CHAPTER 6 THERMOCHEMISTRY: ENERGY FLOW AND CHEMICAL CHANGE

CHEMICAL CONNECTIONS BOXED READING PROBLEMS

B6.1 Plan: Convert the given mass in kg to g, divide by the molar mass to obtain moles, and convert moles to kJ of energy. Sodium sulfate decahydrate will transfer 354 kJ/mol.

Solution:

\[
\text{Heat (kJ)} = \left( 500.0 \text{ kg Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}{322.21 \text{ g Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}} \right) \left( \frac{354 \text{ kJ}}{1 \text{ mol Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}} \right)
\]

\[
= -5.4933 \times 10^5 = -5.49 \times 10^5 \text{ kJ}
\]

B6.2 Plan: Three reactions are given. Equation 1) must be multiplied by 2, and then the reactions can be added, canceling substances that appear on both sides of the arrow. Add the \( \Delta H^\circ_{\text{rxn}} \) values for the three reactions to get the \( \Delta H^\circ_{\text{rxn}} \) for the overall gasification reaction of 2 moles of coal. Use the relationship \( \Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f (\text{products}) - \sum n \Delta H^\circ_f (\text{reactants}) \) to find the heat of combustion of 1 mole of methane. Then find the \( \Delta H^\circ_{\text{rxn}} \) for the gasification of 1.00 kg of coal and \( \Delta H^\circ_{\text{rxn}} \) for the combustion of the methane produced from 1.00 kg of coal and sum these values.

Solution:

a) 1) \( 2\text{C(coal)} + 2\text{H}_2\text{O(g)} \rightarrow 2\text{CO(g)} + 2\text{H}_2\text{(g)} \) \( \Delta H^\circ_{\text{rxn}} = 2(129.7 \text{ kJ}) \)

b) The total may be determined by doubling the value for equation 1) and adding to the other two values. \( \Delta H^\circ_{\text{rxn}} = 2(129.7 \text{ kJ}) + (-41 \text{ kJ}) + (-206 \text{ kJ}) = 12.4 = 12 \text{ kJ} \)

c) Calculating the heat of combustion of \( \text{CH}_4 \):

\( \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O(g)} \)

\( \Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f (\text{products}) - \sum n \Delta H^\circ_f (\text{reactants}) \)

\( \Delta H^\circ_{\text{rxn}} = [(1 \text{ mol CO}_2)(\Delta H^\circ_f \text{ of CO}_2) + (2 \text{ mol H}_2\text{O})(\Delta H^\circ_f \text{ of H}_2\text{O})] - [(1 \text{ mol CH}_4)(\Delta H^\circ_f \text{ of CH}_4) + (2 \text{ mol O}_2)(\Delta H^\circ_f \text{ of O}_2)] \)

\( \Delta H^\circ_{\text{rxn}} = [(1 \text{ mol})(-395.5 \text{ kJ/mol}) + (2 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-74.87 \text{ kJ/mol}) + (2 \text{ mol })(0.0 \text{ kJ/mol})] \)

\( \Delta H^\circ_{\text{rxn}} = -804.282 \text{ kJ/mol CH}_4 \)

Total heat for gasification of 1.00 kg coal:

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

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

\( \Delta H = (1.00 \text{ kg coal}) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol coal}}{12.00 \text{ g coal}} \right) \left( \frac{1 \text{ mol CH}_4}{2 \text{ mol coal}} \right) \left( \frac{-804.282 \text{ kJ}}{1 \text{ mol CH}_4} \right) = -33511.75 \text{ kJ} \)

Total heat = 516.667 kJ + (–33511.75 kJ) = –32995.083 = –3.30 \times 10^4 \text{ kJ}
END–OF–CHAPTER PROBLEMS

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 \( q \) negative.

6.3 \( \Delta E = q + w = w \), since \( q = 0 \).
Thus, the change in work equals the change in internal energy.

6.4 Plan: Remember that an increase in internal energy is a result of the system (body) gaining heat or having work done on it and a decrease in internal energy is a result of the system (body) losing heat or doing work.
Solution:
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 cell)

6.6 Plan: Use the law of conservation of energy.
Solution:
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  (impact)
Kinetic energy  (falling text)
Potential energy  (raised text)
Mechanical energy  (raising of text)
Chemical energy  (biological process to move muscles)

6.8 Plan: 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.
Solution:
\( \Delta E = q + w \)
\( \Delta E = (+425 \text{ J}) + (-425 \text{ J}) = 0 \text{ J} \)

6.9 \( q + w = -255 \text{ cal} + (-428 \text{ cal}) = -683 \text{ cal} \)

6.10 Plan: The change in a system’s energy is \( \Delta E = q + w \). 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. Convert work in calories to work in joules.
Solution:
Work (J) = \( (530 \text{ cal}) \left( \frac{4.184 \text{ J}}{1 \text{ cal}} \right) = 2217.52 \text{ J} \)
\( \Delta E = q + w = -675 \text{ J} + 2217.52 \text{ J} = 1542.52 = 1.54 \times 10^3 \text{ J} \)
6.11 \[ \Delta E = q + w = (0.615 \text{ kJ}) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) + \left( 0.247 \text{ kcal} \right) \left( \frac{10^3 \text{ cal}}{1 \text{ kcal}} \right) \left( \frac{4.184 \text{ J}}{1 \text{ cal}} \right) = 1648.4 = 1.65 \times 10^3 \text{ J} \]

6.12 **Plan:** Convert $6.6 \times 10^9 \text{ J}$ to the other units using conversion factors.

**Solution:**

\[ \text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 6.6 \times 10^9 \text{ J} \]

(2.0 tons)

a) \[ \Delta E (\text{kJ}) = (6.6 \times 10^9 \text{ J}) \left( \frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = 6.6 \times 10^7 \text{ kJ} \]

b) \[ \Delta E (\text{cal}) = (6.6 \times 10^9 \text{ J}) \left( \frac{1 \text{ cal}}{4.184 \text{ J}} \right) \left( \frac{1 \text{ kcal}}{10^3 \text{ cal}} \right) = 1.577 \times 10^7 = 1.6 \times 10^7 \text{ kcal} \]

c) \[ \Delta E (\text{Btu}) = (6.6 \times 10^9 \text{ J}) \left( \frac{1 \text{ Btu}}{1055 \text{ J}} \right) = 6.256 \times 10^7 = 6.3 \times 10^7 \text{ Btu} \]

6.13 \[ \text{CaCO}_3(s) + 9.0 \times 10^6 \text{ kJ} \rightarrow \text{CaO(s)} + \text{CO}_2(\text{g}) \]

(5.0 tons)

a) \[ \Delta E (\text{J}) = (9.0 \times 10^6 \text{ kJ}) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 9.0 \times 10^9 \text{ J} \]

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 \[ \Delta E (\text{J}) = (4.1 \times 10^3 \text{ Calorie}) \left( \frac{10^3 \text{ cal}}{1 \text{ Calorie}} \right) \left( \frac{4.184 \text{ J}}{1 \text{ cal}} \right) = 1.7154 \times 10^7 = 1.7 \times 10^7 \text{ J} \]

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

6.15 **Plan:** 1.0 lb of body fat is equivalent to about $4.1 \times 10^3$ Calories. Convert Calories to kJ with the appropriate conversion factors.

**Solution:**

\[ \text{Time} = (1.0 \text{ lb}) \left( \frac{4.1 \times 10^3 \text{ Cal}}{1 \text{ lb}} \right) \left( \frac{10^3 \text{ cal}}{1 \text{ Cal}} \right) \left( \frac{4.184 \text{ J}}{1 \text{ cal}} \right) \left( \frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \left( \frac{1 \text{ h}}{1950 \text{ kJ}} \right) = 8.79713 = 8.8 \text{ h} \]

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  **Plan:** 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) **Exothermic,** 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  $\Delta H = \Delta E + P \Delta V$ (constant $P$)

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  **Plan:** An exothermic reaction releases heat, so the reactants have greater $H (H_{\text{initial}})$ than the products ($H_{\text{final}}$).

$\Delta H = H_{\text{final}} - H_{\text{initial}} < 0$.

**Solution:**

![Diagram of exothermic reaction](Diagram)

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

6.23  ![Diagram of endothermic reaction](Diagram)

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

6.24  **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 ($H_{\text{final}}$).
Solution:

a) Combustion of ethane: \(2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(g) + \text{heat}\)

\[
\begin{align*}
\text{Increasing, } H \\
\text{2C}_2\text{H}_6 + 7\text{O}_2 \text{ (initial)} & \quad \Delta H = (-), \text{ (exothermic)} \\
\text{4CO}_2 + 6\text{H}_2\text{O} \text{ (final)}
\end{align*}
\]

b) Freezing of water: \(\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s) + \text{heat}\)

\[
\begin{align*}
\text{Increasing, } H \\
\text{H}_2\text{O}(l) \text{ (initial)} & \quad \Delta H = (-), \text{ (exothermic)} \\
\text{H}_2\text{O}(s) \text{ (final)}
\end{align*}
\]

6.25 a) \(\text{Na}(s) + 1/2\text{Cl}_2(g) \rightarrow \text{NaCl}(s) + \text{heat}\)

\[
\begin{align*}
\text{Increasing, } H \\
\text{Na}(s) + 1/2\text{Cl}_2 \text{ (initial)} & \quad \Delta H = (-), \text{ (exothermic)} \\
\text{NaCl}(s)
\end{align*}
\]

b) \(\text{C}_6\text{H}_6(l) + \text{heat} \rightarrow \text{C}_6\text{H}_6(g)\)

\[
\begin{align*}
\text{Increasing, } H \\
\text{C}_6\text{H}_6(l) & \quad \Delta H = (+), \text{ (endothermic)} \\
\text{C}_6\text{H}_6(g)
\end{align*}
\]

6.26 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 \(H \ (H_{\text{final}})\). If heat is absorbed, the reaction is endothermic and the products have greater \(H \ (H_{\text{final}})\) than the reactants \(H \ (H_{\text{initial}})\).

Solution:

a) \(2\text{CH}_2\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g) + \text{heat}\)

\[
\begin{align*}
\text{Increasing, } H \\
\text{2CH}_2\text{OH} + 3\text{O}_2 \text{ (initial)} & \quad \Delta H = (-), \text{ (exothermic)} \\
\text{2CO}_2 + 4\text{H}_2\text{O} \text{ (final)}
\end{align*}
\]
b) Nitrogen dioxide, NO₂, forms from N₂ and O₂.
\[ \frac{1}{2}N_2(g) + O_2(g) + \text{heat} \rightarrow NO_2(g) \]

Increasing, \( H \)

\[ \Delta H = (+), \text{(endothermic)} \]

6.27 a) CO₂(s) + heat → CO₂(g)

Increasing, \( H \)

\[ \Delta H = (+), \text{(endothermic)} \]

b) SO₂(g) + 1/2O₂(g) → SO₃(g) + heat

Increasing, \( H \)

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

6.28 Plan: Recall that \( q_{\text{sys}} \) 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 \( q_{\text{sys}} \) to find \( \Delta E_{\text{sys}} \).

Solution:
a) This is a phase change from the solid phase to the gas phase. Heat is absorbed by the system so \( q_{\text{sys}} \) 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. \( \Delta E_{\text{sys}} = q + w \). Since \( q \) is positive and \( w \) is negative, the sign of \( \Delta E_{\text{sys}} \) cannot be predicted. It will be positive if \( q > w \) and negative if \( q < w \).
c) \( \Delta E_{\text{univ}} = 0 \). 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.

6.29 a) There is a volume decrease; \( V_{\text{final}} < V_{\text{initial}} \) so \( \Delta V \) is negative. Since \( w_{\text{sys}} = -P\Delta V \), \( w \) is positive, +.
b) \( \Delta H_{\text{sys}} \) is – as heat has been removed from the system to liquefy the gas.
c) \( \Delta E_{\text{sys}} = q + w \). Since \( q \) is negative and \( w \) is positive, the sign of \( \Delta E_{\text{sys}} \) and \( \Delta E_{\text{surr}} \) cannot be predicted. \( \Delta E_{\text{sys}} \) will be positive and \( \Delta E_{\text{surr}} \) will be negative if \( w > q \) and \( \Delta E_{\text{sys}} \) will be negative and \( \Delta E_{\text{surr}} \) will be positive if \( w < q \).

6.30 The molar heat capacity of a substance is larger than its specific heat capacity. The specific heat capacity of a substance is the quantity of heat required to change the temperature of 1 g of a substance by 1 K while the molar heat capacity is the quantity of heat required to change the temperature of 1 mole of a substance by 1 K. The specific heat capacity of a substance is multiplied by its molar mass to obtain the molar heat capacity.

6.31 To determine the specific heat capacity of a substance, you need its mass, the heat added (or lost), and the change in temperature.
6.32 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.

6.33 Specific heat capacity is the quantity of heat required to raise 1g of a substance by 1 K. Molar heat capacity is the quantity of heat required to raise 1 mole of substance by 1 K. Heat capacity is also the quantity of heat required for a 1 K temperature change, but it applies to an object instead of a specified amount of a substance. Thus, specific heat capacity and molar heat capacity are used when talking about an element or compound while heat capacity is used for a calorimeter or other object.

6.34 In a coffee-cup calorimeter, reactions occur at constant pressure. \( q_p = \Delta H \).
In a bomb calorimeter, reactions occur at constant volume. \( q_v = \Delta E \).

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

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

6.36
\[
q (J) = c \times \text{mass} \times \Delta T = \left( 2.087 \frac{\text{J}}{\text{g} \cdot \text{K}} \right) (0.10 \text{ g})((-75 - 10.) \text{ K}) = -17.7395 = -18 \text{ J}
\]

6.37 Plan: Use the relationship \( q = c \times \text{mass} \times \Delta T \). We know the heat (change kJ to J), the specific heat capacity, and the mass, so \( \Delta T \) can be calculated. Once \( \Delta T \) is known, that value is added to the initial temperature to find the final temperature.

Solution:
\[
q (J) = c \times \text{mass} \times \Delta T = (75.0 \text{ kJ}) \left( 10^3 \frac{\text{J}}{\text{kJ}} \right) = 7.50 \times 10^4 \text{ J}
\]
\[
7.50 \times 10^4 \text{ J} = (0.900 \text{ J/g} \cdot \text{K})(295 \text{ g})(\Delta T)
\]
\[
\Delta T = \frac{7.50 \times 10^4 \text{ J}}{(295 \text{ g})(0.900 \text{ J/g} \cdot \text{K})} = 282.4859 \text{ K} = 282.4859^\circ\text{C}
\]

(Because the Celsius degree is the same size as the Kelvin degree, \( \Delta T \) is the same in either temperature unit.)
\[
\Delta T = T_{\text{final}} - T_{\text{initial}}
\]
\[
T_{\text{final}} = \Delta T + T_{\text{initial}}
\]
\[
T_{\text{final}} = 282.4859^\circ\text{C} + 13.00^\circ\text{C} = 295.49 = 295^\circ\text{C}
\]

6.38
\[
q (J) = c \times \text{mass} \times \Delta T
\]
\[
-688 \text{ J} = (2.42 \text{ J/g} \cdot \text{K})(27.7 \text{ g})(\Delta T)
\]
\[
(\Delta T) = \frac{-688 \text{ J}}{(27.7 \text{ g})(2.42 \text{ J/g} \cdot \text{K})} = -10.26345 \text{ K} = -10.26345^\circ\text{C}
\]
\[
\Delta T = T_{\text{final}} - T_{\text{initial}}
\]
\[
T_{\text{initial}} = T_{\text{final}} - \Delta T
\]
\[
T_{\text{initial}} = 32.5^\circ\text{C} - (-10.26345^\circ\text{C}) = 42.76345 = 42.8^\circ\text{C}
\]
Plan: 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:
\[
\left[ \frac{T_1 + T_2}{2} \right] = \left[ \frac{(100.0°C + 55°C)}{2} \right] = 77.5°C
\]

6.40 \( q_{\text{lost}} = q_{\text{gained}} \)
- \( 2(\text{mass})(c_{Cu})(T_{\text{final}} - 105)°C = (\text{mass})(c_{Cu})(T_{\text{final}} - 45)°C \)
- \( 2(T_{\text{final}} - 105)°C = (T_{\text{final}} - 45)°C \)
\( 2(105°C) - 2T_{\text{final}} = T_{\text{final}} - 45°C \)
\( 210°C + 45°C = T_{\text{final}} + 2T_{\text{final}} = 3T_{\text{final}} \)
\( 255°C/3 = T_{\text{final}} = 85.0°C \)

6.41 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:

\[
\text{Mass (g) of 75 mL} = \left( 75 \text{ mL} \right) \left( \frac{1.00 \text{ g}}{1 \text{ mL}} \right) = 75 \text{ g}
\]
\[
\text{Mass (g) of 155 mL} = \left( 155 \text{ mL} \right) \left( \frac{1.00 \text{ g}}{1 \text{ mL}} \right) = 155 \text{ g}
\]

\( q_{\text{lost}} = q_{\text{gained}} \)
\( c \times \text{mass} \times \Delta T \ (85°C \text{ water}) = c \times \text{mass} \times \Delta T \ (26°C \text{ water}) \)
- \( (4.184 \text{ J/g°C})(75 \text{ g})(T_{\text{final}} - 85)°C = (4.184 \text{ J/g°C})(155 \text{ g})(T_{\text{final}} - 26)°C \)
\( - (75 \text{ g})(T_{\text{final}} - 85)°C = (155 \text{ g})(T_{\text{final}} - 26)°C \)
\( 6375 - 75T_{\text{final}} = 155T_{\text{final}} - 4030 \)
\( 6375 + 4030 = 155T_{\text{final}} + 75T_{\text{final}} \)
\( 10405 = 230T_{\text{final}} \)
\( T_{\text{final}} = (10405/230.) = 45.24 = 45°C \)

6.42 \( q_{\text{lost}} = q_{\text{gained}} \)
- \( [24.4 \text{ mL}(1.00 \text{ g/mL})](4.184 \text{ J/g°C})(23.5 - 35.0)°C = (\text{mass})(4.184 \text{ J/g°C})(23.5 - 18.2)°C \)
- \( (24.4)(23.5 - 35.0)°C = (\text{mass})(23.5 - 18.2)°C \)
- \( (24.4)(-11.5)°C = (\text{mass})(5.3)°C \)
\( 280.6 = (\text{mass})(5.3)°C \)
\( 52.943 \text{ g} = \text{mass} \)

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

6.43 Plan: Heat gained by water and the container equals the heat lost by the copper tubing so
\( q_{\text{water}} + q_{\text{calorimeter}} = -q_{\text{copper}} \)

Solution:
\[
\Delta T = T_{\text{final}} - T_{\text{initial}}
\]
Specific heat capacity in units of J/g*K has the same value in units of J/g°C since the Celsius and Kelvin unit are the same size.

\( q_{\text{lost}} = q_{\text{gained}} = q_{\text{water}} + q_{\text{calorimeter}} \)
- \( (455 \text{ g Cu})(0.387 \text{ J/g°C})(T_{\text{final}} - 89.5)°C \)
\( = (159 \text{ g H}_2\text{O})(4.184 \text{ J/g°C})(T_{\text{final}} - 22.8)°C + (10.0 \text{ J/°C})(T_{\text{final}} - 22.8)°C \)
\( - (176.085)(T_{\text{final}} - 89.5)°C = (665.256)(T_{\text{final}} - 22.8)°C + (10.0)(T_{\text{final}} - 22.8)°C \)
\( 15759.6075 - 176.085T_{\text{final}} = 665.256T_{\text{final}} - 15167.8368 + 10.0T_{\text{final}} - 228 \)
\( 15759.6075 + 15167.8368 + 228 = 176.085T_{\text{final}} + 665.256T_{\text{final}} + 10.0T_{\text{final}} \)
\( 31155.4443 = 851.341T_{\text{final}} \)
\( T_{\text{final}} = 31155.4443/(851.341) = 36.59573 = 36.6°C \)
6.44

\[ q_{\text{lost}} = q_{\text{gained}} = q_{\text{water}} + q_{\text{calorimeter}} \]

\[ (30.5 \text{ g alloy})(c_{\text{alloy}})(31.1 - 93.0)°C = (50.0 \text{ g H}_2\text{O})(4.184 \text{ J/g°C})(31.1 - 22.0)°C + (9.2 \text{ J/°C})(31.1 - 22.0)°C \]

\[ 1887.95(c_{\text{alloy}}) = 1903.72 + 83.72 = 1987.44 \]

\[ c_{\text{alloy}} = 1987.44/1887.95 = 1.052697 = 1.1 \text{ J/g°C} \]

6.45

Benzoic acid is \( C_6H_5COOH \), and will be symbolized as \( \text{HBz} \).

\[ q_{\text{reaction}} = q_{\text{water}} + q_{\text{calorimeter}} \]

\[ q_{\text{reaction}} = -(1.221 \text{ g HBz})(1 \text{ mol HBz})(122.12 \text{ g HBz})(10^3 \text{ J/1 mol HBz}) = 3.226472 \times 10^4 \text{ J} \]

\[ q_{\text{water}} = c \times \text{mass} \times \Delta T = 4.184 \text{ J/g°C} \times 1200 \text{ g} \times \Delta T \]

\[ q_{\text{calorimeter}} = C \times \Delta T = 1365 \text{ J/C} \times \Delta T \]

\[ q_{\text{reaction}} = q_{\text{water}} + q_{\text{calorimeter}} \]

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

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

\[ \Delta T = 3.226472 \times 10^4 / 6385.8 = 5.052573 = 5.053°C \]

6.46

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 \( q_{\text{calorimeter}} = 0 \).

\[ q_{\text{reaction}} = q_{\text{water}} + q_{\text{calorimeter}} \]

\[ q_{\text{water}} = c \times \text{mass} \times \Delta T = 4.184 \text{ J/g°C} \times 1200 \text{ g} \times \Delta T \]

\[ q_{\text{calorimeter}} = C \times \Delta T = 1365 \text{ J/C} \times \Delta T \]

\[ q_{\text{reaction}} = q_{\text{water}} + q_{\text{calorimeter}} \]

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

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

\[ \Delta T = 3.226472 \times 10^4 / 6385.8 = 5.052573 = 5.053°C \]

6.47

\[ q_{\text{hydrocarbon}} = q_{\text{water}} + q_{\text{calorimeter}} \]

\[ q_{\text{hydrocarbon}} = (2.550 \text{ L H}_2\text{O})(1 \text{ mL} / 10^{-3} \text{ L})(1.00 \text{ g/mL})(4.184 \text{ J/g°C})(23.55 - 20.00)°C \]

\[ + (403 \text{ J/°C})(23.55 - 20.00)°C \]

\[ q_{\text{hydrocarbon}} = (2.550 \text{ g})(4.184 \text{ J/g°C})(3.55°C) + (403 \text{ J/°C})(3.55°C) \]

\[ q_{\text{hydrocarbon}} = (37875.66 \text{ J}) + (1430.65 \text{ J}) = 39306.31 \text{ J} \]

\[ q_{\text{hydrocarbon}}/g = (-3.930631 \times 10^4 \text{ J})/1.520 \text{ g} = -2.5859 \times 10^4 = -2.59 \times 10^4 \text{ J/g} \]

6.48

The reaction is: \( 2\text{KOH(aq)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{K}_2\text{SO}_4(aq) + 2\text{H}_2\text{O(l)} \)

\[ q \text{ (kJ)} = (25.0 + 25.0) \text{ mL}(1.00 \text{ g/mL})(4.184 \text{ J/g°C})(30.17 - 23.50)\text{°C}(1 \text{ kJ/10^3 J}) = 1.395364 \text{ kJ} \]

(The temperature increased so the heat of reaction is exothermic.)

Amount (moles) of \( \text{H}_2\text{SO}_4 \) = (25.0 mL)(0.500 mol \( \text{H}_2\text{SO}_4/L)\times 10^{-3} \text{ L/1 mL} = 0.0125 \text{ mol H}_2\text{SO}_4 \)

Amount (moles) of \( \text{KOH} \) = (25.0 mL)(1.00 mol KOH/L)(10^{-3} \text{ L/1 mL} = 0.0250 \text{ mol KOH} \)

The moles show that both \( \text{H}_2\text{SO}_4 \) and \( \text{KOH} \) 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 \( \text{K}_2\text{SO}_4 \) gives the same value as per mole of \( \text{H}_2\text{SO}_4 \), and per mole of \( \text{H}_2\text{O} \) gives the same value as per mole of \( \text{KOH} \).)

6.49

Reactants \rightarrow \text{Products} + \text{Energy} \]

\[ \Delta H_{\text{rxn}} = (-) \]

Thus, energy is a \textit{product}. 

6-9
6.50 **Plan:** Recall that \( \Delta H \) is positive for an endothermic reaction in which heat is absorbed, while \( \Delta H \) is negative for an exothermic reaction in which heat is released.

**Solution:**
The reaction has a **positive** \( \Delta H_{\text{rxn}} \), because this reaction requires the input of energy to break the oxygen-oxygen bond in \( \text{O}_2 \):

\[
\text{O}_2(g) \rightarrow \text{2O}(g)
\]

6.51 **Plan:** Recall that \( \Delta H \) is positive for an endothermic reaction in which heat is absorbed, while \( \Delta H \) 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 \( \Delta H \) 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 (+\( \Delta H \)).

\[
\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l) + \text{Energy} \quad \text{2H}_2\text{O}(l) \rightarrow \text{2H}_2\text{O}(g)\\
\Delta H_{\text{condensation}} = (-) \quad \Delta H_{\text{vaporization}} = (+2[\Delta H_{\text{condensation}}])
\]
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 \( \text{H}_2\text{O} \) to \( \text{H}_2\text{O} \) vapor.

6.52 **Plan:** Recall that \( \Delta H \) is positive for an endothermic reaction in which heat is absorbed, while \( \Delta H \) is negative for an exothermic reaction in which heat is released. The \( \Delta H_{\text{rxn}} \) 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 \( \Delta H \) to convert between amount of sulfur and heat released.

**Solution:**
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) \( \Delta H_{\text{rxn}} = \left(2.6 \text{ mol } \text{S}_8\right) \left(\frac{-20.2 \text{ kJ}}{1/8 \text{ mol } \text{S}_8}\right) = -420.16 = -4.2 \times 10^2 \text{ kJ} \)

d) The mass of \( \text{S}_8 \) requires conversion to moles and then a calculation identical to part c) can be performed.

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

6.53 \( \text{MgCO}_3(s) \rightarrow \text{MgO}(s) + \text{CO}_2(g) \quad \Delta H_{\text{rxn}} = 117.3 \text{ kJ} \)

**a) Absorbed**

b) \( \Delta H_{\text{rxn}} \) (reverse) = \(-117.3 \text{ kJ} \)

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

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

6.54 **Plan:** A thermochemical equation is a balanced equation that includes the heat of reaction. Since heat is absorbed in this reaction, \( \Delta H \) will be positive. Convert the mass of NO to moles and use the ratio between NO and \( \Delta H \) to find the heat involved for this amount of NO.

**Solution:**
a) \( \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{NO}(g) \quad \Delta H = 90.29 \text{ kJ} \)

b) \( \Delta H_{\text{rxn}} = \left(3.50 \text{ g } \text{NO}\right) \left(\frac{1 \text{ mol } \text{NO}}{30.01 \text{ g } \text{NO}}\right) \left(\frac{-90.29 \text{ kJ}}{1 \text{ mol } \text{NO}}\right) = -10.5303 = -10.5 \text{ kJ} \)
6.55  a) KBr(s) → K(s) + 1/2Br_2(l) \quad \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 \times 10^4 = -3.31 \times 10^4 \text{ kJ}

6.56  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:

\[ 2 \text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \quad \Delta H_{rxn} = -196.1 \text{ kJ} \]

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

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

\[ \text{B}_2\text{H}_6(g) + 6\text{Cl}_2(g) \rightarrow 2\text{BCl}_3(g) + 6\text{HCl}(g) \quad \Delta H_{rxn} = -755.4 \text{ kJ} \]

Heat (kJ) \[ q = \left( \frac{1 \text{ mol B}_2\text{H}_6}{1 \text{ mol B}_2\text{H}_6} \right) \left( \frac{2 \text{ mol Fe}_2\text{O}_3}{2} \right) \left( \frac{159.70 \text{ g Fe}_2\text{O}_3}{1 \text{ mol Fe}_2\text{O}_3} \right) = 938.84 = 939 \text{ g Fe}_2\text{O}_3 \]

6.58  Plan: A thermochemical equation is a balanced equation that includes the heat of reaction. Heat is released in this reaction so \( \Delta H \) is negative. Use the ratio between \( \Delta H \) 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:

\[ 4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s) \quad \Delta H_{rxn} = -1.65 \times 10^3 \text{ kJ} \]

a) Heat (kJ) \[ q = \left( 0.250 \text{ kg Fe} \right) \left( \frac{10^3 \text{ g Fe}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \right) \left( \frac{-1.65 \times 10^3 \text{ kJ}}{4 \text{ mol Fe}} \right) = -1846.46 = -1850 \text{ kJ} \]

b) Mass (g) of Fe_2O_3 \[ \left( \frac{2 \text{ mol Fe}_2\text{O}_3}{1 \text{ mol Fe}_2\text{O}_3} \right) \left( \frac{159.70 \text{ g Fe}_2\text{O}_3}{1 \text{ mol Fe}_2\text{O}_3} \right) = 938.84 = 939 \text{ g Fe}_2\text{O}_3 \]

6.59  Plan: A thermochemical equation is a balanced equation that includes the heat of reaction. Heat is released in this reaction so \( \Delta H \) is negative. Use the ratio between \( \Delta H \) 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:

\[ 2\text{HgO}(s) \rightarrow 2\text{Hg}(l) + \text{O}_2(g) \quad \Delta H_{rxn} = 181.6 \text{ kJ} \]

a) Heat (kJ) \[ q = \left( 555 \text{ g HgO} \right) \left( \frac{1 \text{ mol HgO}}{216.6 \text{ g HgO}} \right) \left( \frac{181.6 \text{ kJ}}{2 \text{ mol HgO}} \right) = 232.659 = 233 \text{ kJ} \]

b) Mass (g) of Hg \[ \left( \frac{2 \text{ mol Hg}}{1 \text{ mol Hg}} \right) \left( \frac{200.6 \text{ g Hg}}{1 \text{ mol Hg}} \right) = 607.544 = 608 \text{ g Hg} \]

6.60  Plan: For the reaction written, 2 moles of C_2H_6 releases 5.64x10^3 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 C_2H_6 must be converted from kg to g to moles.

Solution:

\[ \text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H_{rxn} = -1411 \text{ kJ} \]

b) Mass (g) of C_2H_4 \[ \left( \frac{1 \text{ mol C}_2\text{H}_4}{-1411 \text{ kJ}} \right) \left( \frac{28.05 \text{ g C}_2\text{H}_4}{1 \text{ mol C}_2\text{H}_4} \right) = 1.39157 = 1.39 \text{ g C}_2\text{H}_4 \]

6.61  Plan: For the reaction written, 12 moles of C_12H_22O_11 releases 5.64x10^3 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 C_12H_22O_11 must be converted from kg to g to moles.

Solution:

\[ \text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + 12\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 11\text{H}_2\text{O}(g) \quad \Delta H_{rxn} = -5.64 \times 10^3 \text{ kJ} \]

b) Heat (kJ) \[ q = \left( 1 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \right) \left( \frac{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \right) \left( \frac{-5.64 \times 10^3 \text{ kJ}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \right) = -16.47677 = -16.5 \text{ kJ/g} \]

6.62  Hess’s law: \( \Delta H_{rxn} \) is independent of the number of steps or the path of the reaction.

6.63  Hess’s law provides a useful way of calculating energy changes for reactions which are difficult or impossible to measure directly.
Two chemical equations can be written based on the description given:

\[
\begin{align*}
C(s) + O_2(g) & \rightarrow CO_2(g) \quad \Delta H_1 \\
CO(g) + 1/2O_2(g) & \rightarrow CO_2(g) \quad \Delta H_2
\end{align*}
\]

The second reaction can be reversed and its \(\Delta H\) sign changed. In this case, no change in the coefficients is necessary since the \(CO_2\) cancels. Add the two \(\Delta H\) values together to obtain the \(\Delta H\) of the desired reaction.

**Solution:**

\[
\begin{align*}
C(s) + O_2(g) & \rightarrow CO_2(g) \quad \Delta H_1 \\
CO_2(g) & \rightarrow CO(g) + 1/2O_2(g) \quad -\Delta H_2 \\
\text{Total} & \quad C(s) + 1/2O_2(g) \rightarrow CO(g) \quad \Delta H_{\text{rxn}} = \Delta H_1 + - (\Delta H_2)
\end{align*}
\]

How are the \(\Delta H\) values for each reaction determined? The \(\Delta H_1\) can be found by using the heats of formation in Appendix B:

\[
\Delta H_1 = [\Delta H_f(CO_2)] - [\Delta H_f(C) + \Delta H_f(O_2)] = [-393.5 \text{ kJ/mol}] - [0 + 0] = -393.5 \text{ kJ/mol}.
\]

The \(\Delta H_2\) can be found by using the heats of formation in Appendix B:

\[
\Delta H_2 = [\Delta H_f(CO_2)] - [\Delta H_f(CO) + 1/2\Delta H_f(O_2)] = [-393.5] - [-110.5 \text{ kJ/mol} + 0] = -283 \text{ kJ/mol}.
\]

\[
\Delta H_{\text{rxn}} = \Delta H_1 + - (\Delta H_2) = -393.5 \text{ kJ} + - (-283.0 \text{ kJ}) = \boxed{-110.5 \text{ kJ}}
\]

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.

**Solution:**

\[
\begin{align*}
\text{Ca(s) + 1/2O_2(g) & \rightarrow CaO(g)} \quad \Delta H = -635.1 \text{ kJ} \\
\text{CaO(s) + CO_2(g) & \rightarrow CaCO_3(s)} \quad \Delta H = -178.3 \text{ kJ} \quad \text{(reaction is reversed)} \\
\text{Ca(s) + 1/2O_2(g) + CO_2(g) & \rightarrow CaCO_3(s)} \quad \Delta H = -813.4 \text{ kJ}
\end{align*}
\]

2NOCl(g) \rightarrow 2NO(g) + Cl_2(g) \quad \Delta H = -2(-38.6 \text{ kJ})

2NO(g) \rightarrow N_2(g) + O_2(g) \quad \Delta H = -2(90.3 \text{ kJ})

2NOCl(g) \rightarrow N_2(g) + O_2(g) + Cl_2(g) \quad \Delta H = 77.2 \text{ kJ} + -180.6 \text{ kJ} = \boxed{-103.4 \text{ kJ}}

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 \(\Delta H\) corresponds to an arrow pointing up while a negative \(\Delta H\) corresponds to an arrow pointing down.

**Solution:**

1) \(N_2(g) + O_2(g) \rightarrow 2NO(g)\) \quad \Delta H = 180.6 \text{ kJ}

2) \(2NO(g) + O_2(g) \rightarrow 2NO_2(g)\) \quad \Delta H = -114.2 \text{ kJ}

3) \(N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)\) \quad \boxed{\Delta H_{\text{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.

1) \(P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(g)\) \quad \Delta H_1 = -1148 \text{ kJ}

2) \(4PCl_3(g) + 4Cl_2(g) \rightarrow 4PCl_5(g)\) \quad \Delta H_2 = -460 \text{ kJ}

3) \(P_4(s) + 10Cl_2(g) \rightarrow 4PCl_5(g)\) \quad \boxed{\Delta H_{\text{overall}} = -1608 \text{ kJ}}

Vaporization is the change in state from a liquid to a gas: \(H_2O(l) \rightarrow H_2O(g)\). The two equations describing the chemical reactions for the formation of gaseous and liquid water can be combined to yield the equation for vaporization.

**Solution:**

1) Formation of \(H_2O(g)\): \(H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)\) \quad \Delta H = -241.8 \text{ kJ}

2) Formation of \(H_2O(l)\): \(H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)\) \quad \Delta H = -285.8 \text{ kJ}
Reverse reaction 2 (change the sign of \( \Delta H \)) and add the two reactions:

\[
\begin{align*}
H_2(g) + 1/2O_2(g) & \rightarrow H_2O(g) \quad \Delta H = -241.8 \text{ kJ} \\
H_2O(l) & \rightarrow H_2O(g) + 1/2O_2(g) \quad \Delta H = +285.8 \text{ kJ}
\end{align*}
\]

\[
\begin{align*}
H_2O(l) & \rightarrow H_2O(g) \quad \Delta H_{\text{vap}} = 44.0 \text{ kJ}
\end{align*}
\]

6.70

\[
\begin{align*}
C(s) + 1/4S_8(s) & \rightarrow CS_2(l) \quad \Delta H = +89.7 \text{ kJ} \\
CS_2(l) & \rightarrow CS_2(g) \quad \Delta H = +27.7 \text{ kJ}
\end{align*}
\]

\[
\begin{align*}
C(s) + 1/4S_8(s) & \rightarrow CS_2(g) \quad \Delta H = +117.4 \text{ kJ}
\end{align*}
\]

6.71

\[
\begin{align*}
C \text{(diamond)} + O_2(g) & \rightarrow CO_2(g) \quad \Delta H = -395.4 \text{ kJ} \\
CO_2(g) & \rightarrow C \text{(graphite)} + O_2(g) \quad \Delta H = -(−393.5 \text{ kJ}) \\
C \text{(diamond)} & \rightarrow C \text{(graphite)} \quad \Delta H = -1.9 \text{ kJ}
\end{align*}
\]

6.72 The standard heat of reaction, \( \Delta H_{\text{rxn}} \), 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 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.

6.73 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.

\[
\Delta H_{\text{rxn}} = \sum m \Delta H_f^\circ \text{(products)} - \sum n \Delta H_f^\circ \text{(reactants)}
\]

6.74 **Plan:** \( \Delta H_f^\circ \) is for the reaction that shows the formation of one mole of compound from its elements in their 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

6.75 **Plan:** Formation equations show the formation of one mole of compound from its elements. The elements must be in their most stable states (\( \Delta H_f^\circ = 0 \)).

**Solution:**

a) \( Ca(s) + Cl_2(g) \rightarrow CaCl_2(s) \)

b) \( Na(s) + 1/2H_2(g) + C \text{(graphite)} + 3/2O_2(g) \rightarrow NaHCO_3(s) \)

c) \( C \text{(graphite)} + 2Cl_2(g) \rightarrow CCl_4(l) \)

d) \( 1/2H_2(g) + 1/2N_2(g) + 3/2O_2(g) \rightarrow HNO_3(l) \)

6.76

a) \( 1/2H_2(g) + 1/2I_2(s) \rightarrow HI(g) \)

b) \( Si(s) + 2F_2(g) \rightarrow SiF_4(g) \)

c) \( 3/2O_2(g) \rightarrow O_3(g) \)

d) \( 3Ca(s) + 1/2P_4(s) + 4O_2(g) \rightarrow Ca_3(PO_4)_2(s) \)

6.77 **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 \( \Delta H_f^\circ \) values (Appendix B) are reported as energy per one mole, use the appropriate stoichiometric coefficient to reflect the higher number of moles.
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 \( \Delta H_f^o \) 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, \( \Delta H_{\text{rxn}}^o \) is known and \( \Delta H_f^o \) of CuO must be calculated.

\[
\Delta H_{\text{rxn}}^o = \sum m \Delta H_f^o(\text{products}) - \sum n \Delta H_f^o(\text{reactants})
\]

a) \( \Delta H_{\text{rxn}}^o = \{2 \Delta H_f^o [\text{SO}_2(g)] + 2 \Delta H_f^o [\text{H}_2\text{O}(g)]\} - \{2 \Delta H_f^o [\text{H}_2\text{S}(g)] + 3 \Delta H_f^o [\text{O}_2(g)]\}
\]
\[
= [2 \text{ mol}][-296.8 \text{ kJ/mol}] + [2 \text{ mol}][-214.826 \text{ kJ/mol}] - [2 \text{ mol}][-20.2 \text{ kJ/mol}] + [3 \text{ mol}][0 \text{ kJ/mol}]
\]
\[
= -1036.9 \text{ kJ}
\]
b) 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}}^o = \{1 \Delta H_f^o [\text{CCL}_4(l)] + 4 \Delta H_f^o [\text{HCl}(g)]\} - \{1 \Delta H_f^o [\text{CH}_4(g)] + 4 \Delta H_f^o [\text{Cl}_2(g)]\}
\]
\[
= [(1 \text{ mol})(-139 \text{ kJ/mol}) + (4 \text{ mol})(-92.31 \text{ kJ/mol})] - [(1 \text{ mol})(-74.87 \text{ kJ/mol}) + (4 \text{ mol})(0 \text{ kJ/mol})]
\]
\[
= -433 \text{ kJ}
\]

6.78 \( \Delta H_{\text{rxn}}^o = \sum m \Delta H_f^o(\text{products}) - \sum n \Delta H_f^o(\text{reactants}) \)
a) \( \Delta H_{\text{rxn}}^o = \{1 \Delta H_f^o [\text{SiF}_4(g)] + 2 \Delta H_f^o [\text{H}_2\text{O}(l)]\} - \{1 \Delta H_f^o [\text{SiO}_2(s)] + 4 \Delta H_f^o [\text{HF}(g)]\}
\]
\[
= [(1 \text{ mol})(-1614.9 \text{ kJ/mol}) + (2 \text{ mol})(-285.84 \text{ kJ/mol})]
\]
\[
= -184 \text{ kJ}
\]
b) \( 2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(g) \)

\( \Delta H_{\text{rxn}}^o = \{4 \Delta H_f^o [\text{CO}_2(g)] + 6 \Delta H_f^o [\text{H}_2\text{O}(g)]\} - \{2 \Delta H_f^o [\text{C}_2\text{H}_6(g)] + 7 \Delta H_f^o [\text{O}_2(g)]\}
\]
\[
= [(4 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-241.826 \text{ kJ/mol})] - [(2 \text{ mol})(-84.667 \text{ kJ/mol}) + (7 \text{ mol})(0 \text{ kJ/mol})]
\]
\[
= -2855.6 \text{ kJ} \) (or -1427.8 kJ for reaction of 1 mol of \( \text{C}_2\text{H}_6 \))

6.79 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 \( \Delta H_f^o \) 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, \( \Delta H_{\text{rxn}}^o \) is known and \( \Delta H_f^o \) of CuO must be calculated.

Solution:

\( \Delta H_{\text{rxn}}^o = \sum m \Delta H_f^o(\text{products}) - \sum n \Delta H_f^o(\text{reactants}) \)

\( \text{Cu}_2\text{O}(s) + 1/2\text{O}_2(g) \rightarrow 2\text{CuO}(s) \)
\[ \Delta H_{\text{rxn}}^o = -146.0 \text{ kJ} \]

\( \Delta H_{\text{rxn}}^o = \{2 \Delta H_f^o [\text{Cu}_2\text{O}(s)]\} - \{1 \Delta H_f^o [\text{Cu}_2\text{O}(s)] + 1/2 \Delta H_f^o [\text{O}_2(g)]\}
\]
\[
= -146.0 \text{ kJ} - \{1 \text{ mol}[-168.6 \text{ kJ/mol}] + (1/2 \text{ mol})(0 \text{ kJ/mol})\}
\]
\[
= -146.0 \text{ kJ} = 2 \text{ mol} \Delta H_f^o [\text{Cu}_2\text{O}(s)] + 168.6 \text{ kJ}
\]
\[
\Delta H_f^o [\text{Cu}_2\text{O}(s)] = \frac{-157.3 \text{ kJ/mol}}{2 \text{ mol}}
\]

6.80 \( \Delta H_{\text{rxn}}^o = \sum m \Delta H_f^o(\text{products}) - \sum n \Delta H_f^o(\text{reactants}) \)

\( \text{C}_2\text{H}_2(g) + 5/2\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(g) \)
\[ \Delta H_{\text{rxn}}^o = -1255.8 \text{ kJ} \]

\( \Delta H_{\text{rxn}}^o = \{2 \Delta H_f^o [\text{CO}_2(g)] + 1 \Delta H_f^o [\text{H}_2\text{O}(g)]\} - \{1 \Delta H_f^o [\text{C}_2\text{H}_2(g)] + 5/2 \Delta H_f^o [\text{O}_2(g)]\}
\]
\[
= -1255.8 \text{ kJ} - \{1 \text{ mol}[-241.826 \text{ kJ/mol}] + (5/2 \text{ mol})(0 \text{ kJ/mol})\}
\]
\[
= -787.0 \text{ kJ} = -1 \text{ mol} \Delta H_f^o [\text{C}_2\text{H}_2(g)]
\]
\[
\Delta H_f^o [\text{C}_2\text{H}_2(g)] = \frac{-227.0 \text{ kJ}}{-1 \text{ mol}} = 227.0 \text{ kJ/mol}
\]
6.81  **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 \( \Delta H_f^\circ \) 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 \( \Delta H_f^\circ \)) and multiply the coefficients (and \( \Delta H_f^\circ \)) of the second reaction by 2.

**Solution:**

\[
\begin{align*}
2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) &\rightarrow \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(l) \\
\Delta H_f^\circ_{\text{rxn}} &= \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants}) \\
a) \quad \Delta H_f^\circ_{\text{rxn}} &= \{1 \Delta H_f^\circ[\text{Pb}(s)] + 1 \Delta H_f^\circ[\text{PbO}_2(s)] + 2 \Delta H_f^\circ[\text{H}_2\text{SO}_4(l)]\} \\
&\quad - \{2 \Delta H_f^\circ[\text{PbSO}_4(s)] + 2 \Delta H_f^\circ[\text{H}_2\text{O}(l)]\} \\
&= \frac{503.9 \text{ kJ}}{}
\end{align*}
\]

b) Use Hess’s law:

\[
\begin{align*}
\text{PbSO}_4(s) &\rightarrow \text{Pb}(s) + \text{PbO}_2(s) + 2\text{SO}_3(g) \\
\Delta H_f^\circ_{\text{rxn}} &= -(–768 \text{ kJ}) \quad \text{Equation has been reversed.} \\
2\text{SO}_3(g) + 2\text{H}_2\text{O} (l) &\rightarrow 2\text{H}_2\text{SO}_4(l) \\
\Delta H_f^\circ_{\text{rxn}} &= 2(–132 \text{ kJ}) \\
2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) &\rightarrow \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(l) \\
\Delta H_f^\circ_{\text{rxn}} &= 504 \text{ kJ}
\end{align*}
\]

6.82  **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 \( \Delta H_f^\circ \) 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 \( \Delta H_f^\circ \) 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.

**Solution:**

\[
\begin{align*}
a) \quad \text{C}_{18}\text{H}_{36}\text{O}_2(s) + 26\text{O}_2(g) &\rightarrow 18\text{CO}_2(g) + 18\text{H}_2\text{O}(g) \\
\Delta H_f^\circ_{\text{rxn}} &= \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants}) \\
&= [(18 \text{ mol})(–393.5 \text{ kJ/mol}) + (18 \text{ mol})(–241.826 \text{ kJ/mol})] - [(1 \text{ mol})(–948 \text{ kJ/mol}) + (26 \text{ mol})(0 \text{ kJ/mol})] \\
&= –10,487.868 = –10,488 \text{ kJ} \\
b) \quad \text{PbSO}_4(s) &\rightarrow \text{Pb}(s) + \text{PbO}_2(s) + 2\text{SO}_3(g) \\
\Delta H_f^\circ_{\text{rxn}} &= –(–768 \text{ kJ}) \quad \text{Equation has been reversed.} \\
2\text{SO}_3(g) + 2\text{H}_2\text{O} (l) &\rightarrow 2\text{H}_2\text{SO}_4(l) \\
\Delta H_f^\circ_{\text{rxn}} &= 2(–132 \text{ kJ}) \\
2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) &\rightarrow \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(l) \\
\Delta H_f^\circ_{\text{rxn}} &= 504 \text{ kJ}
\end{align*}
\]

6.83  a) \( \text{H}_2\text{SO}_4(l) \rightarrow \text{H}_2\text{SO}_4(aq) \)

\[
\begin{align*}
\Delta H_f^\circ_{\text{rxn}} &= \{1 \Delta H_f^\circ[\text{H}_2\text{SO}_4(aq)]\} - \{1 \Delta H_f^\circ[\text{H}_2\text{SO}_4(l)]\} \\
&= [(1 \text{ mol})(–907.51 \text{ kJ/mol})] - [(1 \text{ mol})(–813.989 \text{ kJ/mol})] \\
&= –93.52 \text{ kJ}
\end{align*}
\]

Since 1 kcal = 1 Cal, 96.9 kcal = 96.9 Cal. The calculated calorie content is consistent with the package information.
b) \( q \ (J) = c \times \text{mass} \times \Delta T \)

\[
\begin{align*}
93.52 \text{ kJ} \times 10^3 \text{ J/kJ} \times (1000. \text{ mL}) \left( \frac{1.060 \text{ g}}{1 \text{ mL}} \right) \times (T_{\text{final}} - 25.0^\circ \text{C}) \\
9.352 \times 10^4 \text{ J} = \left( \frac{3.50 \text{ J}}{\text{g} \cdot ^\circ \text{C}} \right) \times (1060. \text{ g}) \times (T_{\text{final}} - 25.0^\circ \text{C})
\end{align*}
\]

\( T_{\text{final}} = 50.1995 = 50.2^\circ \text{C} \)

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.

6.84

**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 \( \Delta E \) 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 \( \Delta H = q_p \).

**Solution:**

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) = \( \frac{nRT}{P} = \frac{(0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol} \cdot \text{K})}{(1.00 \text{ atm})} \times (288 \text{ K}) = 23.6448 = 23.6 \text{ L/mol} \)

Final volume (L) = \( \frac{nRT}{P} = \frac{(0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol} \cdot \text{K})}{(1.00 \text{ atm})} \times (303 \text{ K}) = 24.8763 = 24.9 \text{ L/mol} \)

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, \( E = \frac{3}{2}nRT \), 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.

\[
E = \frac{3}{2}nRT = \frac{(3/2)(1.00 \text{ mol}) \times (8.314 \text{ J/mol} \cdot \text{K})(303 - 288)\text{K}}{1.00 \text{ atm}} = 187.065 = 187 \text{ J}
\]

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:

\[
w = -P\Delta V.\text{ When pressure and volume are multiplied together, the unit is L} \cdot \text{atm, so a conversion factor is needed to convert work in units of L} \cdot \text{atm to joules.}
\]

\[
w = -P\Delta V = -\left((1.00 \text{ atm}) \times (24.8763 - 23.6448) \text{ L} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = -124.75 = -1.2 \times 10^2 \text{ J}
\]

d) \( q_p = \Delta E + P\Delta V = (187.065 \text{ J}) + (124.75 \text{ J}) = 311.815 = 3.1 \times 10^2 \text{ J}
\]

e) \( \Delta H = q_p = 310 \text{ J} \).

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: \( \Delta H = \Delta E + P\Delta V = \Delta E - w = (q + w) - w = q_p \).

6.85

a) Respiration:

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) & \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(g) \\
\Delta H_{\text{rxn}} &= \sum_m \Delta H_f^{\circ}(\text{products}) - \sum_n \Delta H_f^{\circ}(\text{reactants}) \\
&= [6 \Delta H_f^{\circ}[\text{CO}_2(g)] + 6 \Delta H_f^{\circ}[\text{H}_2\text{O}(g)]] - [1 \Delta H_f^{\circ}[\text{C}_6\text{H}_{12}\text{O}_6(s)] + 6 \Delta H_f^{\circ}[\text{O}_2(g)]] \\
&= [(6 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-1273.3 \text{ kJ/mol}) + (6 \text{ mol})(0.0 \text{ kJ/mol})] \\
&= -2538.656 = -2538.7 \text{ kJ}
\end{align*}
\]
Fermentation:
\[
C_{6}H_{12}O_{6}(s) \rightarrow 2CO_{2}(g) + 2CH_{3}CH_{2}OH(l)
\]
\[
\Delta H_{\text{rxn}}^{\circ} = \{2 \Delta H_{f}^{\circ} [CO_{2}(g)] + 2 \Delta H_{f}^{\circ} [CH_{3}CH_{2}OH(l)] \} - \{1 \Delta H_{f}^{\circ} [C_{6}H_{12}O_{6}(s)] \}
\]
\[
= [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-277.63 \text{ kJ/mol})] - [(1 \text{ mol})(-1273.3 \text{ kJ/mol})] = -68.96 = -69.0 \text{ kJ}
\]

b) Combustion of ethanol:
\[
CH_{3}CH_{2}OH(l) + 3O_{2}(g) \rightarrow 2CO_{2}(g) + 3H_{2}O(g)
\]
\[
\Delta H_{\text{rxn}}^{\circ} = \{2 \Delta H_{f}^{\circ} [CO_{2}(g)] + 3 \Delta H_{f}^{\circ} [H_{2}O(g)] \} - \{1 \Delta H_{f}^{\circ} [CH_{3}CH_{2}OH(l)] + 3 \Delta H_{f}^{\circ} [O_{2}(g)] \}
\]
\[
= [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (3 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-277.63 \text{ kJ/mol}) + (3 \text{ mol})(0.0 \text{ kJ/mol})]
\]
\[
= -1234.848 = -1234.8 \text{ kJ}
\]

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:
  \[
  \left(\frac{-1234.848 \text{ kJ}}{1 \text{ mol CH}_{3}CH_{2}OH}\right) \left(\frac{1 \text{ mol CH}_{3}CH_{2}OH}{2 \text{ mol C}}\right) = -617.424 = -617.42 \text{ kJ/mol C}
  \]

**Ethanol** has a higher value.

6.86 a) Reactions:
1) \( C_{21}H_{44}(s) + 32O_{2}(g) \rightarrow 21CO_{2}(g) + 22H_{2}O(g) \)
2) \( C_{21}H_{44}(s) + 43/2O_{2}(g) \rightarrow 21CO_{2}(g) + 22H_{2}O(g) \)
3) \( C_{21}H_{44}(s) + 11O_{2}(g) \rightarrow 21C(s) + 22H_{2}O(g) \)

Heats of combustion:
1) \[
\Delta H_{\text{rxn}}^{\circ} = \{21 \Delta H_{f}^{\circ} [CO_{2}(g)] + 22 \Delta H_{f}^{\circ} [H_{2}O(g)] \} - \{1 \Delta H_{f}^{\circ} [C_{21}H_{44}(s)] + 32 \Delta H_{f}^{\circ} [O_{2}(g)] \}
\]
\[
= [(21 \text{ mol})(-74.87 \text{ kJ/mol}) + (22 \text{ mol})(-110.5 \text{ kJ/mol})] - [(1 \text{ mol})(-476 \text{ kJ/mol}) + (32 \text{ mol})(0.0 \text{ kJ/mol})]
\]
\[
= -13,107.672 = -13,108 \text{ kJ}
\]
2) \[
\Delta H_{\text{rxn}}^{\circ} = \{21 \Delta H_{f}^{\circ} [CO(g)] + 22 \Delta H_{f}^{\circ} [H_{2}O(g)] \} - \{1 \Delta H_{f}^{\circ} [C_{21}H_{44}(s)] + 43/2 \Delta H_{f}^{\circ} [O_{2}(g)] \}
\]
\[
= [(21 \text{ mol})(-110.5 \text{ kJ/mol}) + (22 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-476 \text{ kJ/mol}) + (43/2 \text{ mol})(0.0 \text{ kJ/mol})]
\]
\[
= -7,164.672 = -7165 \text{ kJ}
\]
3) \[
\Delta H_{\text{rxn}}^{\circ} = \{21 \Delta H_{f}^{\circ} [C(s)] + 22 \Delta H_{f}^{\circ} [H_{2}O(g)] \} - \{1 \Delta H_{f}^{\circ} [C_{21}H_{44}(s)] + 11 \Delta H_{f}^{\circ} [O_{2}(g)] \}
\]
\[
= [(21 \text{ mol})(0.0 \text{ kJ/mol}) + (22 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-476 \text{ kJ/mol}) + (11 \text{ mol})(0.0 \text{ kJ/mol})]
\]
\[
= -4844.172 = -4844 \text{ kJ}
\]
b) \( q \) (kJ) = \( (254 \text{ g } C_{21}H_{44}) \left(\frac{1 \text{ mol } C_{21}H_{44}}{296.56 \text{ g } C_{21}H_{44}}\right) \left(\frac{-13107.672 \text{ kJ}}{1 \text{ mol } C_{21}H_{44}}\right) = -1.12266 \times 10^{4} = -1.12 \times 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 87.00% of the candle undergoes complete combustion.

Moles \( C_{21}H_{44} \) = \( (254 \text{ g } C_{21}H_{44})(1 \text{ mol } C_{21}H_{44}/296.56 \text{ g } C_{21}H_{44}) \) = 0.856488 mol

\( q = (0.87)(0.856488 \text{ mol})(-13107.672 \text{ kJ/mol}) + (0.0800)(0.856488 \text{ mol})(-7164.672 \text{ kJ/mol}) + (0.0500)(0.856488 \text{ mol})(-4844.172 \text{ kJ/mol}) = -1.04655 \times 10^{4} = -1.05 \times 10^{4} \text{ kJ}
\]

6.87 a) \( EO(l) \rightarrow EO(g) \)
\[
\Delta H_{\text{vap}}^{\circ} = 569.4 \text{ J/(g(44.05 g/mol)(1 kJ/1000 J))} = 25.08 \text{ kJ/mol}
\]
\[
\Delta H_{\text{vap}}^{\circ} = \{1 \Delta H_{f}^{\circ} [EO(g)] \} - \{1 \Delta H_{f}^{\circ} [EO(l)] \}
\]
25.08 kJ/mol = \( \{ \Delta H_{f}^{\circ} [EO(g)] \} - \{ (1 \text{ mol})(-77.4 \text{ kJ/mol}) \}
\]
\[
\Delta H_{f}^{\circ} [EO(g)] = -52.32 \text{ kJ/mol}
\]
\( EO(g) \rightarrow CH_{4}(g) + CO(g) \)
\[
\Delta H_{\text{rxn}}^{\circ} = \{1 \Delta H_{f}^{\circ} [CH_{4}(g)] + 1 \Delta H_{f}^{\circ} [CO(g)] \} - \{1 \Delta H_{f}^{\circ} [EO(g)] \}
\]
\[
= [(1 \text{ mol})(-74.87 \text{ kJ/mol}) + (1 \text{ mol})(-110.5 \text{ kJ/mol})] - [(1 \text{ mol})(-52.32 \text{ kJ/mol})]
\]
\[ \Delta H_{\text{rxn}} = -133.0 \text{ kJ/mol} \]

b) Assume that you have 1.00 mole of EO\((g)\). 1.00 mole of EO\((g)\) produces 1.00 mole or 16.04 g of CH\(_4\)(g) and 1.00 mole or 28.01 g of CO\((g)\). There is a total product mass of 16.04 g + 28.01 g = 44.05 g.

\[ q = c \times \text{mass} \times \Delta T \]

\[ \Delta T = \frac{q}{c \times \text{mass}} = \frac{(133.0 \text{ kJ})(1000 \text{ J})}{(2.5 \text{ J/g°C})(44.05 \text{ g})} \]

\[ \Delta T = 1207.7^\circ \text{C} \]

\[ \Delta T = T_{\text{final}} - T_{\text{initial}} \]

1207.7°C = \(T_{\text{final}} - 93^\circ \text{C}\)

\[ T_{\text{final}} = 1300.72 = 1301^\circ \text{C} \]

6.88

a) 3N\(_2\)O\(_5\)(g) + 3NO\((g)\) → 9NO\(_2\)(g)

\[ \Delta H_{\text{rxn}} = \{9 \Delta H_\text{f}[\text{NO}_2(g)]\} - \{3 \Delta H_\text{f}[\text{N}_2\text{O}_5(g)] + 3 \Delta H_\text{f}[\text{NO}(g)]\} \]

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

\[ = -5.07 = -5 \text{ kJ} \]

b) \(\frac{231.50 \times 10^2 \text{ mol} \times 5.07 \text{ kJ}}{10^2 \text{ J} \times 9 \text{ molecules product} \times 1 \text{ molecule product} \times 9 \text{ moles product} \times 1 \text{ kJ}} = -76.05 = -76.0 \text{ J} \]

6.89

a) Heat (kJ) = \(\frac{3}{81 \times 8 \text{ mL} \times 0.692 \text{ g} \times 5.44 \times 10^6 \text{ kJ}}{20.4 \text{ gal} \times 1 \text{ gal} \times 1.057 \text{ qt} \times 1 \text{ mL} \times 114.22 \text{ g} \times 1 \text{ mol C H}_{10} \times 1 \text{ kJ}} = -2.54435678 \times 10^6 = -2.54 \times 10^6 \text{ kJ} \]

b) Distance (km) = \(-2.54435678 \times 10^6 \text{ kJ} \times 1 \text{ h} \\times 0.62 \text{ mi} \\times 5.5 \times 10^3 \text{ kJ} = 4.84995 \times 10^3 = 4.8 \times 10^3 \text{ km} \)

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.

6.90

\[ q = c \times \text{mass} \times \Delta T \]

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 \(\alpha (c \times \Delta T)\). \(c\), specific heat capacity, and \(\Delta T\) are inversely proportional. The higher the \(\Delta T\), the lower the value of specific heat capacity:

\[ \Delta T: \ B > D > C > A \]

Specific heat capacity: \(B < D < C < A\)

6.91

\[ \text{ClF}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \frac{1}{2} \text{Cl}_2\text{O}(g) + \frac{1}{2} \text{OF}_2(g) \]

\[ \Delta H_{\text{rxn}} = \frac{1}{2}(167.5 \text{ kJ}) = 83.75 \text{ kJ} \]

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

\[ \Delta H_{\text{rxn}} = \frac{1}{2}(-43.5 \text{ kJ}) = -21.75 \text{ kJ} \]

\[ \frac{1}{2} \text{Cl}_2\text{O}(g) + \frac{3}{2} \text{OF}_2(g) \rightarrow \text{ClF}_3(l) + \text{O}_2(g) \]

\[ \Delta H_{\text{rxn}} = -\frac{1}{2}(394.1 \text{ kJ}) = -197.05 \text{ kJ} \]

\[ \text{ClF}(g) + \text{F}_2(g) \rightarrow \text{ClF}_3(l) \]

\[ \Delta H_{\text{rxn}} = -135.1 \text{ kJ} \]

6.92

a) AgNO\(_3\)(aq) + NaI(aq) → AgI(s) + NaNO\(_3\)(aq)

Moles of AgNO\(_3\) = \(50.0 \text{ mL} \times \frac{5.0 \text{ g AgNO}_3}{1 \text{ L} \times 1 \text{ mol AgNO}_3} = 169.9 \text{ g AgNO}_3 \times 1.47145 \times 10^{-3} \text{ mol AgNO}_3 \)

Moles of NaI = \(50.0 \text{ mL} \times \frac{5.0 \text{ g NaI}}{1 \text{ L} \times 1 \text{ mol NaI} = 149.9 \text{ g NaI}} = 1.667785 \times 10^{-3} \text{ mol NaI} \)

6-18
The AgNO₃ is limiting, and will be used to finish the problem:

Mass (g) of AgI = \left(1.47145 \times 10^{-3} \text{ mol AgNO}_3\right) \left(\frac{1 \text{ mol AgI}}{1 \text{ mol AgNO}_3}\right) \left(\frac{234.8 \text{ g AgI}}{1 \text{ mol AgI}}\right) = 0.345496 = 0.35 \text{ g AgI}

\text{b) } \text{Ag}^+ (aq) + I^- (aq) \rightarrow \text{AgI (s)}

\Delta H^\circ_{rxn} = \left\{\Delta H^\circ_{[\text{AgI(s)}]}\right\} - \left\{\Delta H^\circ_{[\text{Ag}^+(aq)]} + \Delta H^\circ_{[I^-(aq)]}\right\}

= [(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^\circ_{rxn} = q = c \times \text{mass} \times \Delta T

\Delta T = \frac{\Delta H^\circ_{rxn}}{c \times \text{mass}} = \left\{\frac{112.3 \text{ kJ}}{1 \text{ mol AgI}}\right\} \left\{\frac{1 \text{ mol AgI}}{1 \text{ mol AgNO}_3}\right\} \left\{1.47145 \times 10^{-3} \text{ mol AgNO}_3\right\} \left\{\frac{10^3 J}{1 \text{ kJ}}\right\} \left\{\frac{4.184 \text{ J}}{\text{g} \cdot \text{K}}\right\} \left\{50.0 + 50.0\right\} \text{mL} \left\{\frac{1.00 \text{ g}}{\text{mL}}\right\}

= 0.39494 = 0.39 \text{ K}

6.93 Plan: Use conversion factors to solve parts a) and b). For part c), first find the heat of reaction for the combustion of methane by using the heats of formation of the reactants and products. 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^\circ values (Appendix B) are reported as energy per one mole, use the appropriate stoichiometric coefficient to reflect the higher number of moles. For part e), convert the amount of water in gal to mass in g and use the relationship \( q = c \times \text{mass} \times \Delta T \) to find the heat needed; then use the conversion factors between joules and therms and the cost per therm to determine the total cost of heating the water.

Solution:

a) \left(\frac{1 \text{ cal}}{\text{g} \cdot \text{C}}\right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}}\right) \left(\frac{453.6 \text{ g}}{1 \text{ lb}}\right) \left(\frac{1.00 \text{ lb} \cdot \text{F}}{1 \text{ C}}\right) \left(\frac{1.00 \text{ lb} \cdot \text{F}}{1 \text{ Btu}}\right) = 1054.368 = 1.1 \times 10^3 \text{ J/Btu}

b) \( E = \left(1.00 \text{ therm}\right) \left(\frac{100,000 \text{ Btu}}{1 \text{ therm}}\right) \left(\frac{1054.368 \text{ J}}{1 \text{ Btu}}\right) = 1.054368 \times 10^8 = 1.1 \times 10^8 \text{ J} \)

c) \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)

\Delta H^\circ_{rxn} = \left\{\Delta H^\circ_{[\text{CO}_2(g)]} + 2 \Delta H^\circ_{[\text{H}_2\text{O}(g)]}\right\} - \left\{\Delta H^\circ_{[\text{CH}_4(g)]} + 2 \Delta H^\circ_{[\text{O}_2(g)]}\right\}

= [(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 = -802.3 \text{ kJ/mol CH}_4

Moles of CH\(_4\) = (1.00 \text{ therm}) \left(\frac{1.054368 \times 10^8 \text{ J}}{1 \text{ therm}}\right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) \left(\frac{1 \text{ mol CH}_4}{802.282 \text{ kJ}}\right)

= 131.4211 = 1.3 \times 10^2 \text{ mol CH}_4

d) \text{Cost} = \left(\frac{\$0.66}{\text{therm}}\right) \left(\frac{1 \text{ therm}}{131.4211 \text{ mol}}\right) = 0.005022 = \$0.0050/\text{mol}

e) \text{Mass (g) of} = (318 \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{1.0 \text{ g}}{\text{mL}}\right) = 1.203406 \times 10^6 \text{ g}

q = c \times \text{mass} \times \Delta T = \left(\frac{4.184 \text{ J}}{\text{g} \cdot \text{C}}\right) \left(\frac{1.203406 \times 10^6 \text{ g}}{(42.0 - 15.0) \text{C}}\right) = 1.359464 \times 10^8 \text{ J}

\text{Cost} = \left(1.359494 \times 10^8 \text{ J}\right) \left(\frac{\$0.66}{1 \text{ therm}}\right) \left(\frac{1 \text{ therm}}{1.054368 \times 10^8 \text{ J}}\right) = 0.850999 = \$0.85
6.94 a) Mass (kg) of $=(5600 \text{ EJ}) \left( \frac{10^{18} \text{ J}}{1 \text{ EJ}} \right) \left( \frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \left( \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \right) \left( \frac{1 \text{ kg}}{1 \text{ mol CH}_4} \right) = 1.12 \times 10^{14} \text{ kg CH}_4$

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

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

d) Volume (ft$^3$) of CH$_4$ = $(2 \times 10^3 \text{ J}) \left( \frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \left( \frac{1 \text{ mol CH}_4}{802 \text{ kJ}} \right) \left( \frac{16.04 \text{ g CH}_4}{1 \text{ mol CH}_4} \right) \left( \frac{1 \text{ L}}{0.72 \text{ g CH}_4} \right) \left( \frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right) \left( \frac{35.3 \text{ ft}^3}{1 \text{ m}^3} \right) = 1.961105 \times 10^7 \text{ ft}^3$

6.95 The reaction is exothermic. The argon atoms in the chamber after the reaction are moving with greater kinetic energy, indicating an increase in temperature.

6.96 H$_2$SO$_4$(aq) + 2NaOH(aq) → Na$_2$SO$_4$(aq) + 2H$_2$O(l)

2H$^+$ (aq) + 2OH$^-$ (aq) → 2H$_2$O(l)

$\Delta H_{\text{rxn}} = \{2 \Delta H_f^\circ [\text{H}_2\text{O}(l)] - \{2 \Delta H_f^\circ [\text{H}^+(aq)] + 2 \Delta H_f^\circ [\text{OH}^-(aq)]\} = [(2 \text{ mol})(-285.84 \text{ kJ/mol})] - [(2 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(-229.94 \text{ kJ/mol})] = -111.8 \text{ kJ}$

1 mole of H$_2$SO$_4$ reacts with 2 moles of NaOH.

Mass (g) of H$_2$SO$_4$ solution = $(1 \text{ mol H}_2\text{SO}_4) \left( \frac{1.00 \text{ L}}{0.50 \text{ mol H}_2\text{SO}_4} \right) \left( \frac{1.00 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1.030 \text{ g}}{1 \text{ mL}} \right) = 2060 \text{ g H}_2\text{SO}_4$ solution

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

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

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

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

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

6.97 a) 2C$_{12}$H$_{26}$(l) + 37O$_2$(g) → 24CO$_2$(g) + 26H$_2$O(g)

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

$-1.50 \times 10^4 \text{ kJ} = [(24 \text{ mol})(-393.5 \text{ kJ/mol}) + (26 \text{ mol})(-241.826 \text{ kJ/mol})] - [(2 \text{ mol}) \Delta H_f^\circ [\text{C}_{12}\text{H}_{26}(g)] + (37 \text{ mol})(0.0 \text{ kJ/mol})]$

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

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

$-1.50 \times 10^4 \text{ kJ} + 15,731.476 \text{ kJ} = -2 \text{ mol} \Delta H_f^\circ [\text{C}_{12}\text{H}_{26}(g)]$
Heat of reaction is calculated using the relationship
\[ \Delta H_{\text{rxn}}^\circ = \sum_m \Delta H_f^\circ(\text{products}) - \sum_n \Delta H_f^\circ(\text{reactants}) \]

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) SiCl₄(g) + 2H₂O(g) → SiO₂(s) + 4HCl(g)
\[ \Delta H_{\text{rxn}}^\circ = \{ 1 \Delta H_f^\circ [\text{SiO}_2(s)] + 4 \Delta H_f^\circ [\text{HCl(g)}] - \{ 1 \Delta H_f^\circ [\text{SiCl}_4(g)] + 2 \Delta H_f^\circ [\text{H}_2\text{O(g)}] \} \]
\[ -139.5 \text{ kJ} = [(1 \text{ mol})(-910.9 \text{ kJ/mol}) + (4 \text{ mol})(-92.31 \text{ kJ})] - [\Delta H_f^\circ [\text{SiCl}_4(g)] + (2 \text{ mol})(-241.826 \text{ kJ/mol})] \]
\[ -139.5 \text{ kJ} = -1280.14 - [ \Delta H_f^\circ [\text{SiCl}_4(g)] + (-483.652 \text{ kJ}) ] \]
\[ 1140.64 \text{ kJ} = - \Delta H_f^\circ [\text{SiCl}_4(g)] + 483.652 \text{ kJ} \]
\[ \Delta H_f^\circ [\text{SiCl}_4(g)] = -656.988 \text{ kJ/mol} \]

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

1) Si(s) + 2Cl₂(g) → SiCl₄(g)
\[ \Delta H_{\text{rxn}}^\circ = \{ 1 \Delta H_f^\circ [\text{SiCl}_4(g)] - \{ 1 \Delta H_f^\circ [\text{Si}(s)] + 2 \Delta H_f^\circ [\text{Cl}_2(g)] \} \]
\[ = [(1 \text{ mol})(-656.988 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})] = -656.988 = -657.0 \text{ kJ} \]

2) SiO₂(s) + 2C(graphite) + 2Cl₂(g) → SiCl₄(g) + 2CO(g)
\[ \Delta H_{\text{rxn}}^\circ = \{ 1 \Delta H_f^\circ [\text{SiCl}_4(g)] + 2 \Delta H_f^\circ [\text{CO(g)}] \}
\[ = [(1 \text{ mol})(-656.988 \text{ kJ/mol})] + (2 \text{ mol})(-110.5 \text{ kJ/mol}) \]
\[ = [(1 \text{ mol})(-656.988 \text{ kJ/mol})] + (2 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol}) \]
\[ = 32.912 = 32.9 \text{ kJ} \]

b) Adding reactions 2 and 3 yields:

(2) SiO₂(s) + 2C(graphite) + 2Cl₂(g) → SiCl₄(g) + 2CO(g)
\[ \Delta H_{\text{rxn}}^\circ = 32.912 \text{ kJ} \]

(3) SiCl₄(g) + 2H₂O(g) → SiO₂(g) + 4HCl(g)
\[ \Delta H_{\text{rxn}}^\circ = -139.5 \text{ kJ} \]

\[ 2 \text{C(graphite)} + 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O(g)} \rightarrow 2\text{CO(g)} + 4\text{HCl(g)} \]
\[ \Delta H_{\text{rxn}}^\circ = [-2 \Delta H_f^\circ [\text{CO(g)}] + 4 \Delta H_f^\circ [\text{HCl(g)}] - [2 \Delta H_f^\circ [\text{C(graphite)}] + 2 \Delta H_f^\circ [\text{Cl}_2(g)] + 2 \Delta H_f^\circ [\text{H}_2\text{O(g)}]] \]
\[ = [(2 \text{ mol})(-110.5 \text{ kJ/mol})] + (4 \text{ mol})(-92.31 \text{ kJ}) \]
\[ = -106.588 = -106.6 \text{ kJ} \]
6.99 **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.

**Solution:**

a) $PV = nRT$

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

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

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

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

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

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

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

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

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

**Solution:**

Only reaction 3 contains N$_2$O$_4$(g), and only reaction 1 contains N$_2$O$_3$(g), so we can use those reactions as a starting point. N$_2$O$_3$ 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) $\quad \text{N}_2\text{O}_3(g) \rightarrow \text{NO}(g) + \text{NO}_2(g) \quad \Delta H^\circ_{\text{rxn}} = -(-39.8 \text{ kJ}) = \quad 39.8 \text{ kJ}$

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

(5) $\quad \text{N}_2\text{O}_5(s) \rightarrow \text{N}_2\text{O}_5(g) \quad \Delta H^\circ_{\text{rxn}} = 54.1 \text{ kJ} = 54.1 \text{ kJ}$

To cancel out the N$_2$O$_3(g)$ intermediate, reverse equation 2. This also cancels out some of the undesired NO$_2(g)$ but adds NO(g) and O$_2(g)$.

Reverse (2) $\quad \text{N}_2\text{O}_5(g) \rightarrow \text{NO}(g) + \text{NO}_2(g) + \text{O}_2(g) \quad \Delta H^\circ_{\text{rxn}} = -(-112.5 \text{ kJ}) = 112.5 \text{ kJ}$

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

Reverse (4) $\quad 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \quad \Delta H^\circ_{\text{rxn}} = 54.1 \text{ kJ}$

Total: $\quad \text{N}_2\text{O}_3(g) + \text{N}_2\text{O}_5(s) \rightarrow 2\text{N}_2\text{O}_4(g) \quad \Delta H^\circ_{\text{rxn}} = -22.2 \text{ kJ}$
6.101 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 $\Delta H^\circ_r$ 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, $\Delta H^\circ_{rxn}$ of the second reaction is known and $\Delta H^\circ_r$ of $\text{N}_2\text{H}_4(aq)$ must be calculated. For part b), calculate $\Delta H^\circ_{rxn}$ for the reaction between $\text{N}_2\text{H}_4(aq)$ and $\text{O}_2$, using the value of $\Delta H^\circ_r$ for $\text{N}_2\text{H}_4(aq)$ found in part a); then determine the moles of $\text{O}_2$ present by multiplying volume and molarity and multiply by the $\Delta H^\circ_{rxn}$ for the reaction.

Solution:

a) \[ \text{2NH}_3(aq) + \text{NaOCl}(aq) \rightarrow \text{N}_2\text{H}_4(aq) + \text{NaCl}(aq) + \text{H}_2\text{O}(l) \]

$\Delta H^\circ_{rxn} = \{1 \Delta H^\circ_r[\text{N}_2\text{H}_4(aq)] + 1 \Delta H^\circ_r[\text{NaCl}(aq)] + 1 \Delta H^\circ_r[\text{H}_2\text{O}(l)]\}

- \{2 \Delta H^\circ_r[\text{NH}_3(aq)] + 1 \Delta H^\circ_r[\text{NaOCl}(aq)]\}

Note that the Appendix B value for $\text{N}_2\text{H}_4$ is for $\text{N}_2\text{H}_4(l)$, not for $\text{N}_2\text{H}_4(aq)$, so this term must be calculated. In addition, Appendix B does not list a value for $\text{NaCl}(aq)$, so this term must be broken down into $\Delta H^\circ_r[\text{Na}^{+}(aq)]$ and $\Delta H^\circ_r[\text{Cl}^{-}(aq)]$.

\[ -151 \text{ kJ} = [ \Delta H^\circ_r[\text{N}_2\text{H}_4(aq)] + 1 \text{ mol}(–239.66 \text{ kJ/mol}) + 1 \text{ mol}(–167.46 \text{ kJ/mol}) + 1 \text{ mol}(–285.840 \text{ kJ/mol})]

- \{2 \text{ mol}(–80.83 \text{ kJ/mol}) + 1 \text{ mol}(–346 \text{ kJ/mol})\]

\[ -151 \text{ kJ} = \Delta H^\circ_r[\text{N}_2\text{H}_4(aq)] + (–692.96 \text{ kJ}) \]

\[ \Delta H^\circ_r[\text{N}_2\text{H}_4(aq)] = 34.3 = 34 \text{ kJ} \]

b) Moles of $\text{O}_2 = \left( \frac{4}{3} \times \frac{1}{10^3} \text{ L} \right) \left( \frac{2.50 \times 10^{-4} \text{ mol}}{1 \text{ L}} \right) = 1.25 \text{ mol} \text{ O}_2$

\[ \text{N}_2\text{H}_4(aq) + \text{O}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l) \]

$\Delta H^\circ_{rxn} = \{1 \Delta H^\circ_r[\text{N}_2(g)] + 2 \Delta H^\circ_r[\text{H}_2\text{O}(l)]\} - \{1 \Delta H^\circ_r[\text{N}_2\text{H}_4(aq)] + 1 \Delta H^\circ_r[\text{O}_2(g)]\}

= [(1 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(–285.840 \text{ kJ/mol})] - [(1 \text{ mol})(34.3 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]

= –605.98 \text{ kJ}

Heat (kJ) = \left( \frac{1.25 \text{ mol} \text{ O}_2}{1 \text{ mol} \text{ O}_2} \right) \left( \frac{–605.98 \text{ kJ}}{1 \text{ mol} \text{ O}_2} \right) = –757.475 = –757 \text{ kJ}

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

$\Delta H^\circ_{rxn} = \{1 \Delta H^\circ_r[\text{CH}_3\text{OH}(l)]\} - \{1 \Delta H^\circ_r[\text{CO}(g)] + 2 \Delta H^\circ_r[\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 $\text{CO} = \frac{PV}{RT} = \left( \frac{112 \text{ kPa}}{0.0821 \text{ L} \text{ atm} \text{ mol}^{-1} \text{ K}^{-1}} \right) \left( \frac{15.0 \text{ L}}{101.325 \text{ kPa}} \right) = 0.5641135 \text{ mol} \text{ CO}$

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

Moles of $\text{H}_2 = \frac{PV}{RT} = \left( \frac{744 \text{ torr}}{0.0821 \text{ L} \text{ atm} \text{ mol}^{-1} \text{ K}^{-1}} \right) \left( \frac{18.5 \text{ L}}{760 \text{ torr}} \right) = 0.6338824 \text{ mol} \text{ H}_2$

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

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

6.103 **Plan:** 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 \( \Delta H_f^\circ \) 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 methane to moles and multiply that mole number by the heat of combustion.

**Solution:**

a) The balanced chemical equation for this reaction is:

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)
\]

\[
\Delta H_{\text{rxn}}^\circ = \{1 \Delta H_f^\circ [\text{CO}_2(g)] + 2 \Delta H_f^\circ [\text{H}_2\text{O}(g)]\} - \{1 \Delta H_f^\circ [\text{CH}_4(g)] + 2 \Delta H_f^\circ [\text{O}_2(g)]\}
\]

\[
= [(1 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-74.87 \text{ kJ/mol}) + (2 \text{ mol})(0.0 \text{ kJ/mol})]
\]

\[
= -802.282 \text{ kJ}
\]

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

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

b) The heat released by the reaction is "stored" in the gaseous molecules by virtue of their specific heat capacities, \( c \), using the equation \( q = c \times \text{mass} \times \Delta T \). 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 \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). All of the methane and oxygen molecules were consumed. However, the oxygen was added as a component of air, which is 78% \( \text{N}_2 \) and 21% \( \text{O}_2 \), and there is leftover \( \text{N}_2 \).

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

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

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

Mole fraction \( \text{N}_2 \) = (79%/100%) = 0.79

Mole fraction \( \text{O}_2 \) = (21%/100%) = 0.21

Moles of \( \text{N}_2(g) \) = \( \left( 3.1172 \text{ mol O}_2 \right) \left( \frac{0.79 \text{ mol N}_2}{0.21 \text{ mol O}_2} \right) = 11.72661 \text{ mol N}_2 \)

\[
q = c \times \text{mass} \times \Delta T
\]

\[
q = (1250.4 \text{ kJ}) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 1.2504 \times 10^6 \text{ J}
\]

\[
1.2504 \times 10^6 \text{ J} = (1.5586 \text{ mol CO}_2)(57.2 \text{ J/mol°C})(T_{\text{final}} - 0.0)^\circ \text{C}
\]

\[
+ (3.1172 \text{ mol H}_2\text{O})(36.0 \text{ J/mol°C})(T_{\text{final}} - 0.0)^\circ \text{C}
\]

\[
+ (11.72661 \text{ mol N}_2)(30.5 \text{ J/mol°C})(T_{\text{final}} - 0.0)^\circ \text{C}
\]

\[
1.2504 \times 10^6 \text{ J} = 89.15192 \text{ J/°C}(T_{\text{final}}) + 112.2192 \text{ J/°C}(T_{\text{final}}) + 357.6616 \text{ J/°C}(T_{\text{final}})
\]

\[
1.2504 \times 10^6 \text{ J} = (559.03272 \text{ J/°C})T_{\text{final}}
\]

\[
T_{\text{final}} = (1.2504 \times 10^6 \text{ J})/(559.0324 \text{ J/°C}) = 2236.72 = 2.24 \times 10^3 \text{ °C}
\]