

CHAPTER 6 THERMOCHEMISTRY: ENERGY FLOW AND CHEMICAL CHANGE

END-OF-CHAPTER PROBLEMS

6.1 **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 (impact)
 ↓
 Kinetic energy (falling text)
 ↓
 Potential energy (raised text)
 ↓
 Mechanical energy (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:

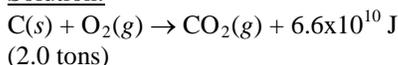
$$\Delta E = q + w$$

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

6.6 $q + w = -255 \text{ cal} + (-428 \text{ cal}) = \mathbf{-683 \text{ cal}}$

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

Solution:



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

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

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

6.8 $\text{CaCO}_3(s) + 9.0 \times 10^6 \text{ kJ} \rightarrow \text{CaO}(s) + \text{CO}_2(g)$
(5.0 tons)

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

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

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

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

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

6.10 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) **Endothermic**, the wood being chopped absorbs heat (and work).

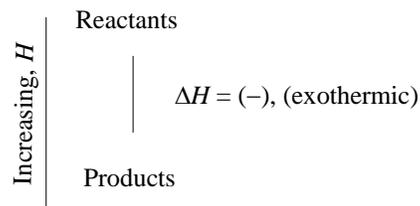
g) **Exothermic**, the furnace releases heat from fuel combustion. Alternatively, if the system is defined as the air in the house, the change is endothermic since the air's temperature is increasing by the input of heat energy from the furnace.

6.11 Absolute enthalpy values, like absolute energy values, are unknown.

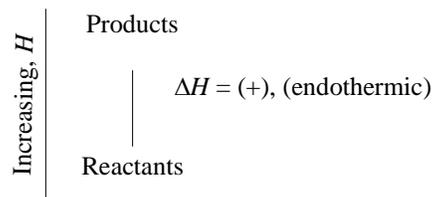
6.12 Plan: An exothermic reaction releases heat, so the reactants have greater H (H_{initial}) than the products (H_{final}).

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

Solution:

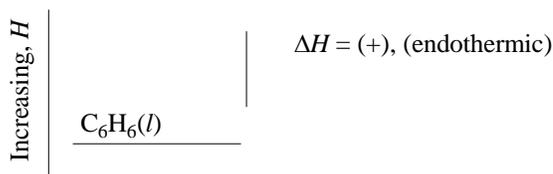
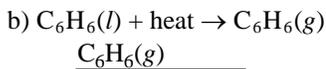
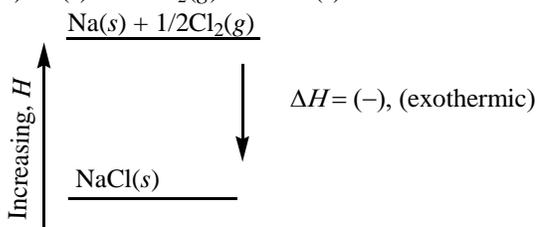
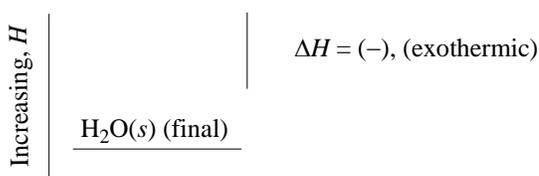
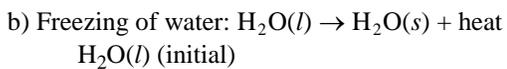
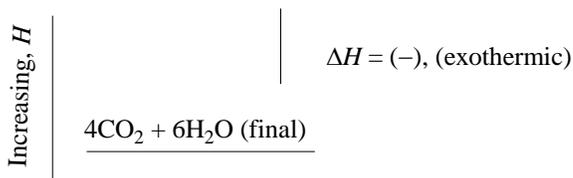
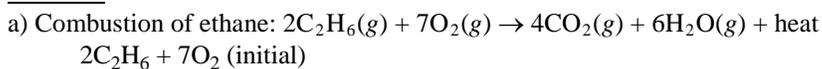


6.13



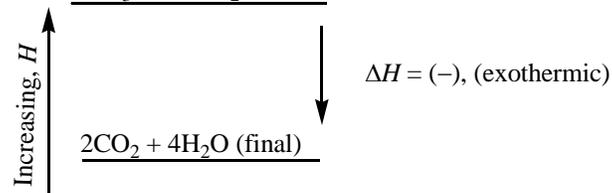
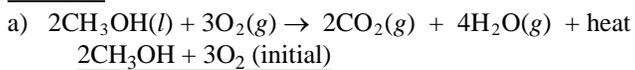
6.14 Plan: Combustion of hydrocarbons and related compounds require oxygen (and a heat catalyst) to yield carbon dioxide gas, water vapor, and heat. Combustion reactions are exothermic. The freezing of liquid water is an exothermic process as heat is removed from the water in the conversion from liquid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

Solution:

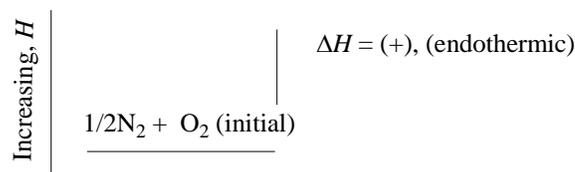
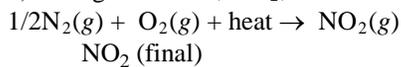


6.16 Plan: Combustion of hydrocarbons and related compounds require oxygen (and a heat catalyst) to yield carbon dioxide gas, water vapor, and heat. Combustion reactions are exothermic. An exothermic reaction releases heat, so the reactants have greater H (H_{initial}) than the products (H_{final}). If heat is absorbed, the reaction is endothermic and the products have greater H (H_{final}) than the reactants (H_{initial}).

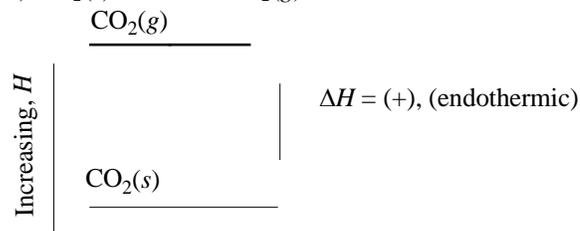
Solution:



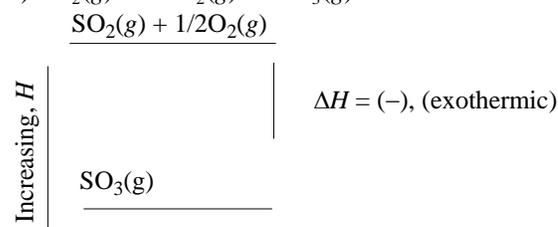
b) Nitrogen dioxide, NO_2 , forms from N_2 and O_2 .



6.17 a) $\text{CO}_2(\text{s}) + \text{heat} \rightarrow \text{CO}_2(\text{g})$



b) $\text{SO}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) + \text{heat}$



6.18 Plan: Recall that q_{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_{sys} to find ΔE_{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. $\Delta E_{\text{sys}} = q + w$. Since q is positive and w is negative, the sign of ΔE_{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.

6.19 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) $\Delta E_{\text{sys}} = q + w$. Since q is negative and w is positive, the sign of ΔE_{sys} and ΔE_{surr} cannot be predicted. ΔE_{sys} will be positive and ΔE_{surr} will be negative if $w > q$ and ΔE_{sys} will be negative and ΔE_{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 $q = c \times \text{mass} \times \Delta T$. The specific heat capacity, c_{water} , is found in Table 6.2. Because the Celsius degree is the same size as the Kelvin degree, $\Delta T = 100^\circ\text{C} - 25^\circ\text{C} = 75^\circ\text{C} = 75\text{ K}$.

Solution:

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

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

- 6.24 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 ΔT can be calculated. Once ΔT is known, that value is added to the initial temperature to find the final temperature.

Solution:

$$q (\text{J}) = c \times \text{mass} \times \Delta T \quad T_{\text{initial}} = 13.00^\circ\text{C} \quad T_{\text{final}} = ? \quad \text{mass} = 295 \text{ g} \quad c = 0.900 \text{ J/g}\cdot\text{K}$$

$$q = (75.0 \text{ kJ}) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 7.50 \times 10^4 \text{ J}$$

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

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

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

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

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

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

6.25 $q (\text{J}) = c \times \text{mass} \times \Delta T$
 $-688 \text{ J} = (2.42 \text{ J/g}\cdot\text{K})(27.7 \text{ g})(\Delta T)$
 $(\Delta T) = \frac{(-688 \text{ J})}{(27.7 \text{ g}) \left(\frac{2.42 \text{ J}}{\text{g}\cdot\text{K}} \right)} = -10.26345 \text{ K} = -10.26345^\circ\text{C}$

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

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

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

- 6.26 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:

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

6.27 $-q_{\text{lost}} = q_{\text{gained}}$
 $-2(\text{mass})(c_{\text{Cu}})(T_{\text{final}} - 105)^\circ\text{C} = (\text{mass})(c_{\text{Cu}})(T_{\text{final}} - 45)^\circ\text{C}$
 $-2(T_{\text{final}} - 105)^\circ\text{C} = (T_{\text{final}} - 45)^\circ\text{C}$
 $2(105^\circ\text{C}) - 2T_{\text{final}} = T_{\text{final}} - 45^\circ\text{C}$
 $210^\circ\text{C} + 45^\circ\text{C} = T_{\text{final}} + 2T_{\text{final}} = 3T_{\text{final}}$
 $(255^\circ\text{C})/3 = T_{\text{final}} = \mathbf{85.0^\circ\text{C}}$

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:

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

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

$$c \times \text{mass} \times \Delta T (85^\circ\text{C water}) = c \times \text{mass} \times \Delta T (26^\circ\text{C water})$$

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

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

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

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

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

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

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

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

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

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

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

$$52.943 \text{ g} = \text{mass}$$

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

6.30 Benzoic acid is $\text{C}_6\text{H}_5\text{COOH}$, and will be symbolized as HBz.

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

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

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

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

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

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

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

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

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

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 $q_{\text{calorimeter}} = 0$.

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

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

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

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

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

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

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

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.)

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

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

The moles show that both H_2SO_4 and KOH are limiting.

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

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

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

(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:

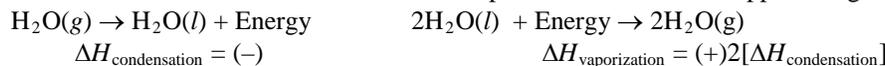
The reaction has a **positive** ΔH_{rxn} , because this reaction requires the input of energy to break the oxygen-oxygen bond in O_2 :



- 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 ($+\Delta H$).



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 ΔH_{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, $\Delta H = \mathbf{+20.2 \text{ kJ}}$.

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

d) The mass of S_8 requires conversion to moles and then a calculation identical to part c) can be performed.

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

- 6.36 $\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g}) \qquad \Delta H_{\text{rxn}} = 117.3 \text{ kJ}$

a) **Absorbed**

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

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

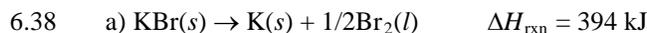
$$\text{d) } \Delta H_{\text{rxn}} = (35.5 \text{ g CO}_2) \left(\frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \right) \left(\frac{-117.3 \text{ kJ}}{1 \text{ mol CO}_2} \right) = -94.618 = \mathbf{-94.6 \text{ kJ}}$$

- 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:



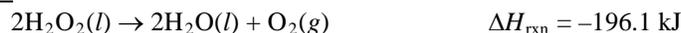
b) $\Delta H_{\text{rxn}} = (3.50 \text{ g NO}) \left(\frac{1 \text{ mol NO}}{30.01 \text{ g NO}} \right) \left(\frac{-90.29 \text{ kJ}}{1 \text{ mol NO}} \right) = -10.5303 = \mathbf{-10.5 \text{ kJ}}$



b) $\Delta H_{\text{rxn}} = (10.0 \text{ kg KBr}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol KBr}}{119.00 \text{ g KBr}} \right) \left(\frac{-394 \text{ kJ}}{1 \text{ mol KBr}} \right) = -3.3109 \times 10^4 = \mathbf{-3.31 \times 10^4 \text{ kJ}}$

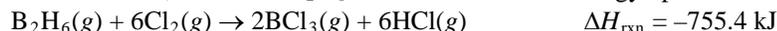
6.39 Plan: For the reaction written, 2 moles of H_2O_2 release 196.1 kJ of energy upon decomposition. Use this ratio to convert between the given amount of reactant and the amount of heat released. The amount of H_2O_2 must be converted from kg to g to moles.

Solution:



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

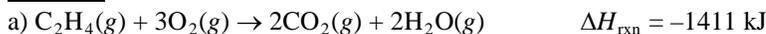
6.40 For the reaction written, 1 mole of B_2H_6 releases 755.4 kJ of energy upon reaction.



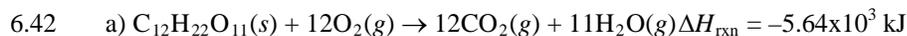
Heat (kJ) = $q = (1 \text{ kg}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol B}_2\text{H}_6}{27.67 \text{ g B}_2\text{H}_6} \right) \left(\frac{-755.4 \text{ kJ}}{1 \text{ mol B}_2\text{H}_6} \right) = -2.73003 \times 10^4 = \mathbf{-2.730 \times 10^4 \text{ kJ/kg}}$

6.41 Plan: 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:



b) Mass (g) of $\text{C}_2\text{H}_4 = (-70.0 \text{ kJ}) \left(\frac{1 \text{ mol C}_2\text{H}_4}{-1411 \text{ kJ}} \right) \left(\frac{28.05 \text{ g C}_2\text{H}_4}{1 \text{ mol C}_2\text{H}_4} \right) = 1.39157 = \mathbf{1.39 \text{ g C}_2\text{H}_4}$



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

6.43 Hess's law: ΔH_{rxn} is independent of the number of steps or the path of the reaction.

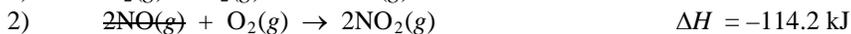
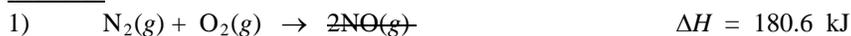
6.44 Plan: To obtain the overall reaction, add the first reaction to the reverse of the second. When the second reaction is reversed, the sign of its enthalpy change is reversed from positive to negative.

Solution:

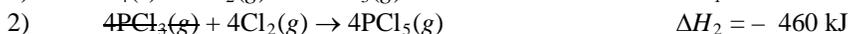
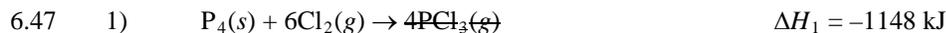


6.46 Plan: Add the two equations, canceling substances that appear on both sides of the arrow. When matching the equations with the arrows in the Figure, remember that a positive ΔH corresponds to an arrow pointing up while a negative ΔH corresponds to an arrow pointing down.

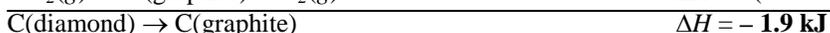
Solution:



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.



Equation 1) = B, equation 2) = C, equation 3) = A



6.49 The standard heat of reaction, $\Delta H_{\text{rxn}}^\circ$, is the enthalpy change for any reaction where all substances are in their standard states. The standard heat of formation, ΔH_f° , 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.

6.50 Plan: ΔH_f° is for the reaction that shows the formation of one mole of compound from its elements in their standard states.

Solution:

a) $1/2\text{Cl}_2(\text{g}) + \text{Na}(\text{s}) \rightarrow \text{NaCl}(\text{s})$ The element chlorine occurs as Cl_2 , not Cl.

b) $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ 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 ($\Delta H_f^\circ = 0$).

Solution:

a) $\text{Ca}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$

b) $\text{Na}(\text{s}) + 1/2\text{H}_2(\text{g}) + \text{C}(\text{graphite}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{NaHCO}_3(\text{s})$

c) $\text{C}(\text{graphite}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{l})$

d) $1/2\text{H}_2(\text{g}) + 1/2\text{N}_2(\text{g}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{HNO}_3(\text{l})$

6.52 a) $1/2\text{H}_2(\text{g}) + 1/2\text{I}_2(\text{s}) \rightarrow \text{HI}(\text{g})$

b) $\text{Si}(\text{s}) + 2\text{F}_2(\text{g}) \rightarrow \text{SiF}_4(\text{g})$

c) $3/2\text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$

d) $3\text{Ca}(\text{s}) + 1/2\text{P}_4(\text{s}) + 4\text{O}_2(\text{g}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$

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 ΔH_f° values (Appendix B) are reported as energy per one mole, use the appropriate stoichiometric coefficient to reflect the higher number of moles.

Solution:

$$\Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta H_{\text{f}}^{\circ}(\text{reactants})$$

$$\begin{aligned} \text{a) } \Delta H_{\text{rxn}}^{\circ} &= \{2 \Delta H_{\text{f}}^{\circ} [\text{SO}_2(\text{g})] + 2 \Delta H_{\text{f}}^{\circ} [\text{H}_2\text{O}(\text{g})]\} - \{2 \Delta H_{\text{f}}^{\circ} [\text{H}_2\text{S}(\text{g})] + 3 \Delta H_{\text{f}}^{\circ} [\text{O}_2(\text{g})]\} \\ &= [(2 \text{ mol})(-296.8 \text{ kJ/mol}) + (2 \text{ mol})(-241.826 \text{ kJ/mol})] - [(2 \text{ mol})(-20.2 \text{ kJ/mol}) + (3 \text{ mol})(0.0 \text{ kJ/mol})] \\ &= \mathbf{-1036.9 \text{ kJ}} \end{aligned}$$

b) The balanced equation is $\text{CH}_4(\text{g}) + 4\text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{l}) + 4\text{HCl}(\text{g})$

$$\Delta H_{\text{rxn}}^{\circ} = \{1 \Delta H_{\text{f}}^{\circ} [\text{CCl}_4(\text{l})] + 4 \Delta H_{\text{f}}^{\circ} [\text{HCl}(\text{g})]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{CH}_4(\text{g})] + 4 \Delta H_{\text{f}}^{\circ} [\text{Cl}_2(\text{g})]\}$$

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= [(1 \text{ mol})(-139 \text{ kJ/mol}) + (4 \text{ mol})(-92.31 \text{ kJ/mol})] - [(1 \text{ mol})(-74.87 \text{ kJ/mol}) + (4 \text{ mol})(0 \text{ kJ/mol})] \\ &= \mathbf{-433 \text{ kJ}} \end{aligned}$$

$$6.54 \quad \Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta H_{\text{f}}^{\circ}(\text{reactants})$$

$$\begin{aligned} \text{a) } \Delta H_{\text{rxn}}^{\circ} &= \{1 \Delta H_{\text{f}}^{\circ} [\text{SiF}_4(\text{g})] + 2 \Delta H_{\text{f}}^{\circ} [\text{H}_2\text{O}(\text{l})]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{SiO}_2(\text{s})] + 4 \Delta H_{\text{f}}^{\circ} [\text{HF}(\text{g})]\} \\ &= [(1 \text{ mol})(-1614.9 \text{ kJ/mol}) + (2 \text{ mol})(-285.840 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol})(-910.9 \text{ kJ/mol}) + (4 \text{ mol})(-273 \text{ kJ/mol})] \\ &= \mathbf{-184 \text{ kJ}} \end{aligned}$$

b) $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

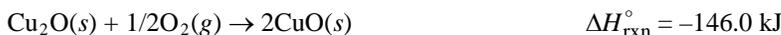
$$\Delta H_{\text{rxn}}^{\circ} = \{4 \Delta H_{\text{f}}^{\circ} [\text{CO}_2(\text{g})] + 6 \Delta H_{\text{f}}^{\circ} [\text{H}_2\text{O}(\text{g})]\} - \{2 \Delta H_{\text{f}}^{\circ} [\text{C}_2\text{H}_6(\text{g})] + 7 \Delta H_{\text{f}}^{\circ} [\text{O}_2(\text{g})]\}$$

$$\begin{aligned} &= [(4 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-241.826 \text{ kJ/mol})] - [(2 \text{ mol})(-84.667 \text{ kJ/mol}) + (7 \text{ mol})(0 \text{ kJ/mol})] \\ &= \mathbf{-2855.6 \text{ kJ}} \text{ (or } -1427.8 \text{ kJ for reaction of 1 mol of } \text{C}_2\text{H}_6\text{)} \end{aligned}$$

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 $\Delta H_{\text{f}}^{\circ}$ 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, $\Delta H_{\text{rxn}}^{\circ}$ is known and $\Delta H_{\text{f}}^{\circ}$ of CuO must be calculated.

Solution:

$$\Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta H_{\text{f}}^{\circ}(\text{reactants})$$



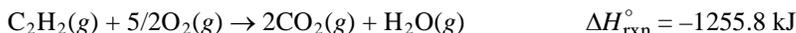
$$\Delta H_{\text{rxn}}^{\circ} = \{2 \Delta H_{\text{f}}^{\circ} [\text{CuO}(\text{s})]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{Cu}_2\text{O}(\text{s})] + 1/2 \Delta H_{\text{f}}^{\circ} [\text{O}_2(\text{g})]\}$$

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

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

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

$$6.56 \quad \Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta H_{\text{f}}^{\circ}(\text{reactants})$$



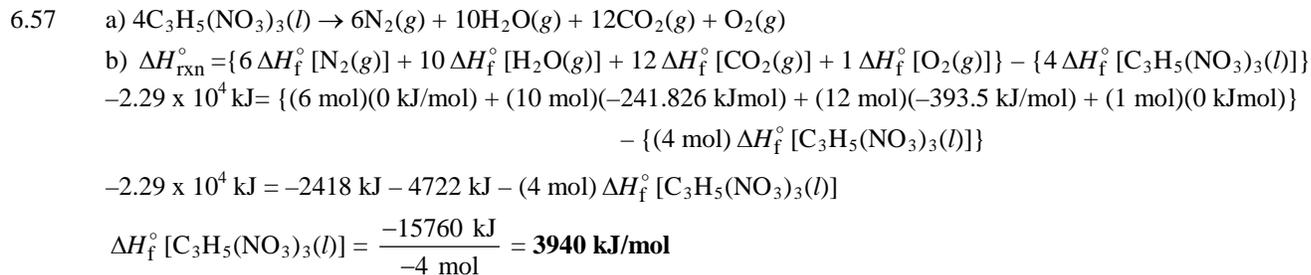
$$\Delta H_{\text{rxn}}^{\circ} = \{2 \Delta H_{\text{f}}^{\circ} [\text{CO}_2(\text{g})] + 1 \Delta H_{\text{f}}^{\circ} [\text{H}_2\text{O}(\text{g})]\} - \{1 \Delta H_{\text{f}}^{\circ} [\text{C}_2\text{H}_2(\text{g})] + 5/2 \Delta H_{\text{f}}^{\circ} [\text{O}_2(\text{g})]\}$$

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

$$- \{(1 \text{ mol}) \Delta H_{\text{f}}^{\circ} [\text{C}_2\text{H}_2(\text{g})] + (5/2 \text{ mol})(0.0 \text{ kJ/mol})\}$$

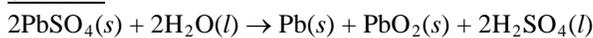
$$-1255.8 \text{ kJ} = -787.0 \text{ kJ} - 241.8 \text{ kJ} - (1 \text{ mol}) \Delta H_{\text{f}}^{\circ} [\text{C}_2\text{H}_2(\text{g})]$$

$$\Delta H_{\text{f}}^{\circ} [\text{C}_2\text{H}_2(\text{g})] = \frac{-227.0 \text{ kJ}}{-1 \text{ mol}} = \mathbf{227.0 \text{ kJ/mol}}$$



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 ΔH_f° 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 $\Delta H_{\text{rxn}}^\circ$) and multiply the coefficients (and $\Delta H_{\text{rxn}}^\circ$) of the second reaction by 2.

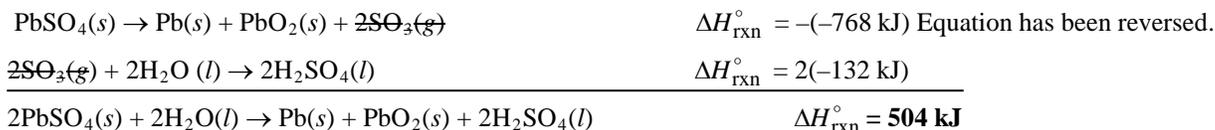
Solution:



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

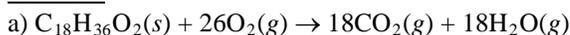
$$\begin{aligned} \text{a) } \Delta H_{\text{rxn}}^\circ &= \{1 \Delta H_f^\circ [\text{Pb}(s)] + 1 \Delta H_f^\circ [\text{PbO}_2(s)] + 2 \Delta H_f^\circ [\text{H}_2\text{SO}_4(l)]\} \\ &\quad - \{2 \Delta H_f^\circ [\text{PbSO}_4(s)] + 2 \Delta H_f^\circ [\text{H}_2\text{O}(l)]\} \\ &= \{(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(-276.6 \text{ kJ/mol}) + (2 \text{ mol})(-813.989 \text{ kJ/mol})\} \\ &\quad - \{(2 \text{ mol})(-918.39 \text{ kJ/mol}) + (2 \text{ mol})(-285.840 \text{ kJ/mol})\} \\ &= \mathbf{503.9 \text{ kJ}} \end{aligned}$$

b) Use Hess's law:



6.59 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 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 stearic acid to moles and use the ratio between stearic acid and $\Delta H_{\text{rxn}}^\circ$ 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.

Solution:



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

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \{18 \Delta H_f^\circ [\text{CO}_2(g)] + 18 \Delta H_f^\circ [\text{H}_2\text{O}(g)]\} - \{1 \Delta H_f^\circ [\text{C}_{18}\text{H}_{36}\text{O}_2(s)] + 26 \Delta H_f^\circ [\text{O}_2(g)]\} \\ &= \{(18 \text{ mol})(-393.5 \text{ kJ/mol}) + (18 \text{ mol})(-241.826 \text{ kJ/mol})\} - \{(1 \text{ mol})(-948 \text{ kJ/mol}) + (26 \text{ mol})(0 \text{ kJ/mol})\} \\ &= -10,487.868 = \mathbf{-10,488 \text{ kJ}} \end{aligned}$$

$$\text{c) } q (\text{kJ}) = (1.00 \text{ g C}_{18}\text{H}_{36}\text{O}_2) \left(\frac{1 \text{ mol C}_{18}\text{H}_{36}\text{O}_2}{284.47 \text{ C}_{18}\text{H}_{36}\text{O}_2} \right) \left(\frac{-10,487.868 \text{ kJ}}{1 \text{ mol C}_{18}\text{H}_{36}\text{O}_2} \right) = -36.8681 = \mathbf{-36.9 \text{ kJ}}$$

$$q (\text{kcal}) = (-36.8681 \text{ kJ}) \left(\frac{1 \text{ kcal}}{4.184 \text{ kJ}} \right) = -8.811688 = \mathbf{-8.81 \text{ kcal}}$$

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

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 $\Delta H = q_P$.

Solution:

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

$$T = 273 + 15 = 288 \text{ K} \quad \text{and} \quad T = 273 + 30 = 303 \text{ K}$$

$$\text{Initial volume (L)} = V = \frac{nRT}{P} = \frac{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(288 \text{ K})}{(1.00 \text{ atm})} = 23.6448 = \mathbf{23.6 \text{ L/mol}}$$

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

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.

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

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 $\text{L}\cdot\text{atm}$, so a conversion factor is needed to convert work in units of $\text{L}\cdot\text{atm}$ to joules.

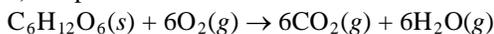
$$w = -P\Delta V = -(1.00 \text{ atm})((24.8763 - 23.6448) \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} \right) = -124.75 = \mathbf{-1.2 \times 10^2 \text{ J}}$$

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

$$e) \Delta H = q_P = \mathbf{310 \text{ J}}$$

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: $\Delta H = \Delta E + P\Delta V = \Delta E - w = (q + w) - w = q_P$

- 6.61 a) Respiration:



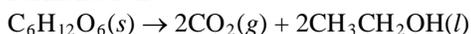
$$\Delta H_{\text{rxn}}^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$$

$$= \{6 \Delta H_f^\circ[\text{CO}_2(g)] + 6 \Delta H_f^\circ[\text{H}_2\text{O}(g)]\} - \{1 \Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6(s)] + 6 \Delta H_f^\circ[\text{O}_2(g)]\}$$

$$= [(6 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-1273.3 \text{ kJ/mol}) + (6 \text{ mol})(0.0 \text{ kJ/mol})]$$

$$= -2538.656 = \mathbf{-2538.7 \text{ kJ}}$$

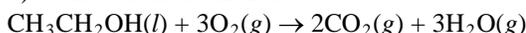
Fermentation:



$$\Delta H_{\text{rxn}}^\circ = \{2 \Delta H_f^\circ[\text{CO}_2(g)] + 2 \Delta H_f^\circ[\text{CH}_3\text{CH}_2\text{OH}(l)]\} - [1 \Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6(s)]]$$

$$= [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-277.63 \text{ kJ/mol})] - [(1 \text{ mol})(-1273.3 \text{ kJ/mol})] = -68.96 = \mathbf{-69.0 \text{ kJ}}$$

b) Combustion of ethanol:



$$\Delta H_{\text{rxn}}^\circ = \{2 \Delta H_f^\circ[\text{CO}_2(g)] + 3 \Delta H_f^\circ[\text{H}_2\text{O}(g)]\} - \{1 \Delta H_f^\circ[\text{CH}_3\text{CH}_2\text{OH}(l)] + 3 \Delta H_f^\circ[\text{O}_2(g)]\}$$

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

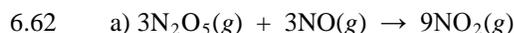
$$= -1234.848 = -\mathbf{1234.8 \text{ kJ}}$$

Heats of combustion/mol C:

$$\text{Sugar: } \left(\frac{-2538.656 \text{ kJ}}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} \right) \left(\frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{6 \text{ mol C}} \right) = -423.1093 = -423.11 \text{ kJ/mol C}$$

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

Ethanol has a higher value.

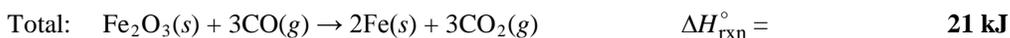
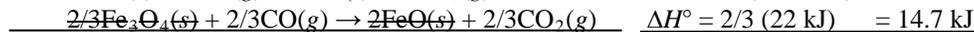
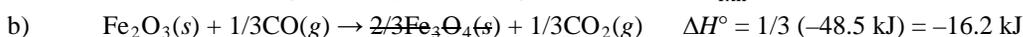
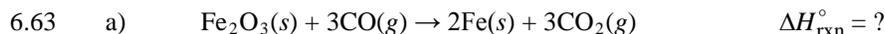


$$\Delta H_{\text{rxn}}^{\circ} = \{9 \Delta H_f^{\circ} [\text{NO}_2(\text{g})]\} - \{3 \Delta H_f^{\circ} [\text{N}_2\text{O}_5(\text{g})] + 3 \Delta H_f^{\circ} [\text{NO}(\text{g})]\}$$

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

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

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



6.64 a) Heat = $(20.4 \text{ gal}) \left(\frac{4 \text{ qt}}{1 \text{ gal}} \right) \left(\frac{1 \text{ L}}{1.057 \text{ qt}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{0.702 \text{ g}}{\text{mL}} \right) \left(\frac{1 \text{ mol C}_8\text{H}_{18}}{114.22 \text{ g}} \right) \left(\frac{-5.45 \times 10^3 \text{ kJ}}{1 \text{ mol C}_8\text{H}_{18}} \right)$

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

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

c) Only a small percentage of the chemical energy in the fuel is converted to work to move the car; most of the chemical energy is lost as waste heat flowing into the surroundings.

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

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

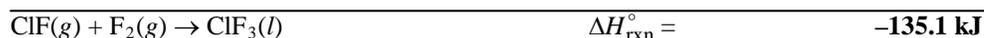
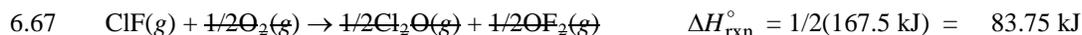
All also have the same q value, 450. J. So, 450. J $\propto (c \times \Delta T)$. c , specific heat capacity, and ΔT are inversely proportional. The higher the ΔT , the lower the value of specific heat capacity:

ΔT : $\mathbf{B > D > C > A}$

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



$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol sucrose})(-2226 \text{ kJ/mol}) + (1 \text{ mol H}_2\text{O})(-285.840 \text{ kJ/mol})] - [(1 \text{ mol glucose})(-1273 \text{ kJ/mol}) + (1 \text{ mol fructose})(-1266 \text{ kJ/mol})] = \mathbf{27 \text{ kJ/mol sucrose}}$$



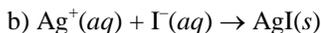


$$\begin{aligned} \text{Moles of AgNO}_3 &= (50.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{5.0 \text{ g AgNO}_3}{1 \text{ L}} \right) \left(\frac{1 \text{ mol AgNO}_3}{169.9 \text{ g AgNO}_3} \right) \\ &= 1.47145 \times 10^{-3} \text{ mol AgNO}_3 \end{aligned}$$

$$\begin{aligned} \text{Moles of NaI} &= (50.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{5.0 \text{ g NaI}}{1 \text{ L}} \right) \left(\frac{1 \text{ mol NaI}}{149.9 \text{ g NaI}} \right) \\ &= 1.6677785 \times 10^{-3} \text{ mol NaI} \end{aligned}$$

The AgNO_3 is limiting, and will be used to finish the problem:

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



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \{1 \Delta H_f^\circ [\text{AgI}(s)]\} - \{1 \Delta H_f^\circ [\text{Ag}^+(aq)] + 1 \Delta H_f^\circ [\text{I}^-(aq)]\} \\ &= [(1 \text{ mol})(-62.38 \text{ kJ/mol})] - [(1 \text{ mol})(105.9 \text{ kJ/mol}) + (1 \text{ mol})(-55.94 \text{ kJ/mol})] \\ &= \mathbf{-112.3 \text{ kJ}} \end{aligned}$$

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

$$\begin{aligned} \Delta T = \Delta H_{\text{rxn}}^\circ / c \times \text{mass} &= \frac{\left[\left(\frac{112.3 \text{ kJ}}{\text{mol AgI}} \right) \left(\frac{1 \text{ mol AgI}}{1 \text{ mol AgNO}_3} \right) (1.47145 \times 10^{-3} \text{ mol AgNO}_3) \right]}{\left(\frac{4.184 \text{ J}}{\text{g} \cdot \text{K}} \right) \left[(50.0 + 50.0) \text{ mL} \left(\frac{1.00 \text{ g}}{\text{mL}} \right) \right]} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) \\ &= 0.39494 = \mathbf{0.39 \text{ K}} \end{aligned}$$

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

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

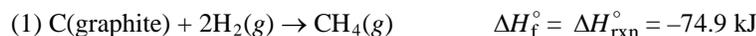
c) Moles of $\text{CH}_4 = (1.00 \text{ qt}) \left(\frac{1 \text{ L}}{1.057 \text{ qt}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1.00 \text{ g}}{\text{mL}} \right) \left(\frac{4.184 \text{ J}}{\text{g} \cdot \text{C}} \right) ((100.0 - 25.0)^\circ\text{C}) \left(\frac{1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

Volume (ft^3) of $\text{CH}_4 = (0.370172 \text{ mol CH}_4) \left(\frac{16.04 \text{ g CH}_4}{1 \text{ mol CH}_4} \right) \left(\frac{1 \text{ L}}{0.72 \text{ g CH}_4} \right) \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right) \left(\frac{35.3 \text{ ft}^3}{1 \text{ m}^3} \right)$
 $= 0.291105 = \mathbf{0.29 \text{ ft}^3}$

d) Volume = $(2 \times 10^{13} \text{ J}) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \left(\frac{1 \text{ mol CH}_4}{802 \text{ kJ}} \right) \left(\frac{16.04 \text{ g CH}_4}{1 \text{ mol CH}_4} \right) \left(\frac{1 \text{ L}}{0.72 \text{ g CH}_4} \right) \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right) \left(\frac{35.3 \text{ ft}^3}{1 \text{ m}^3} \right)$
 $= 1.9611 \times 10^7 = \mathbf{2 \times 10^7 \text{ ft}^3}$

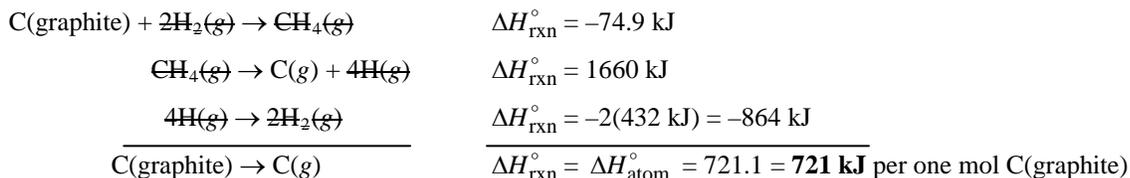
6.70 Plan: Chemical equations can be written that describe the three processes. Assume one mole of each substance of interest so that units are expressed as kJ. To obtain the overall reaction, reverse the third reaction and multiply its coefficients by two and add to the first two reactions. When the third reaction is reversed, the sign of its enthalpy change is reversed from positive to negative.

Solution:





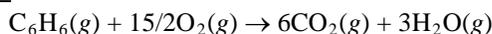
The third equation is reversed and its coefficients are multiplied by 2 to add the three equations.



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

Solution:

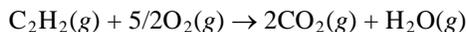


$$\Delta H_{\text{rxn}}^{\circ} = \{6 \Delta H_f^{\circ} [\text{CO}_2(g)] + 3 \Delta H_f^{\circ} [\text{H}_2\text{O}(g)]\} - \{1 \Delta H_f^{\circ} [\text{C}_6\text{H}_6(g)] + 15/2 \Delta H_f^{\circ} [\text{O}_2(g)]\}$$

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

$$= -3169.378$$

$$\Delta H_{\text{rxn}}^{\circ} \text{ per mole of CH} = \left(\frac{-3169.378 \text{ kJ}}{\text{mol C}_6\text{H}_6} \right) \left(\frac{1 \text{ mol C}_6\text{H}_6}{6 \text{ mol CH}} \right) = -528.2297 = \mathbf{-528.2 \text{ kJ/mol CH}}$$



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

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

$$= -1255.826 \text{ kJ}$$

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

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



$$\Delta H_{\text{rxn}}^{\circ} = \{2 \Delta H_f^{\circ} [\text{H}_2\text{O}(l)]\} - \{2 \Delta H_f^{\circ} [\text{H}^+(aq)] + 2 \Delta H_f^{\circ} [\text{OH}^-(aq)]\}$$

$$= [(2 \text{ mol})(-285.84 \text{ kJ/mol})] - [(2 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(-229.94 \text{ kJ/mol})]$$

$$= -111.8 \text{ kJ}$$

1 mole of H_2SO_4 reacts with 2 moles of NaOH.

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

$$= 2060 \text{ g H}_2\text{SO}_4 \text{ solution}$$

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

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

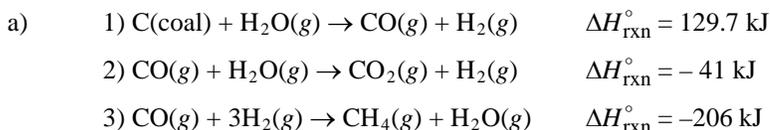
$$\Delta T = \frac{q}{c \times \text{mass}} = \frac{(111.8 \text{ kJ}) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right)}{4.184 \text{ J/g}^{\circ}\text{C}((2060 + 200) \text{ g})} = 11.82^{\circ}\text{C}$$

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

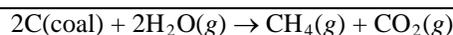
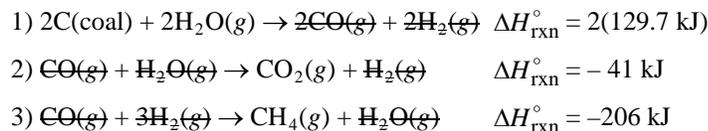
This temperature is above the temperature at which a flammable vapor could be formed so the temperature increase could cause the vapor to explode.

6.74 a) $2\text{C}_{12}\text{H}_{26}(l) + 37\text{O}_2(g) \rightarrow 24\text{CO}_2(g) + 26\text{H}_2\text{O}(g)$
 b) $\Delta H_{\text{rxn}}^{\circ} = \{24 \Delta H_f^{\circ} [\text{CO}_2(g)] + 26 \Delta H_f^{\circ} [\text{H}_2\text{O}(g)]\} - \{2 \Delta H_f^{\circ} [\text{C}_{12}\text{H}_{26}(g)] + 37 \Delta H_f^{\circ} [\text{O}_2(g)]\}$
 $-1.50 \times 10^4 \text{ kJ} = [(24 \text{ mol})(-393.5 \text{ kJ/mol}) + (26 \text{ mol})(-241.826 \text{ kJ/mol})]$
 $- [(2 \text{ mol}) \Delta H_f^{\circ} [\text{C}_{12}\text{H}_{26}(g)] + (37 \text{ mol})(0.0 \text{ kJ/mol})]$
 $-1.50 \times 10^4 \text{ kJ} = -9444.0 \text{ kJ} + -6287.476 \text{ kJ} - [(2 \text{ mol}) \Delta H_f^{\circ} [\text{C}_{12}\text{H}_{26}(g)] + 0.0 \text{ kJ}]$
 $-1.50 \times 10^4 \text{ kJ} = -15,731.476 \text{ kJ} - (2 \text{ mol}) \Delta H_f^{\circ} [\text{C}_{12}\text{H}_{26}(g)]$
 $-1.50 \times 10^4 \text{ kJ} + 15,731.476 \text{ kJ} = -(2 \text{ mol}) \Delta H_f^{\circ} [\text{C}_{12}\text{H}_{26}(g)]$
 $731.476 \text{ kJ} = -(2 \text{ mol}) \Delta H_f^{\circ} [\text{C}_{12}\text{H}_{26}(g)]$
 $\Delta H_f^{\circ} [\text{C}_{12}\text{H}_{26}(g)] = -365.738 = -\mathbf{3.66 \times 10^2 \text{ kJ}}$
 c) Heat (kJ) = $(0.50 \text{ gal}) \left(\frac{4 \text{ qt}}{1 \text{ gal}} \right) \left(\frac{1 \text{ L}}{1.057 \text{ qt}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{0.749 \text{ g C}_{12}\text{H}_{26}}{\text{mL}} \right) \left(\frac{1 \text{ mol C}_{12}\text{H}_{26}}{170.33 \text{ g C}_{12}\text{H}_{26}} \right) \left(\frac{-1.50 \times 10^4 \text{ kJ}}{2 \text{ mol C}_{12}\text{H}_{26}} \right)$
 $= -6.2403 \times 10^4 = -\mathbf{6.2 \times 10^4 \text{ kJ}}$
 d) Volume (gal) = $(1250. \text{ Btu}) \left(\frac{1.055 \text{ kJ}}{1 \text{ Btu}} \right) \left(\frac{0.50 \text{ gal}}{6.2403 \times 10^4 \text{ kJ}} \right) = 0.010566 = \mathbf{1.1 \times 10^{-2} \text{ gal}}$

6.75 Use Hess's Law:



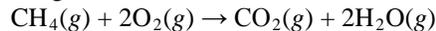
Equation 1) must be multiplied by 2 and then the reactions are added:



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

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

c) Calculating the heat of combustion of CH_4 :



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

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

$$- [(1 \text{ mol})(-74.87 \text{ kJ/mol}) - (2 \text{ mol})(0.0 \text{ kJ/mol})]$$

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

Total heat for gasification of 1.00 kg coal:

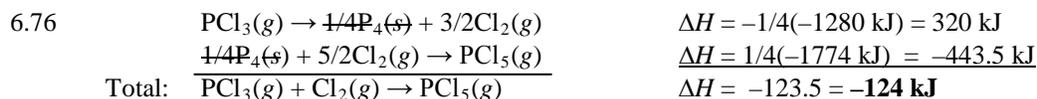
$$\Delta H^{\circ} = (1.00 \text{ kg coal}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol coal}}{12.00 \text{ g coal}} \right) \left(\frac{12.4 \text{ kJ}}{2 \text{ mol coal}} \right) = 516.667 \text{ kJ}$$

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

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

$$= -33511.75 \text{ kJ}$$

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



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

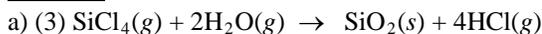
$$\text{b) Energy} = E = \text{mass} \times g \times \text{height} = mgh$$

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

c) Energy is also converted to heat.

6.78 Plan: 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 SiCl_4 , are found in Appendix B. Use reaction 3, with its given $\Delta H_{\text{rxn}}^\circ$, to find the heat of formation of $\text{SiCl}_4(g)$. Once the heat of formation of SiCl_4 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:

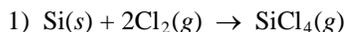


$$\begin{aligned}
 \Delta H_{\text{rxn}}^\circ &= \{1 \Delta H_f^\circ [\text{SiO}_2(s)] + 4 \Delta H_f^\circ [\text{HCl}(g)]\} - \{1 \Delta H_f^\circ [\text{SiCl}_4(g)] + 2 \Delta H_f^\circ [\text{H}_2\text{O}(g)]\} \\
 -139.5 \text{ kJ} &= [(1 \text{ mol})(-910.9 \text{ kJ/mol}) + (4 \text{ mol})(-92.31 \text{ kJ/mol})] - [\Delta H_f^\circ [\text{SiCl}_4(g)] + (2 \text{ mol})(-241.826 \text{ kJ/mol})] \\
 -139.5 \text{ kJ} &= -1280.14 - [\Delta H_f^\circ [\text{SiCl}_4(g)] + (-483.652 \text{ kJ})]
 \end{aligned}$$

$$1140.64 \text{ kJ} = -\Delta H_f^\circ [\text{SiCl}_4(g)] + 483.652 \text{ kJ}$$

$$\Delta H_f^\circ [\text{SiCl}_4(g)] = -656.988 \text{ kJ/mol}$$

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

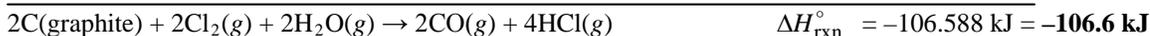
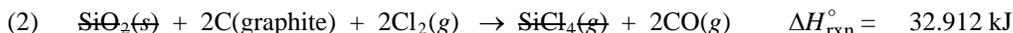


$$\begin{aligned}
 \Delta H_{\text{rxn}}^\circ &= \{1 \Delta H_f^\circ [\text{SiCl}_4(g)]\} - \{1 \Delta H_f^\circ [\text{Si}(s)] + 2 \Delta H_f^\circ [\text{Cl}_2(g)]\} \\
 &= [(1 \text{ mol})(-656.988 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})] = -656.988 = \mathbf{-657.0 \text{ kJ}}
 \end{aligned}$$



$$\begin{aligned}
 \Delta H_{\text{rxn}}^\circ &= \{1 \Delta H_f^\circ [\text{SiCl}_4(g)] + 2 \Delta H_f^\circ [\text{CO}(g)]\} \\
 &\quad - \{1 \Delta H_f^\circ [\text{SiO}_2(s)] + 2 \Delta H_f^\circ [\text{C}(\text{graphite})] + 2 \Delta H_f^\circ [\text{Cl}_2(g)]\} \\
 &= [(1 \text{ mol})(-656.988 \text{ kJ/mol}) + (2 \text{ mol})(-110.5 \text{ kJ/mol})] \\
 &\quad - [(1 \text{ mol})(-910.9 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})] \\
 &= 32.912 = \mathbf{32.9 \text{ kJ}}
 \end{aligned}$$

b) Adding reactions 2 and 3 yields:



Confirm this result by calculating $\Delta H_{\text{rxn}}^\circ$ using Appendix B values.

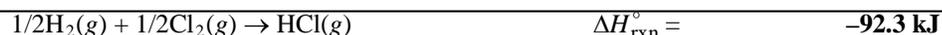
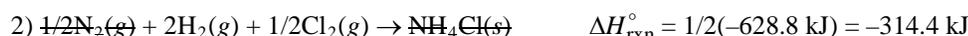


$$\begin{aligned}
 \Delta H_{\text{rxn}}^\circ &= \{2 \Delta H_f^\circ [\text{CO}(g)] + 4 \Delta H_f^\circ [\text{HCl}(g)]\} - \{2 \Delta H_f^\circ [\text{C}(\text{graphite})] + 2 \Delta H_f^\circ [\text{Cl}_2(g)] + 2 \Delta H_f^\circ [\text{H}_2\text{O}(g)]\} \\
 &= [(2 \text{ mol})(-110.5 \text{ kJ/mol}) + (4 \text{ mol})(-92.31 \text{ kJ/mol})] \\
 &\quad - [(2 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(-241.826 \text{ kJ/mol})] \\
 &= -106.588 = \mathbf{-106.6 \text{ kJ}}
 \end{aligned}$$

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



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



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

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

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

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

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

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

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

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

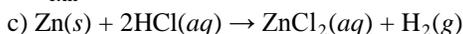
Zn is the limiting reactant.

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

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

$$= 3.0803 \text{ kJ}$$

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



$$\Delta H_{\text{rxn}}^\circ = \{1 \Delta H_f^\circ [\text{ZnCl}_2(\text{aq})] + 1 [\Delta H_f^\circ \text{H}_2(\text{g})]\} - \{1 \Delta H_f^\circ [\text{Zn}(\text{s})] + 2 \Delta H_f^\circ [\text{HCl}(\text{aq})]\}$$

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

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

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

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

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.

Solution:

a) $PV = nRT$

$$\text{Initial volume at } 0^\circ\text{C} + 273 = 273 \text{ K} = V = \frac{nRT}{P} = \frac{(1 \text{ mol})\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(273 \text{ K})}{(1.00 \text{ atm})} = 22.4133 \text{ L}$$

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

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

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

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

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

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

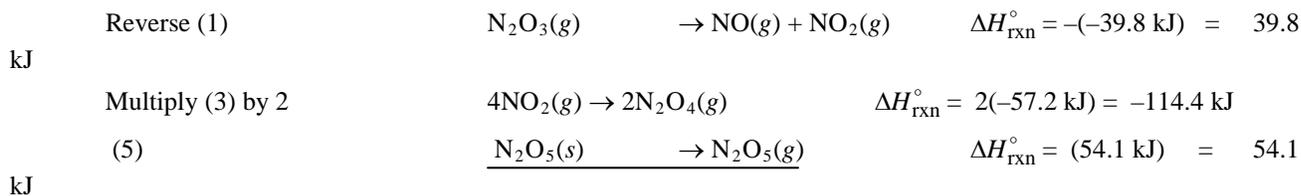
$$\Delta T = \frac{q}{(c)(\text{mass})} = \frac{6.812553 \times 10^3 \text{ J}}{(28.02 \text{ g})(1.00 \text{ J/g}\cdot\text{K})} = 243.132 = 243 \text{ K} = \mathbf{243^\circ\text{C}}$$

6.82 Plan: 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

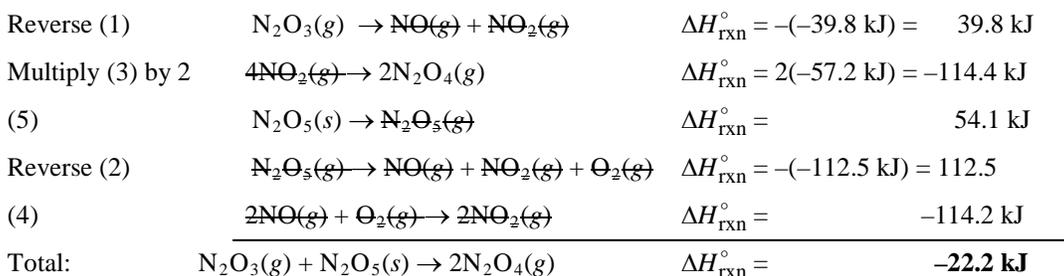
$\Delta H_{\text{rxn}}^\circ$ values will add to give the $\Delta H_{\text{rxn}}^\circ$ value of the target equation.

Solution:

Only reaction 3 contains $\text{N}_2\text{O}_4(\text{g})$, and only reaction 1 contains $\text{N}_2\text{O}_3(\text{g})$, 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:



To cancel out the $\text{N}_2\text{O}_5(\text{g})$ intermediate, reverse equation 2. This also cancels out some of the undesired $\text{NO}_2(\text{g})$ but adds $\text{NO}(\text{g})$ and $\text{O}_2(\text{g})$. Finally, add equation 4 to remove those intermediates:



6.83 $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \{1 \Delta H_f^\circ [\text{CH}_3\text{OH}(\text{l})]\} - \{1 \Delta H_f^\circ [\text{CO}(\text{g})] + 2 \Delta H_f^\circ [\text{H}_2(\text{g})]\} \\ &= [(1 \text{ mol})(-238.6 \text{ kJ/mol})] - [(1 \text{ mol})(-110.5 \text{ kJ/mol}) + (2 \text{ mol})(0.0 \text{ kJ/mol})] \\ &= -128.1 \text{ kJ}\end{aligned}$$

Find the limiting reactant:

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

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

$$\text{Moles of H}_2 = \frac{PV}{RT} = \frac{(744 \text{ torr})(18.5 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)((273 + 75) \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.6338824 \text{ mol H}_2$$

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

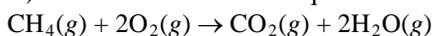
H₂ is limiting.

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

- 6.84 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 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:



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \{1 \Delta H_f^\circ [\text{CO}_2(\text{g})] + 2 \Delta H_f^\circ [\text{H}_2\text{O}(\text{g})]\} - \{1 \Delta H_f^\circ [\text{CH}_4(\text{g})] + 2 \Delta H_f^\circ [\text{O}_2(\text{g})]\} \\ &= [(1 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol})(-74.87 \text{ kJ/mol}) + (2 \text{ mol})(0.0 \text{ kJ/mol})] \\ &= -802.282 \text{ kJ} \end{aligned}$$

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

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

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 CO₂ and H₂O. All of the methane and oxygen molecules were consumed. However, the oxygen was added as a component of air, which is 78% N₂ and 21% O₂, and there is leftover N₂.

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

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

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

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

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

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

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

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

$$1.2504 \times 10^6 \text{ J} = (1.5586 \text{ mol CO}_2)(57.2 \text{ J/mol}^\circ\text{C})(T_{\text{final}} - 0.0)^\circ\text{C} \\ + (3.1172 \text{ mol H}_2\text{O})(36.0 \text{ J/mol}^\circ\text{C})(T_{\text{final}} - 0.0)^\circ\text{C} \\ + (11.72661 \text{ mol N}_2)(30.5 \text{ J/mol}^\circ\text{C})(T_{\text{final}} - 0.0)^\circ\text{C}$$

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

$$1.2504 \times 10^6 \text{ J} = (559.03272 \text{ J/}^\circ\text{C})T_{\text{final}}$$

$$T_{\text{final}} = (1.2504 \times 10^6 \text{ J}) / (559.0324 \text{ J/}^\circ\text{C}) = 2236.72 = \mathbf{2.24 \times 10^3}^\circ\text{C}$$