SO₄ reacts with 2 moles of NaOH.

$$\begin{aligned} \text{Mass (g) of H_2SO$_4 solution} &= \Big(1 \text{ mol } H_2\text{SO}_4\Big) \!\! \left(\frac{1.00 \text{ L}}{0.50 \text{ mol } H_2\text{SO}_4} \right) \!\! \left(\frac{1.00 \text{ mL}}{10^{-3} \text{ L}} \right) \!\! \left(\frac{1.030 \text{ g}}{1.00 \text{ mL}} \right) \\ &= 2060 \text{ g } H_2\text{SO}_4 \text{ solution} \end{aligned}$$

Mass (g) of NaOH solution =
$$(2 \text{ mol NaOH}) \left(\frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}} \right) \left(\frac{100 \text{ g solution}}{40 \text{ g NaOH}} \right) = 200. \text{ g NaOH solution}$$

 $q = c \times \text{mass } \times \Delta T$

$$\Delta T = \frac{q}{c \text{ x mass}} = \frac{\left(111.8 \text{ kJ}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right)}{4.184 \text{ J/g} \, \text{°C}\left(\left(2060 + 200\right)\text{g}\right)} = 11.82 \, \text{°C}$$

$$31^{\circ}\text{C} + 11.82^{\circ}\text{C} = 42.82 = 43^{\circ}\text{C}$$

This temperature is above the temperature at which a flammable vapor could be formed so the temperature increase could cause the vapor to explode.

6.74 a)
$$2C_{12}H_{26}(l) + 37O_2(g) \rightarrow 24CO_2(g) + 26H_2O(g)$$

b)
$$\Delta H_{\text{rxn}}^{\circ} = \{24 \,\Delta H_{\text{f}}^{\circ} \,[\text{CO}_2(g)] + 26 \,\Delta H_{\text{f}}^{\circ} \,[\text{H}_2\text{O}(g)]\} - \{2 \,\Delta H_{\text{f}}^{\circ} \,[\text{C}_{12}\text{H}_{26}(g)] + 37 \,\Delta H_{\text{f}}^{\circ} \,[\text{O}_2(g)]\}$$

$$-1.50 \times 10^4 \text{ kJ} = [(24 \text{ mol})(-393.5 \text{ kJ/mol}) + (26 \text{ mol})(-241.826 \text{ kJ/mol})]$$

$$-[(2 \text{ mol}) \Delta H_f^{\circ} [C_{12}H_{26}(g)] + (37 \text{ mol})(0.0 \text{ kJ/mol})]$$

$$-1.50 \times 10^4 \text{ kJ} = -9444.0 \text{ kJ} + -6287.476 \text{ kJ} - [(2 \text{ mol}) \Delta H_f^{\circ} [C_{12} H_{26}(g)] + 0.0 \text{ kJ}]$$

$$-1.50 \times 10^4 \text{ kJ} = -15,731.476 \text{ kJ} - (2 \text{ mol}) \Delta H_f^{\circ} [C_{12} H_{26}(g)]$$

$$-1.50 \times 10^4 \text{ kJ} + 15,731.476 \text{ kJ} = -(2 \text{ mol}) \Delta H_f^{\circ} [C_{12} H_{26}(g)]$$

731.476 kJ =
$$-(2 \text{ mol}) \Delta H_{\rm f}^{\circ} [C_{12} H_{26}(g)]$$

$$\Delta H_{\rm f}^{\circ} [C_{12}H_{26}(g)] = -365.738 = -3.66 \times 10^2 \text{ kJ}$$

c) Heat (kJ) =
$$(0.50 \text{ gal}) \left(\frac{4 \text{ qt}}{1 \text{ gal}}\right) \left(\frac{1 \text{ L}}{1.057 \text{ qt}}\right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right) \left(\frac{0.749 \text{ g } C_{12} H_{26}}{\text{mL}}\right) \left(\frac{1 \text{ mol } C_{12} H_{26}}{170.33 \text{ g } C_{12} H_{26}}\right) \left(\frac{-1.50 \text{x} 10^4 \text{ kJ}}{2 \text{ mol } C_{12} H_{26}}\right) = -6.2403 \text{x} 10^4 = -\textbf{6.2} \textbf{x} 10^4 \text{ kJ}$$

d) Volume (gal) =
$$\left(1250. \text{ Btu}\right) \left(\frac{1.055 \text{ kJ}}{1 \text{ Btu}}\right) \left(\frac{0.50 \text{ gal}}{6.2403 \text{x} 10^4 \text{ kJ}}\right) = 0.010566 = \textbf{1.1x} \textbf{10}^{-2} \text{ gal}$$

6.75 Use Hess's Law:

a) 1)
$$C(coal) + H_2O(g) \rightarrow CO(g) + H_2(g)$$
 $\Delta H_{rxn}^{\circ} = 129.7 \text{ kJ}$

2)
$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
 $\Delta H_{rxn}^{\circ} = -41 \text{ kJ}$

3)
$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$$
 $\Delta H_{rxn}^{\circ} = -206 \text{ kJ}$

Equation 1) must be multiplied by 2 and then the reactions are added:

1)
$$2C(coal) + 2H_2O(g) \rightarrow \frac{2CO(g)}{2} + \frac{2H_2(g)}{2} \Delta H_{rxn}^{\circ} = 2(129.7 \text{ kJ})$$

2)
$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
 $\Delta H_{rxn}^{\circ} = -41 \text{ kJ}$

3)
$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$$
 $\Delta H_{rxn}^{\circ} = -206 \text{ kJ}$

$$2C(coal) + 2H_2O(g) \rightarrow CH_4(g) + CO_2(g)$$

b) The total may be determined by doubling the value for equation 1) and adding to the other two values.

$$\Delta H_{\text{rxn}}^{\circ} = 2(129.7 \text{ kJ}) + (-41 \text{ kJ}) + (-206 \text{ kJ}) = 12.4 = 12 \text{ kJ}$$

c) Calculating the heat of combustion of CH₄:

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

$$\Delta H_{\mathrm{comb}}^{\circ} = \left\{1 \, \Delta H_{\mathrm{f}}^{\circ} \left[\mathrm{CO}_{2}(g)\right] + 2 \, \Delta H_{\mathrm{f}}^{\circ} \left[\mathrm{H}_{2}\mathrm{O}(g)\right]\right\} - \left\{1 \, \Delta H_{\mathrm{f}}^{\circ} \left[\mathrm{CH}_{4}(g)\right]\right\} - 2 \, \Delta H_{\mathrm{f}}^{\circ} \left[\mathrm{O}_{2}(g)\right]\right\}$$

$$\Delta H_{\text{comb}}^{\circ} = [(1 \text{ mol})(-395.5 \text{ kJ/mol}) + (2 \text{ mol})(-241.826 \text{ kJ/mol})]$$

-[(1 mol)(-74.87kJ/mol) - (2 mol)(0.0 kJ/mol)]

$$= -804.282 \text{ kJ/mol CH}_4$$

Total heat for gasification of 1.00 kg coal:

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

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

$$\Delta H^{\circ} = \left(1.00 \text{ kg coal}\right) \left(\frac{10^{3} \text{ g}}{1 \text{ kg}}\right) \left(\frac{1 \text{ mol coal}}{12.00 \text{ g coal}}\right) \left(\frac{1 \text{ mol CH}_{4}}{2 \text{ mol coal}}\right) \left(\frac{-804.282 \text{ kJ}}{1 \text{ mol CH}_{4}}\right)$$

=-33511.75 kJ

Total heat = $516.667 \text{ kJ} - 33511.75 \text{ kJ} = 32995.083 = 3.30 \text{ x } 10^4 \text{ kJ}$

6.76
$$PCl_{3}(g) \rightarrow \frac{1}{4}P_{4}(s) + \frac{3}{2}Cl_{2}(g) \qquad \Delta H = -\frac{1}{4}(-1280 \text{ kJ}) = 320 \text{ kJ}$$

$$\frac{1}{4}P_{4}(s) + \frac{5}{2}Cl_{2}(g) \rightarrow PCl_{5}(g) \qquad \Delta H = \frac{1}{4}(-1774 \text{ kJ}) = -443.5 \text{ kJ}$$

$$Total: PCl_{3}(g) + Cl_{2}(g) \rightarrow PCl_{5}(g) \qquad \Delta H = -123.5 = -124 \text{ kJ}$$

6.77 a) Energy (kJ) =
$$(2 \text{ oz}) \left(\frac{28.4 \text{ g}}{1.00 \text{ oz}} \right) \left(\frac{4.0 \text{ Cal}}{1.0 \text{ g}} \right) \left(\frac{1 \text{ kcal}}{1 \text{ Cal}} \right) \left(\frac{4.184 \text{ kJ}}{1 \text{ kcal}} \right) = 950.60 = \mathbf{1} \times \mathbf{10}^3 \text{ kJ}$$

b) Energy = E = mass x g x height = mgh

$$h = \frac{E}{mg} = \frac{(950.60 \text{ kJ})}{(58 \text{ kg})(9.8 \text{ m/s}^2)} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}}\right) = 1672.41 = 2 \text{ x } 10^3 \text{ m}$$

- c) Energy is also converted to heat.
- 6.78 <u>Plan:</u> Heat of reaction is calculated using the relationship $\Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f (products)}}^{\circ} - \sum n \Delta H_{\text{f (reactants)}}^{\circ}$. The heats of formation for all of the species, except SiCl₄, are found in Appendix B. Use reaction 3, with its given $\Delta H_{\text{rxn}}^{\circ}$, to find the heat of formation of SiCl₄(g). Once the heat of formation of SiCl₄ is known, the heat of reaction of the other two reactions can be calculated. When reactions 2 and 3 are added to obtain a fourth reaction, the heats of reaction of reactions 2 and 3 are also added to obtain the heat of reaction for the fourth reaction.

Solution:

a) (3)
$$SiCl_4(g) + 2H_2O(g) \rightarrow SiO_2(s) + 4HCl(g)$$

$$\Delta H_{rxn}^{\circ} = \{1 \Delta H_{f}^{\circ} [SiO_2(s)] + 4 \Delta H_{f}^{\circ} [HCl(g)]\} - \{1 \Delta H_{f}^{\circ} [SiCl_4(g)] + 2 \Delta H_{f}^{\circ} [H_2O(g)]\}$$

$$-139.5 \text{ kJ} = [(1 \text{ mol})(-910.9 \text{ kJ/mol}) + (4 \text{ mol})(-92.31 \text{ kJ/mol})] - [\Delta H_{f}^{\circ} [SiCl_4(g)] + (2 \text{ mol})(-241.826 \text{ kJ/mol})]$$

$$-139.5 \text{ kJ} = [(1 \text{ mol})(-910.9 \text{ kJ/mol}) + (4 \text{ mol})(-92.31 \text{ kJ/mol})] - [\Delta H_f [SiCl_4(g)] + (2 \text{ mol})(-241.826 \text{ kJ/mol})]$$

$$-139.5 \text{ kJ} = -1280.14 - [\Delta H_{\text{f}}^{\circ} [\text{SiCl}_4(g)] + (-483.652 \text{ kJ})]$$

1140.64 kJ =
$$-\Delta H_{\rm f}^{\circ}$$
 [SiCl₄(g)] + 483.652 kJ

$$\Delta H_{\rm f}^{\circ} [{\rm SiCl_4}(g)] = -656.988 \, {\rm kJ/mol}$$

The heats of reaction for the first two steps can now be calculated.

1) $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(g)$

$$\Delta H_{\text{rxn}}^{\circ} = \{1 \Delta H_{\text{f}}^{\circ} [\text{SiCl}_{4}(g)]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{Si}(s)] + 2 \Delta H_{\text{f}}^{\circ} [\text{Cl}_{2}(g)]\}$$

$$= [(1 \text{ mol})(-656.988 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})] = -656.988 = -657.0 \text{ kJ}$$
2) SiO (a) + 2C(araphita) +

2)
$$SiO_2(s) + 2C(graphite) + 2Cl_2(g) \rightarrow SiCl_4(g) + 2CO(g)$$

$$\Delta H_{\text{rxn}}^{\circ} = \{1 \, \Delta H_{\text{f}}^{\circ} \left[\text{SiCl}_4(g) \right] + 2 \, \Delta H_{\text{f}}^{\circ} \left[\text{CO}(g) \right] \}$$

$$-\left\{1\,\Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{SiO}_{2}(g)\right]+2\,\Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{C}(\mathrm{graphite})\right]+2\,\Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{Cl}_{2}(g)\right]\right\}$$

=
$$[(1 \text{ mol})(-656.988 \text{ kJ/mol}) + (2 \text{ mol})(-110.5 \text{ kJ/mol})]$$

$$- [(1 \text{ mol})(-910.9 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})]$$

$$= 32.912 = 32.9 \text{ kJ}$$

b) Adding reactions 2 and 3 yields:

(2)
$$\frac{\text{SiO}_2(s)}{2} + 2\text{C(graphite)} + 2\text{Cl}_2(g) \rightarrow \frac{\text{SiCl}_4(g)}{2} + 2\text{CO}(g)$$
 $\Delta H_{\text{rxn}}^{\circ} = 32.912 \text{ kJ}$

(3)
$$\frac{\text{SiCl}_4(g)}{\text{SiCl}_4(g)} + 2\text{H}_2\text{O}(g) \rightarrow \frac{\text{SiO}_2(g)}{\text{SiO}_2(g)} + 4\text{HCl}(g)$$
 $\Delta H_{\text{rxn}}^{\circ} = -139.5 \text{ kJ}$

$$2C(\text{graphite}) + 2Cl_2(g) + 2H_2O(g) \rightarrow 2CO(g) + 4HCl(g)$$
 $\Delta H_{\text{rxn}}^{\circ} = -106.588 \text{ kJ} = -106.6 \text{ kJ}$

Confirm this result by calculating ΔH_{rxn}^0 using Appendix B values.

$$2C(graphite) + 2Cl_2(g) + 2H_2O(g) \rightarrow 2CO(g) + 4HCl(g)$$

$$\begin{split} \Delta H_{\rm rxn}^{\circ} &= \{2 \, \Delta H_{\rm f}^{\circ} \, [{\rm CO}(g)] + 4 \, \Delta H_{\rm f}^{\circ} \, [{\rm HCl}(g)]\} - \{2 \, \Delta H_{\rm f}^{\circ} \, [{\rm C}({\rm graphite})] + 2 \, \Delta H_{\rm f}^{\circ} \, [{\rm Cl}_2(g)] + 2 \, \Delta H_{\rm f}^{\circ} \, [{\rm H}_2{\rm O}(g)]\} \\ &= [(2 \, {\rm mol})(-110.5 \, {\rm kJ/mol}) + (4 \, {\rm mol})(-92.31 \, {\rm kJ}) \\ &\qquad \qquad - [(2 \, {\rm mol})(0 \, {\rm kJ/mol}) + (2 \, {\rm mol})(0 \, {\rm kJ/mol}) + (2 \, {\rm mol})(-241.826 \, {\rm kJ/mol})] \end{split}$$

$$=-106.588 = -106.6 \text{ kJ}$$

6.79 This is a Hess's Law problem. $\Delta H_{\rm f}^{\circ}$ of HCl $[1/2{\rm H}_2(g) + 1/2{\rm Cl}_2(g) \rightarrow {\rm HCl}(g)]$ must be found using the following equations:

1)
$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

$$\Delta H_{\rm rxn}^{\circ} = -91.8 \text{ kJ}$$

2)
$$N_2(g) + 4H_2(g) + Cl_2(g) \rightarrow 2NH_4Cl(s)$$

$$\Delta H_{\rm rxn}^{\circ} = -628.8 \text{ kJ}$$

3)
$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

$$\Delta H_{\rm rxn}^{\circ} = -176.2 \text{ kJ}$$

Reverse equation 1 and divide by 2; divide equation 2 by 2; finally, reverse equation 3. This gives:

1)
$$NH_3(g) \rightarrow 1/2N_2(g) + 3/2H_2(g)$$

$$\Delta H_{\rm rxn}^{\circ} = -1/2(-91.8 \text{ kJ}) = 45.9 \text{ kJ}$$

2)
$$\frac{1/2N_2(g)}{g} + 2H_2(g) + 1/2Cl_2(g) \rightarrow NH_4Cl(s)$$

$$\Delta H_{\rm rxn}^{\circ} = 1/2(-628.8 \text{ kJ}) = -314.4 \text{ kJ}$$

3)
$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

$$\Delta H_{\rm rxn}^{\circ} = -(-176.2 \text{ kJ}) = 176.2 \text{ kJ}$$

$$1/2H_2(g) + 1/2Cl_2(g) \rightarrow HCl(g)$$

$$H_{\rm rxn}^{\circ} = -92.3 \text{ kg}$$

6.80 a) $-q_{\text{rxn}} = q_{\text{water}} + q_{\text{calorimeter}}$

$$-q_{\rm rxn} = (50.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) \left(\frac{2.00 \text{ mol}}{\text{L}}\right) \left(\frac{-57.32 \text{ kJ}}{\text{mol}}\right) = 5.732 \text{ kJ}$$

 $q_{\text{water}} = (\text{mass})(c)(\Delta T)$

$$\left[100.0 \text{ mL} \left(\frac{1.04 \text{ g}}{\text{mL}}\right)\right] \left(3.93 \frac{\text{J}}{\text{g}^{\circ}\text{C}}\right) \left(\left(30.4 - 16.9\right)^{\circ}\text{C}\right) \left(\frac{1 \text{ kJ}}{10^{3} \text{ J}}\right) = 5.51772 \text{ kJ}$$

 $q_{\text{calorimeter}} = q_{\text{rxn}} - q_{\text{water}} = (5.732 \text{ kJ}) - (5.51772 \text{ kJ}) = 0.21428 \text{ kJ}$

 $C_{calorimeter} = q_{calorimeter}/\Delta T = (0.21428 \text{ kJ})/(30.4 - 16.9)^{\circ}C = 0.01587 = 0.016 \text{ kJ/}^{\circ}C$

b) Mole HCl =
$$(100.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{1.00 \text{ mol HCl}}{\text{L}} \right) = 0.100 \text{ mol HCl}$$

Mole Zn =
$$(1.3078 \text{ g Zn}) \left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}} \right) = 0.01999 \text{ mol Zn}$$

Zn is the limiting reactant.

 $-q_{\rm rxn} = q_{\rm water} + q_{\rm calorimeter}$

$$= \left[100.0 \text{ mL} \left(\frac{1.015 \text{ g}}{\text{mL}}\right) + 1.3078 \text{ g}\right] \left(3.95 \frac{\text{J}}{\text{g}^{\circ}\text{C}}\right) \left(\left(24.1 - 16.8\right)^{\circ}\text{C}\right) \left(\frac{1 \text{ kJ}}{10^{3} \text{ J}}\right) + \left(0.01587 \frac{\text{kJ}}{^{\circ}\text{C}}\right) \left(\left(24.1 - 16.8\right)^{\circ}\text{C}\right) = 3.0803 \text{ kJ}$$

 $\Delta H_{\text{rxn}}^{\circ} = (-3.0803 \text{ kJ})/(0.01999 \text{ mol Zn}) = -154.1 = -1.5 \text{x} 10^2 \text{ kJ/mol}$

c)
$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

$$\Delta H_{\text{rxn}}^{\circ} = \{1 \, \Delta H_{\text{f}}^{\circ} \, [\text{ZnCl}_{2}(aq)] + 1[\, \Delta H_{\text{f}}^{\circ} \, \text{H}_{2}(g)]\} - \{1 \, \Delta H_{\text{f}}^{\circ} \, [\text{Zn}(s)] + 2 \, \Delta H_{\text{f}}^{\circ} \, [\text{HCl}(aq)]\}$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol})(-4.822 \text{x} 10^2 \text{ kJ/mol}) + (1 \text{ mol})(0.0 \text{ kJ/mol})]$$

$$-[(1 \text{ mol})(0.0 \text{ kJ/mol}) + (2 \text{ mol})(-1.652 \text{x} 10^2 \text{ kJ/mol})]$$

 $\Delta H_{\rm rxn}^{\circ} = -151.8 \text{ kJ}$

Error =
$$\left| \frac{-151.8 - (-154.1)}{-151.8} \right| (100\%) = 1.515 = 2\%$$

6.81 Plan: Use PV = nRT to find the initial volume of nitrogen gas at 0°C and then the final volume at 819°C. Then the relationship $w = -P\Delta V$ can be used to calculate the work of expansion.

a)
$$PV = nRT$$

Initial volume at 0°C + 273 = 273 K =
$$V = \frac{nRT}{P} = \frac{(1 \text{ mol})(0.0821 \frac{\text{L•atm}}{\text{mol•K}})(273 \text{ K})}{(1.00 \text{ atm})} = 22.4133 \text{ L}$$

Final volume at 819°C + 273 = 1092 K =
$$V = \frac{nRT}{P} = \frac{(1 \text{ mol}) \left(0.0821 \frac{\text{L•atm}}{\text{mol•K}}\right) (1092 \text{ K})}{(1.00 \text{ atm})} = 89.6532 \text{ L}$$

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 89.6532 \text{ L} - 22.4133 \text{ L} = 67.2399 \text{ L}$$

 $w = -P\Delta V = -(1 \text{ atm}) \times 67.2399 \text{ L} = -67.2399 \text{ atm} \cdot \text{L}$

$$w (J) = (-67.2399 \text{ atm} \cdot L) \left(\frac{1 \text{ J}}{9.87 \text{ x } 10^{-3} \text{ atm} \cdot L} \right) = -6812.553 = -6.81 \text{x} \cdot 10^{3} \text{ J}$$

b) $q = c \times \text{mass } \times \Delta T$

Mass (g) of N₂ =
$$(1 \text{ mol N}_2) \left(\frac{28.02 \text{ g}}{1 \text{ mol N}_2} \right) = 28.02 \text{ g}$$

$$\Delta T = \frac{q}{(c)(\text{mass})} = \frac{6.812553 \times 10^3 \text{ J}}{(28.02 \text{ g})(1.00 \text{ J/g} \cdot \text{K})} = 243.132 = 243 \text{ K} = 243^{\circ} \text{C}$$

6.82 <u>Plan:</u> Note the numbers of moles of the reactants and products in the target equation and manipulate equations 1-5 and their $\Delta H_{\text{rxn}}^{\circ}$ values so that these equations sum to give the target equation. Then the manipulated $\Delta H_{\text{rxn}}^{\circ}$ values will add to give the $\Delta H_{\text{rxn}}^{\circ}$ value of the target equation.

Solution:

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 yields the desired reactants and products, with some undesired intermediates:

Reverse (1)
$$N_2O_3(g) \rightarrow NO(g) + NO_2(g) \qquad \Delta H_{rxn}^{\circ} = -(-39.8 \text{ kJ}) = 39.8$$

kJ

Multiply (3) by 2
$$4\text{NO}_2(g) \rightarrow 2\text{N}_2\text{O}_4(g)$$
 $\Delta H_{\text{rxn}}^{\circ} = 2(-57.2 \text{ kJ}) = -114.4 \text{ kJ}$

(5)
$$N_2O_5(s) \rightarrow N_2O_5(g) \qquad \Delta H_{rxn}^{\circ} = (54.1 \text{ kJ}) = 54.1$$

kJ

$$N_2O_3(g) + 4NO_2(g) + N_2O_5(s) \rightarrow NO(g) + NO_2(g) + 2N_2O_4(g) + N_2O_5(g)$$

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:

Reverse (1)
$$N_2O_3(g) \to \frac{NO(g)}{HO_2(g)} + \frac{NO_2(g)}{HO_2(g)} \qquad \Delta H_{rxn}^{\circ} = -(-39.8 \text{ kJ}) = 39.8 \text{ kJ}$$

Multiply (3) by 2
$$4NO_2(g) \rightarrow 2N_2O_4(g)$$
 $\Delta H_{rxn}^{\circ} = 2(-57.2 \text{ kJ}) = -114.4 \text{ kJ}$

(5)
$$N_2O_5(s) \rightarrow N_2O_5(g)$$
 $\Delta H_{rxn}^{\circ} = 54.1 \text{ kJ}$

Reverse (2)
$$N_2O_5(g) \to NO(g) + NO_2(g) + O_2(g) \to \Delta H_{rxn}^{\circ} = -(-112.5 \text{ kJ}) = 112.5$$

(4)
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
 $\Delta H_{TXII}^{\circ} = -114.2 \text{ kJ}$
Total: $N_2O_3(g) + N_2O_5(s) \rightarrow 2N_2O_4(g)$ $\Delta H_{TXII}^{\circ} = -22.2 \text{ kJ}$

6.83
$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

$$\Delta H_{\text{rxn}}^{\circ} = \{1 \Delta H_{\text{f}}^{\circ} [\text{CH}_{3}\text{OH}(l)]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{CO}(g)] + 2 \Delta H_{\text{f}}^{\circ} [\text{H}_{2}(g)]\}$$

$$= [(1 \text{ mol})(-238.6 \text{ kJ/mol})] - [(1 \text{ mol})(-110.5 \text{ kJ mol}) + (2 \text{ mol})(0.0 \text{ kJ/mol})]$$

$$= -128.1 \text{ kJ}$$

Find the limiting reactant:

Moles of CO =
$$\frac{PV}{RT} = \frac{(112 \text{ kPa})(15.0 \text{ L})}{(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})((273 + 85) \text{ K})} \left(\frac{1 \text{ atm}}{101.325 \text{ kPa}}\right) = 0.5641135 \text{ mol CO}$$

Moles of CH₃OH from CO =
$$(0.5641135 \text{ mol CO}) \left(\frac{1 \text{ mol CH}_3\text{OH}}{1 \text{ mol CO}} \right) = 0.5641135 \text{ mol CH}_3\text{OH}$$

Moles of
$$H_2 = \frac{PV}{RT} = \frac{(744 \text{ torr})(18.5 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \left((273 + 75) \text{K}\right)} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.6338824 \text{ mol } H_2$$

Moles of CH₃OH from H₂ =
$$(0.6338824 \text{ mol H}_2) \left(\frac{1 \text{ mol CH}_3\text{OH}}{2 \text{ mol H}_2} \right) = 0.3169412 \text{ mol CH}_3\text{OH}$$

H₂ is limiting.

Heat (kJ) =
$$(0.6338824 \text{ mol H}_2) \left(\frac{-128.1 \text{ kJ}}{2 \text{ mol H}_2} \right) = -40.6002 = -40.6002 = -40.6 \text{ kJ}$$

6.84 <u>Plan:</u> First find the heat of reaction for the combustion of methane. The enthalpy change of a reaction is the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants. Since the

 ΔH_f° values (Appendix B) are reported as energy per one mole, use the appropriate stoichiometric coefficient to reflect the higher number of moles. Convert the mass of methane to moles and multiply that mole number by the heat of combustion.

Solution:

a) The balanced chemical equation for this reaction is:

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

$$\begin{split} \Delta H_{\text{rxn}}^{\circ} &= \{1 \, \Delta H_{\text{f}}^{\circ} \, [\text{CO}_{2}(g)] + 2 \, \Delta H_{\text{f}}^{\circ} \, [\text{H}_{2}\text{O}(g)]\} - \{1 \, \Delta H_{\text{f}}^{\circ} \, [\text{CH}_{4}(g)] + 2 \, \Delta H_{\text{f}}^{\circ} \, [\text{O}_{2}(g)]\} \\ &= [(1 \, \text{mol})(-393.5 \, \text{kJ/mol}) + (2 \, \text{mol})(-241.826 \, \text{kJ/mol})] - [(1 \, \text{mol})(-74.87 \, \text{kJ/mol}) + (2 \, \text{mol})(0.0 \, \text{kJ/mol})] \\ &= -802.282 \, \text{kJ} \end{split}$$

Moles of CH₄ =
$$(25.0 \text{ g CH}_4) \left(\frac{1 \text{ mol}}{16.04 \text{ g CH}_4} \right) = 1.5586 \text{ mol CH}_4$$

Heat (kJ) =
$$(1.5586 \text{ mol CH}_4) \left(\frac{-802.282 \text{ kJ}}{1 \text{ mol CH}_4} \right) = -1250.4 = -1.25 \text{x} \cdot 10^3 \text{ kJ}$$

b) The heat released by the reaction is "stored" in the gaseous molecules by virtue of their specific heat capacities, c, using the equation q = c x mass x ΔT . 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_2 and 21% O_2 , and there is leftover N_2 .

Moles of
$$CO_2(g) = (1.5586 \text{ mol CH}_4) \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} \right) = 1.5586 \text{ mol CO}_2(g)$$

Moles of
$$H_2O(g) = (1.5586 \text{ mol CH}_4) \left(\frac{2 \text{ mol H}_2O}{1 \text{ mol CH}_4} \right) = 3.1172 \text{ mol H}_2O(g)$$

Moles of
$$O_2(g)$$
 reacted = $(1.5586 \text{ mol CH}_4) \left(\frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4}\right) = 3.1172 \text{ mol O}_2(g)$

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

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

Moles of
$$N_2(g) = (3.1172 \text{ mol } O_2 \text{ reacted}) \left(\frac{0.79 \text{ mol } N_2}{0.21 \text{ mol } O_2} \right) = 11.72661 \text{ mol } N_2$$

```
\begin{split} q &= c \text{ x mass x } \Delta T \\ q &= \left(1250.4 \text{ kJ}\right) \!\! \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) = 1.2504 \text{x} 10^6 \text{ J} \\ 1.2504 \text{x} 10^6 \text{ J} &= (1.5586 \text{ mol CO}_2)(57.2 \text{ J/mol}^\circ\text{C})(T_{\text{final}} - 0.0)^\circ\text{C} \\ &\quad + (3.1172 \text{ mol H}_2\text{O})(36.0 \text{ J/mol}^\circ\text{C})(T_{\text{final}} - 0.0)^\circ\text{C} \\ &\quad + (11.72661 \text{ mol N}_2)(30.5 \text{ J/mol}^\circ\text{C})(T_{\text{final}} - 0.0)^\circ\text{C} \\ 1.2504 \text{x} 10^6 \text{ J} &= 89.15192 \text{ J/}^\circ\text{C}(T_{\text{final}}) + 112.2192 \text{ J/}^\circ\text{C}(T_{\text{final}}) + 357.6616 \text{ J/}^\circ\text{C}(T_{\text{final}}) \\ 1.2504 \text{x} 10^6 \text{ J} &= (559.03272 \text{ J/}^\circ\text{C})T_{\text{final}} \\ T_{\text{final}} &= (1.2504 \text{x} 10^6 \text{ J})/(559.0324 \text{ J/}^\circ\text{C}) = 2236.72 = \textbf{2.24x} \textbf{10}^3^\circ\text{C} \end{split}
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