5 Thermochemistry

Visualizing Concepts

5.2 (a) The internal energy, E, of the products is greater than that of the reactants, so the diagram represents an increase in the internal energy of the system.

(b) ΔE for this process is positive, +.

(c) If no work is associated with the process, it is endothermic.

5.3 (a) For an endothermic process, the sign of q is positive; the system gains heat. This is true only for system (iii).

(b) In order for ΔE to be less than 0, there is a net transfer of heat or work from the system to the surroundings. The magnitude of the quantity leaving the system is greater than the magnitude of the quantity entering the system. In system (i), the magnitude of the heat leaving the system is less than the magnitude of the work done on the system. In system (iii), the magnitude of the work done by the system is less than the magnitude of the heat entering the system. None of the systems has $\Delta E < 0$.

(c) In order for ΔE to be greater than 0, there is a net transfer of work or heat to the system from the surroundings. In system (i), the magnitude of the work done on the system is greater than the magnitude of the heat leaving the system. In system (ii), work is done on the system with no change in heat. In system (iii) the magnitude of the heat gained by the system is greater than the magnitude of the work done on the surroundings. $\Delta E > 0$ for all three systems.

5.5 $w = -P\Delta V$. Since ΔV for the process is (–), the sign of w is (+).

$\Delta E = q + w$. At constant pressure, $\Delta H = q$. If the reaction is endothermic, the signs of ΔH and q are (+). The sign of w is (+), so the sign of ΔE is (+). The internal energy of the system increases during the change. (This situation is described by the diagram (ii) in Exercise 5.3.)

5.7 (a) $N_2(g) + O_2(g) \rightarrow 2NO(g)$. Since $\Delta V = 0$, $w = 0$.

(b) $\Delta H = 90.37$ kJ for production of 1 mol of NO(g). The definition of a formation reaction is one where elements combine to form one mole of a single product. The enthalpy change for such a reaction is the enthalpy of formation.

5.8 (a) $\Delta H_A = \Delta H_B + \Delta H_C$. The net enthalpy change associated with going from the initial state to the final state does not depend on path. The change can be accomplished via reaction A, or via two successive reactions, B then C, with the same net enthalpy change.

(b) $\Delta H_Z = \Delta H_X + \Delta H_Y$. The diagram indicates that Reaction Z can be written as the sum of reactions X and Y. Hess's Law states that the enthalpy change for the net reaction Z is the sum of the enthalpy changes of the steps X and Y, regardless of whether the reaction actually occurs via this path. $\Delta H_Z = \Delta H_X + \Delta H_Y$ because ΔH is a state function, independent of path.

The Nature of Energy

5.10 (a) The kinetic energy of the ball **decreases** as it moves higher. As the ball moves higher and opposes gravity, kinetic energy is changed into potential energy.

(b) The potential energy of the ball **increases** as it moves higher.

(c) The heavier ball would go **half as high** as the tennis ball. At the apex of the trajectory, all initial kinetic energy has been changed into potential energy. The magnitude of the change in potential energy is $m\ g\ \Delta h$, which is equal to the energy initially imparted to the ball. If the same amount of energy is imparted to a ball with twice the mass, m doubles so Δh is half as large.

5.12 (a) *Plan.* Convert lb → kg, mi/hr → m/s.

Solve. $950 \text{ lb} \times \dfrac{1 \text{ kg}}{2.205 \text{ lb}} = 430.84 = 431 \text{ kg}$

$$\frac{68 \text{ mi}}{1 \text{ hr}} \times \frac{1.6093 \text{ km}}{1 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ sec}} = 30.398 = 30 \text{ m/s}$$

$$E_k = 1/2\ mv^2 = 1/2 \times 430.84 \text{ kg} \times (30.398)^2 \text{ m}^2/\text{s}^2 = 2.0 \times 10^5 \text{ J}$$

(b) E_k is proportional to v^2, so if speed decreases by a factor of 2, kinetic energy decreases by a factor of 4.

(c) Brakes stop a moving vehicle, so the kinetic energy of the motorcycle is primarily transferred to friction between brakes and wheels, and somewhat to deformation of the tire and friction between the tire and road.

5.14 (a) *Analyze.* Given: 1 kwh; 1 watt = 1 J/s; 1 watt • s = 1 J.

Find: conversion factor for joules and kwh.

Plan. kwh → wh → ws → J

Solve. $1 \text{ kwh} \times \dfrac{1000 \text{ w}}{1 \text{ kw}} \times \dfrac{60 \text{ min}}{\text{h}} \times \dfrac{60 \text{ s}}{\text{min}} \times \dfrac{1 \text{ J}}{1 \text{ w} \bullet \text{s}} = 3.6 \times 10^6 \text{ J}$

$1 \text{ kwh} = 3.6 \times 10^6 \text{ J}$

(b) *Analyze.* Given: 100 watt bulb. Find: heat in kcal radiated by bulb or person in 24 hr.

Plan. 1 watt = 1 J/s; 1 kcal = 4.184×10^3 J; watt → J/s → J → kcal. *Solve.*

$$100 \text{ watt} = \frac{100 \text{ J}}{1 \text{ s}} \times \frac{60 \text{ sec}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times 24 \text{ hr} \times \frac{1 \text{ kcal}}{4.184 \times 10^3 \text{ J}} = 2065 = 2.1 \times 10^3 \text{ kcal}$$

24 hr has 2 sig figs, but 100 watt is ambiguous. The answer to 1 sig fig would be 2×10^3 kcal.

Check. $(1 \times 10^2 \times 6 \times 10^1 \times 6/10^3) \approx 6^3 \times 10 \approx 2000$ kcal

5.16 The air gun imparts a certain amount of kinetic energy to the pellet. As the pellet rises against the force of gravity, kinetic energy is changed to potential energy. When all kinetic energy has been transferred to potential energy (or lost as heat through friction) the pellet stops rising and falls to earth. In principle, if enough kinetic energy could be imparted to the pellet, it could escape the force of gravity and move into space. For an air gun and a pellet, this is practically impossible.

5.18 (a) The system is not closed, because it is exchanging mass with the surroundings. That is, solution flows into and out of the flask.

(b) If the system is defined as shown, it can be closed by blocking the flow in and out, but leaving the flask full of solution.

5.20 (a) Heat is the energy transferred from a hotter object to a colder object.

(b) Heat is transferred from one object (system) to another until the two objects (systems) are at the same temperature.

5.22 (a) Electrostatic attraction; no work is done because the particles are held stationary.

(b) Magnetic attraction; work is done because the nail is moved a distance.

The First Law of Thermodynamics

5.24 (a) $\Delta E_{sys} = -\Delta E_{surr}$; $\Delta E_{sys} = q + w$

(b) The quantities q and w are negative when the system loses heat to the surroundings (it cools), or does work on the surroundings.

5.26 In each case, evaluate q and w in the expression $\Delta E = q + w$. For an exothermic process, q is negative; for an endothermic process, q is positive.

(a) q is positive and w is negative. $\Delta E = 900\text{ J} - 422\text{ J} = 478\text{ J}$. The process is endothermic.

(b) q is negative and w is essentially zero. $\Delta E = -3140$ J. The process is exothermic.

(c) q is negative and w is zero. $\Delta E = -8.65$ kJ. The process is exothermic.

5.28 $E_{el} = \dfrac{\kappa Q_1 Q_2}{r^2}$ For two oppositely charged particles, the sign of E_{el} is negative; the closer the particles, the greater the magnitude of E_{el}.

(a) The potential energy becomes less negative as the particles are separated (r increases).

(b) ΔE for the process is positive; the internal energy of the system increases as the oppositely charged particles are separated.

(c) Work is done on the system to separate the particles so w is positive. We have no direct knowledge of the change in q, except that it cannot be large and negative, because overall $\Delta E = q + w$ is positive.

5.30 (a) Independent. Potential energy is a state function.

(b) Dependent. Some of the energy released could be employed in performing work, as is done in the body when sugar is metabolized; heat is not a state function.

(c) Dependent. The work accomplished depends on whether the gasoline is used in an engine, burned in an open flame, or in some other manner. Work is not a state function.

Enthalpy

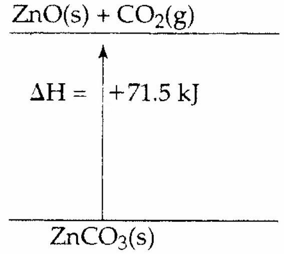
5.32 (a) When a process occurs under constant external pressure, the enthalpy change (ΔH) equals the amount of heat transferred. $\Delta H = q_p$.

(b) $\Delta H = q_p$. If the system absorbs heat, q and ΔH are positive and the enthalpy of the system increases.

5.34 (a) $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

$\Delta H = 71.5$ kJ

(b)



5.36 *Plan.* Consider the sign of an enthalpy change that would convert one of the substances into the other. *Solve.*

(a) $CO_2(s) \rightarrow CO_2(g)$. This change is sublimation, which is endothermic, $+\Delta H$. $CO_2(g)$ has the higher enthalpy.

(b) $H_2 \rightarrow 2H$. Breaking the H–H bond requires energy, so the process is endothermic, $+\Delta H$. Two moles of H atoms have higher enthalpy.

(c) $H_2O(g) \rightarrow H_2(g) + 1/2\ O_2(g)$. Decomposing H_2O into its elements requires energy and is endothermic, $+\Delta H$. One mole of $H_2(g)$ and 0.5 mol $O_2(g)$ at 25°C have the higher enthalpy.

(d) $N_2(g)$ at 100° → $N_2(g)$ at 300°. An increase in the temperature of the sample requires that heat is added to the system, +q and $+\Delta H$. $N_2(g)$ at 300° has the higher enthalpy.

5.38 (a) The reaction is endothermic, so heat is absorbed by the system during the course of reaction.

(b) $$45.0\text{ g } CH_3OH \times \frac{1\text{ mol } CH_3OH}{32.04\text{ g } CH_3OH} \times \frac{90.7\text{ kJ}}{1\text{ mol } CH_3OH} = 127\text{ kJ heat transferred (absorbed)}$$

(c) $$18.5\text{ kJ} \times \frac{2\text{ mol } H_2}{90.7\text{ kJ}} \times \frac{2.016\text{ g } H_2}{1\text{ mol } H_2} = 0.822\text{ g } H_2\text{ produced}$$

(d) The sign of ΔH is reversed for the reverse reaction: $\Delta H = -90.7$ kJ

$$27.0\text{ g CO} \times \frac{1\text{ mol CO}}{28.01\text{ g CO}} \times \frac{-90.7\text{ kJ}}{1\text{ mol CO}} = -87.4\text{ kJ heat transferred (released)}$$

5.40 (a) $0.855\text{ mol } O_2 \times \frac{-89.4\text{ kJ}}{3\text{ mol } O_2} = -25.48 = -25.5\text{ kJ}$

(b) $10.75\text{ g KCl} \times \frac{1\text{ mol KCl}}{74.55\text{ g KCl}} \times \frac{-89.4\text{ kJ}}{2\text{ mol KCl}} = -6.4457 = -6.45\text{ kJ}$

(c) Since the sign of ΔH is reversed for the reverse reaction, it seems reasonable that other characteristics would be reversed, as well. If the forward reaction proceeds spontaneously, the reverse reaction is probably not spontaneous. Also, we know from experience that KCl(s) does not spontaneously react with atmospheric $O_2(g)$, even at elevated temperature.

5.42 At constant volume ($\Delta V = 0$), $\Delta E = q_v$. According to the definition of enthalpy, $H = E + PV$, so $\Delta H = \Delta E + \Delta(PV)$. For an ideal gas at constant temperature and volume, $\Delta PV = V\Delta P = RT\Delta n$. For this reaction, there are 2 mol of gaseous product and 3 mol of gaseous reactants, so $\Delta n = -1$. Thus $V\Delta P$ or $\Delta(PV)$ is negative. Since $\Delta H = \Delta E + \Delta(PV)$, the negative $\Delta(PV)$ term means that ΔH will be smaller or more negative than ΔE.

5.44 The gas is the system. If 418 J of heat is added, $q = +418$ J. Work done by the system decreases the overall energy of the system, so $w = -107$ J.

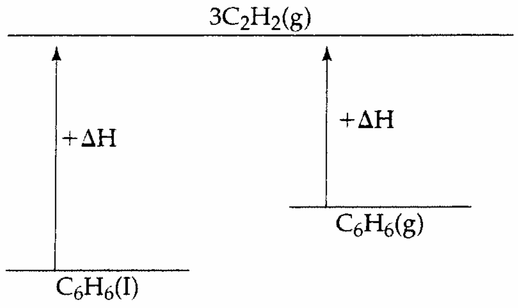
$\Delta E = q + w = 418\text{ J} - 107\text{ J} = 311\text{ J}$. $\Delta H = q = 418$ J (at constant pressure).

5.46 (a) $3C_2H_2(g) \rightarrow C_6H_6(l)$ $\Delta H = -630\text{ kJ}$

(b) $C_6H_6(l) \rightarrow 3C_2H_2(g)$ $\Delta H = 630\text{ kJ}$
ΔH for the formation of 3 mol of acetylene is 630 kJ. ΔH for the formation of 1 mol of C_2H_2 is then 630 kJ/3 = 210 kJ.

(c) The exothermic reverse reaction is more likely to be thermodynamically favored.

(d)



If the reactant is in the higher enthalpy gas phase, the overall ΔH for the reaction has a smaller positive value.

Calorimetry

The specific heat of water to four significant figures, **4.184 J/g • K**, will be used in many of the following exercises; temperature units of K and °C will be used interchangeably.

5.48 *Analyze.* Both objects are heated to 100°C. The two hot objects are placed in the same amount of cold water at the same temperature. Object A raises the water temperature more than object B. *Plan.* Apply the definition of heat capacity to heating the water and heating the objects to determine which object has the greater heat capacity. *Solve.*

(a) Both beakers of water contain the same mass of water, so they both have the same heat capacity. Object A raises the temperature of its water more than object B, so more heat was transferred from object A than from object B. Since both objects were heated to the same temperature initially, object A must have absorbed more heat to reach the 100° temperature. The greater the heat capacity of an object, the greater the heat required to produce a given rise in temperature. Thus, object A has the greater heat capacity.

(b) Since no information about the masses of the objects is given, we cannot compare or determine the specific heats of the objects.

5.50 (a) In Table 5.2, Hg(l) has the smallest specific heat, so it will require the smallest amount of energy to heat 50.0 g of the substance 10 k.

(b) $$50.0\,\text{g Hg(l)} \times 10\,\text{K} \times \frac{0.14\,\text{J}}{\text{g} \bullet \text{K}} = 70\,\text{J}$$

5.52 $$62.0\,\text{g ethylene glycol} \times \frac{2.42\,\text{J}}{\text{g} \bullet \text{K}} \times (40.8^{\circ}\text{C} - 15.2^{\circ}\text{C}) = 3.84 \times 10^3\,\text{J}$$

5.54 (a) Following the logic in Solution 5.53, the dissolving process is endothermic, ΔH is positive. The total mass of the solution is (60.0 g H_2O + 3.88 g NH_4NO_3) = 63.88 = 63.9 g. The temperature change of the solution is 23.0 - 18.4 = 4.6°C. The heat lost by the solution is

$$63.88\,\text{g solution} \times \frac{4.184\,\text{J}}{1\,\text{g} \bullet {}^{\circ}\text{C}} \times 4.6^{\circ}\text{C} \times \frac{1\,\text{kJ}}{1000\,\text{J}} = 1.229 = 1.2\,\text{kJ}$$

Thus, 1.2 kJ is absorbed when 3.88 g $NH_4NO_3(s)$ dissolves.

$$\frac{+1.229\,\text{kJ}}{3.88\,NH_4NO_3} \times \frac{80.05\,\text{g}\,NH_4NO_3}{1\,\text{mol}\,NH_4NO_3} = +25.36 = +25\,\text{kJ/mol}\,NH_4NO_3$$

(b) This process is endothermic, because the temperature of the surroundings decreases, indicating that heat is absorbed by the system.

5.56 (a) $C_6H_5OH(s) + 7O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

(b) $q_{bomb} = -q_{rxn}$; ΔT = 26.37°C - 21.36°C = 5.01°C

$$q_{bomb} = \frac{11.66\,\text{kJ}}{1^{\circ}\text{C}} \times 5.01^{\circ}\text{C} = 58.417 = 58.4\,\text{kJ}$$

At constant volume, $q_v = \Delta E$. ΔE and ΔH are very similar.

$$\Delta H_{rxn} \approx \Delta E_{rxn} = q_{rxn} = -q_{bomb} = \frac{-58.417\,\text{kJ}}{1.800\,\text{g}\,C_6H_5OH} = -32.454 = -32.5\,\text{kJ/g}\,C_6H_5OH$$

$$\Delta H_{rxn} = \frac{-32.454\,\text{kJ}}{1\,\text{g}\,C_6H_5OH} \times \frac{94.11\,\text{g}\,C_6H_5OH}{1\,\text{mol}\,C_6H_5OH} = \frac{-3.054 \times 10^3\,\text{kJ}}{\text{mol}\,C_6H_5OH}$$

$$= -3.05 \times 10^3\,\text{kJ/mol}\,C_6H_5OH$$

5.58 (a) $$C = 1.640\,\text{g}\,HC_7H_5O_2 \times \frac{26.38\,\text{kJ}}{1\,\text{g}\,HC_7H_5O_2} \times \frac{1}{4.95^{\circ}\text{C}} = 8.740 = 8.74\,\text{kJ/}^{\circ}\text{C}$$

(b) $\frac{8.740\ \text{kJ}}{{}^{\circ}\text{C}} \times 4.68^{\circ}\text{C} \times \frac{1}{1.320\ \text{g sample}} = 30.99 = 31.0\ \text{kJ/g sample}$

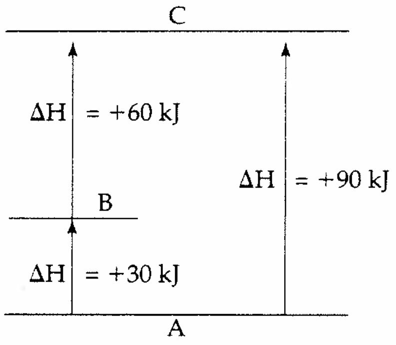
(c) If water is lost from the calorimeter, there is less water to heat, so the same amount of heat (kJ) from a reaction would cause a larger increase in the calorimeter temperature. The calorimeter constant, kJ/°C, would decrease, because °C is in the denominator of the expression.

Hess's Law

5.60 (a) *Analyze/Plan.* Arrange the reactions so that in the overall sum, B, appears in both reactants and products and can be canceled. This is a general technique for using Hess's Law. *Solve.*

$$\begin{array}{ll} \text{A} \rightarrow \text{B} & \Delta\text{H} = +30\ \text{kJ} \\ \text{B} \rightarrow \text{C} & \Delta\text{H} = +60\ \text{kJ} \\ \hline \text{A} \rightarrow \text{C} & \Delta\text{H} = +30\ \text{kJ} \end{array}$$

(b)



Check. The process of A forming C can be described as A forming B and B forming C.

5.62
$$\begin{array}{lll} 3\text{H}_2(g) + 3/2\,\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(g) & \Delta\text{H} = 3/2(-483.6\ \text{kJ}) \\ \text{O}_3(g) \rightarrow 3/2\,\text{O}_2(g) & \Delta\text{H} = 1/2(-284.6\ \text{kJ}) \\ \hline 3\text{H}_2(g) + \text{O}_3(g) \rightarrow \text{P}_4\text{O}_{10}(s) & \Delta\text{H} = -867.7\ \text{kJ} \end{array}$$

5.64
$$\begin{array}{ll} \text{N}_2\text{O}(g) \rightarrow \text{N}_2(g) + 1/2\,\text{O}_2(g) & \Delta\text{H} = 1/2\ (-163.2\ \text{kJ}) \\ \text{NO}_2(g) \rightarrow \text{NO}(g) + 1/2\,\text{O}_2(g) & \Delta\text{H} = 1/2(113.1\ \text{kJ}) \\ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) & \Delta\text{H} = 180.7\ \text{kJ} \\ \hline \text{N}_2\text{O}(g) + \text{NO}_2(g) \rightarrow 3\text{NO}(g) & \Delta\text{H} = 155.7\ \text{kJ} \end{array}$$

Enthalpies of Formation

5.66 (a) Tables of ΔH_f° are useful because, according to Hess's law, the standard enthalpy of any reaction can be calculated from the standard enthalpies of formation for the reactants and products.

$$\Delta\text{H}_{\text{rxn}}^{\circ} = \Sigma\Delta\text{H}_f^{\circ}\,(\text{products}) - \Sigma\Delta\text{H}_f^{\circ}\,(\text{reactants})$$

(b) The standard enthalpy of formation for any element in its standard state is zero. Elements in their standard states are the reference point for the enthalpy of formation scale.

(c) $6C(s) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$

5.68 (a) $1/2\ H_2(g) + 1/2\ Br_2(l) \rightarrow HBr(g)$ $\Delta H_f^\circ = -36.23$ kJ

(b) $Ag(s) + 1/2\ N_2(g) + 3/2\ O_2(g) \rightarrow AgNO_3(s)$ $\Delta H_f^\circ = -124.4$ kJ

(c) $2Hg(l) + Cl_2(g) \rightarrow Hg_2Cl_2(s)$ $\Delta H_f^\circ = -264.9$ kJ

(d) $2C(s, gr) + 1/2\ O_2(g) + 3H_2(g) \rightarrow C_2H_5OH(l)$ $\Delta H_f^\circ = -277.7$ kJ

5.70 Use heats of formation to calculate ΔH° for the combustion of butane.

$$C_4H_{10}(l) + 13/2\ O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

$$\Delta H^\circ_{rxn} = 4\Delta H\ CO_2(g) + 5\Delta H_f^\circ\ H_2O(l) - \Delta H_f^\circ\ C_4H_{10}(l) - 13/2\ \Delta H_f^\circ\ O_2(g)$$

$$\Delta H^\circ_{rxn} = 4(-393.5\text{ kJ}) + 5(-285.83\text{ kJ}) - (-147.6\text{ kJ}) - 13/2(0) = -2855.6 = -2856\text{ kJ/mol } C_4H_{10}$$

$$1.0\text{ g } C_4H_{10} \times \frac{1\text{ mol } C_4H_{10}}{58.123\text{ g } C_4H_{10}} \times \frac{-2855.6\text{ kJ}}{1\text{ mol } C_4H_{10}} = -49\text{ kJ}$$

5.72 (a) $\Delta H^\circ_{rxn} = 4\Delta H_f^\circ\ H_2O(g) + \Delta H_f^\circ\ N_2(g) - \Delta H_f^\circ\ N_2O_4(g) - 4\Delta H_f^\circ\ H_2(g)$

$= 4(-241.82) + 0 - (9.66) - 4(0) = -976.94$ kJ

(b) $\Delta H^\circ_{rxn} = \Delta H_f^\circ\ K_2CO_3(s) + \Delta H_f^\circ\ H_2O(g) - 2\Delta H_f^\circ\ KOH(s) - \Delta H_f^\circ\ CO_2(g)$

$= -1150.18$ kJ $- 241.82$ kJ $- 2(-424.7)$ kJ $- (-393.5$ kJ$) = -149.1$ Kj

(c) $\Delta H^\circ_{rxn} = 3/\ 8\Delta H_f^\circ\ S_8(s) + 2\Delta H_f^\circ\ H_2O(g) - \Delta H_f^\circ\ SO_2(g) - 2\Delta H_f^\circ\ H_2S(g)$

$= 3/8(\overset{102.3}{\cancel{0}}) + 2(-241.82) - (-\overset{246.9}{\cancel{269.9}}) - 2(-20.17) = -\cancel{173}.4$ kJ -108.0 kJ/mol

(d) $\Delta H^\circ_{rxn} = 2\Delta H_f^\circ\ FeCl_3(s) + 3\Delta H_f^\circ\ H_2O(g) - \Delta H_f^\circ\ Fe_2O(g) - 6\Delta H_f^\circ\ HCl(g)$

$= 2(-400$ kJ$) + 3(-241.82$ kJ$) - (-822.16$ kJ$) - 6(-92.30$ kJ$) = -149.5$ kJ

5.74 $\Delta H^\circ_{rxn} = \Delta H_f^\circ\ Ca(OH)_2(s) + \Delta H_f^\circ\ C_2H_2(g) - 2\Delta H_f^\circ\ H_2O(l) - \Delta H_f^\circ\ CaC_2(s)$

$-127.2\text{ kJ} = -986.2\text{ kJ} + 226.7\text{ kJ} - 2(-285.83\text{ kJ}) - \Delta H_f^\circ\ CaC_2(s)$

ΔH_f° for $CaC_2(s) = -60.6$ kJ

5.76 (a)

$$\begin{array}{ll} 2B(s) + 3/2\ O_2(g) \rightarrow B_2O_3(s) & \Delta H^\circ = 1/2(-2509.1\text{ kJ}) \\ 3H_2(g) + 3/2\ O_2(g) \rightarrow 3H_2O(l) & \Delta H^\circ = 3/2(-571.7\text{ kJ}) \\ B_2O_3(s) + 3H_2O(l) \rightarrow B_2H_6(g) + 3O_2(g) & \Delta H^\circ = -(-2147.5\text{ kJ}) \\ \hline 2B(s) + 3H_2(g) \rightarrow B_2H_6(g) & \Delta H_f^\circ = +35.4\text{ kJ} \end{array}$$

(b) If, like B_2H_6, the combustion of B_5H_9 produces B_2O_3 as the boron-containing product, the heat of combustion of B_5H_9 in addition to data given in part (a) would enable calculation of the heat of formation of B_5H_9.

The combustion reaction is: $B_5H_9(l) + 6O_2(g) \rightarrow 5/2\ B_2O_3(s) + 9/2\ H_2O(l)$

$$\begin{array}{ll} 5/4\,[4B(s) + 3O_2(g) \rightarrow 2B_2O_3(s)] & \Delta H = 5/4(-2509.1\ kJ) \\ 9/4\,[2H_2(g) + O_2(g) \rightarrow 2H_2O(l)] & \Delta H = 9/4\,(-571.7\ kJ) \\ 5/2\ B_2O_3(s) + 9/2\ H_2O(l) \rightarrow B_5H_9(l) + 6O_2(g) & \Delta H = -\,(\text{heat of combustion}) \\ \hline 5B(s) + 9/2\ H_2(g) \rightarrow B_5H_9(l) & \Delta H_f^\circ \text{ of } B_5H_9(l) \end{array}$$

$[\Delta H_f^\circ\ B_5H_9(l) = -\,[\text{heat of combustion of } B_5H_9(l)] - 3136.4\ kJ - 1286\ kJ]$

We need to measure the heat of combustion of $B_5H_9(l)$.

5.78 (a) $10C(s) + 4H_2(g) \rightarrow C_{10}H_8(s)$ formation

$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l)$ combustion, $\Delta H^\circ = -5154\ kJ$

(b) $\Delta H_{rxn}^\circ = 10\Delta H_f^\circ\ CO_2(g) + 4\Delta H_f^\circ\ H_2O(l) - \Delta H_f^\circ\ C_{10}H_8 - 12\Delta H_f^\circ\ O_2(g)$

$-5154 = 10(-393.5\ kJ) + 4(-285.83\ kJ) - \Delta H_f^\circ\ C_{10}H_8(s) - 12(0)$

$\Delta H_f^\circ\ C_{10}H_8(s) = 10(-393.5\ kJ) + 4(-285.83\ kJ) + 5154\ kJ = 76\ kJ$

Check. The result has 0 decimal places because the heat of combustion has 0 decimal places.

Foods and Fuels

5.80 (a) Fats are appropriate for fuel storage because they are insoluble in water (and body fluids) and have a high fuel value.

(b) For convenience, assume 100 g of chips.

$$12\text{ g protein} \times \frac{17\text{ kJ}}{1\text{ g protein}} \times \frac{1\text{ Cal}}{4.184\text{ kJ}} = 48.76 = 49\text{ Cal}$$

$$14\text{ g fat} \times \frac{38\text{ kJ}}{1\text{ g fat}} \times \frac{1\text{ Cal}}{4.184\text{ kJ}} = 127.15 = 130\text{ Cal}$$

$$74\text{ g carbohydrates} \times \frac{17\text{ kJ}}{1\text{ g carbohydrates}} \times \frac{1\text{ Cal}}{4.184\text{ kJ}} = 300.67 = 301\text{ Cal}$$

total Cal = (48.76 + 127.15 + 300.67) = 476.58 = 480 Cal

$$\%\text{ Cal from fat} = \frac{127.15\text{ Cal fat}}{476.58\text{ total Cal}} \times 100 = 26.68 = 27\%$$

(Since the conversion from kJ to Cal was common to all three components, we would have determined the same percentage by using kJ.)

(c) $25\text{ g fat} \times \dfrac{38\text{ kJ}}{\text{g fat}} = x\text{ g protein} \times \dfrac{17\text{ kJ}}{\text{g protein}};\quad x = 56\text{ g protein}$

5.82 Calculate the fuel value in a pound of M&M® candies.

$$96\text{ fat} \times \frac{38\text{ kJ}}{1\text{ g fat}} = 3648\text{ kJ} = 3.6 \times 10^3\text{ kJ}$$

$$320\text{ g carbohydrate} \times \frac{17\text{ kJ}}{1\text{ g carbohydrate}} = 5440\text{ kJ} = 5.4 \times 10^3\text{ kJ}$$

$$21\text{ g protein} \times \frac{17\text{ kJ}}{1\text{ g protein}} = 357\text{ kJ} = 3.6 \times 10^2\text{ kJ}$$

total fuel value = 3648 kJ + 5440 kJ + 357 kJ = 9445 kJ = 9.4×10^3 kJ/lb

$$\frac{9445\text{ kJ}}{\text{lb}} \times \frac{1\text{ lb}}{453.6\text{ g}} \times \frac{42\text{ g}}{\text{serving}} = 874.5\text{ kJ} = 8.7 \times 10^2\text{ kJ/serving}$$

$$\frac{874.5\text{ kJ}}{\text{serving}} \times \frac{1\text{ kcal}}{4.184\text{ kJ}} \times \frac{1\text{ Cal}}{1\text{ kcal}} = 209.0\text{ Cal} = 2.1 \times 10^2\text{ Cal/serving}$$

Check. 210 Cal is the approximate food value of a candy bar, so the result is reasonable.

5.84

$$177\text{ mL} \times \frac{1.0\text{ g wine}}{1\text{ mL}} \times \frac{0.106\text{ g ethanol}}{1\text{ g wine}} \times \frac{1\text{ mol ethanol}}{46.1\text{ g ethanol}} \times \frac{1367\text{ kJ}}{1\text{ mol ethanol}} \times \frac{1\text{ Cal}}{4.184\text{ kJ}}$$
$$= 133 = 1.3 \times 10^2\text{ Cal}$$

Check. A "typical" 6 oz. glass of wine has 150–250 Cal, so this is a reasonable result. Note that alcohol is responsible for most of the food value of wine.

5.86

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f\ CO_2(g) + 2\Delta H^\circ_f\ H_2O(g) - \Delta H^\circ_f\ CH_4(g) - \Delta H^\circ_f\ O_2(g)$$
$$= -393.5\text{ kJ} + 2(-241.82\text{ kJ}) - (-74.8\text{ kJ}) - 0\text{ kJ} = -802.3\text{ kJ}$$

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f\ CF_4(g) + 4\Delta H^\circ_f\ HF(g) - \Delta H^\circ_f\ CH_4(g) - 4\Delta H^\circ_f\ F_2(g)$$
$$= -679.9\text{ kJ} + 4(-268.61\text{ kJ}) - (-74.8\text{ kJ}) - 0\text{ kJ} = -1679.5\text{ kJ}$$

The second reaction is twice as exothermic as the first. The "fuel values" of hydrocarbons in a fluorine atmosphere are approximately twice those in an oxygen atmosphere. Note that the difference in ΔH° values for the two reactions is in the ΔH°_f for the products, since the ΔH°_f for the reactants is identical.

Additional Exercises

5.88 (a) $E_p = mgh = 52.0\text{ kg} \times 9.81\text{ m/s}^2 \times 10.8\text{ m} = 5509.3\text{ J} = 5.51\text{ kJ}$

(b) $E_k = 1/2\, mv^2;\ v = (2E_k/m)^{1/2} = \left(\frac{2 \times 5509\text{ kg} \bullet \text{m}^2/\text{s}^2}{52.0\text{ kg}}\right)^{1/2} = 14.6\text{ m/s}$

(c) Yes, the diver does work on entering (pushing back) the water in the pool.

5.89 In the process described, one mole of solid CO_2 is converted to one mole of gaseous CO_2. The volume of the gas is much greater than the volume of the solid. Thus the system (that is, the mole of CO_2) must work against atmospheric pressure when it expands. To accomplish this work while maintaining a constant temperature requires the absorption of additional heat beyond that required to increase the internal energy of the CO_2. The remaining energy is turned into work.

5.91 Freezing is an exothermic process (the opposite of melting, which is clearly endothermic). When the system, the soft drink, freezes, it releases energy to the surroundings, the can. Some of this energy does the work of splitting the can.

5.92 (a) $q = 0$, $w > 0$ (work done to system), $\Delta E > 0$

(b) Since the system (the gas) is losing heat, the sign of q is negative. The changes in state described in cases (a) and (b) are identical and ΔE is the same in both cases. The distribution of energy transferred as either work or heat is different in the two scenarios. In case (b), more work is required to compress the gas because some heat is lost to the surroundings. (The moral of this story is that the more energy lost by the system as heat, the greater the work on the system required to accomplish the desired change.)

5.94 If a function sometimes depends on path, then it is simply not a state function. Enthalpy is a state function, so ΔH for the two pathways leading to the same change of state pictured in Figure 5.10 must be the same. However, q is not the same for the both. Our conclusion must be that $\Delta H \neq q$ for these pathways. The condition for $\Delta H = q_p$ (other than constant pressure) is that the only possible work on or by the system is pressure-volume work. Clearly, the work being done in this scenario is not pressure-volume work, so $\Delta H \neq q$, even though the two changes occur at constant pressure.

5.96 (a) $$q_{Cu} = \frac{0.385\text{ J}}{\text{g} \bullet \text{K}} \times 121.0\text{ g Cu} \times (30.1^\circ\text{C} - 100.4^\circ\text{C}) = -3274.9 = -3.27 \times 10^3\text{ J}$$

The negative sign indicates the 3.27×10^3 J are lost by the Cu block.

(b) $$q_{H_2O} = \frac{4.184\text{ J}}{\text{g} \bullet \text{K}} \times 150.0\text{ g } H_2O \times (30.1^\circ\text{C} - 25.1^\circ\text{C}) = 3138 = 3.1 \times 10^3\text{ J}$$

The positive sign indicates that 3.14×10^3 J are gained by the H_2O.

(c) The difference in the heat lost by the Cu and the heat gained by the water is $3.275 \times 10^3\text{ J} - 3.138 \times 10^3\text{ J} = 0.137 \times 10^3\text{ J} = 1 \times 10^2$ J. The temperature change of the calorimeter is 5.0°C. The heat capacity of the calorimeter in J/K is

$$0.137 \times 10^3\text{ J} \times \frac{1}{5.0^\circ\text{C}} = 27.4 = 3 \times 10\text{ J/K.}$$

Since q_{H_2O} is known to one decimal. place, the difference has one decimal place and the result has 1 sig fig.

If the rounded results from (a) and (b) are used,

$$C_{\text{calorimeter}} = \frac{0.2 \times 10^3\text{ J}}{5.0^\circ\text{C}} = 4 \times 10\text{ J/K.}$$

(d) $$q_{H_2O} = 3.275 \times 10^3\text{ J} = \frac{4.184\text{ J}}{\text{g} \bullet \text{K}} \times 150.0\text{ g} \times (\Delta T)$$

$\Delta T = 5.22^\circ\text{C}$; $T_f = 25.1^\circ\text{C} + 5.22^\circ\text{C} = 30.3^\circ\text{C}$

5.97 (a) From the mass of benzoic acid that produces a certain temperature change, we can calculate the heat capacity of the calorimeter.

$$\frac{0.235\text{ g benzoic acid}}{1.642^\circ\text{C change observed}} \times \frac{26.38\text{ kJ}}{1\text{ g benzoic acid}} = 3.7755 = 3.78\text{ kJ/}^\circ\text{C}$$

Now we can use this experimentally determined heat capacity with the data for caffeine.

$$\frac{1.525^\circ\text{C rise}}{0.265\text{ g caffeine}} \times \frac{3.7755\text{ kJ}}{1^\circ\text{C}} \times \frac{194.2\text{ g caffeine}}{1\text{ mol caffeine}} = 4.22 \times 10^3\text{ kJ/mol caffeine}$$

(b) The overall uncertainty is approximately equal to the sum of the uncertainties due to each effect. The uncertainty in the mass measurement is 0.001/0.235 or 0.001/0.265, about 1 part in 235 or 1 part in 265. The uncertainty in the temperature measurements is 0.002/1.642 or 0.002/1.525, about 1 part in 820 or 1 part in 760. Thus the uncertainty in heat of combustion from each measurement is

$$\frac{4220}{235} = 18\text{ kJ};\quad \frac{4220}{265} = 16\text{ kJ};\quad \frac{4220}{820} = 5\text{ kJ};\quad \frac{4220}{760} = 6\text{ kJ}$$

The sum of these uncertainties is 45 kJ. In fact, the overall uncertainty is less than this because independent errors in measurement do tend to partially cancel.

5.99 (a) For comparison, balance the equations so that 1 mole of CH_4 is burned in each.

$CH_4(g) + O_2(g) \rightarrow C(s) + 2H_2O(l)$ $\Delta H^\circ = -496.9$ kJ

$CH_4(g) + 3/2\ O_2(g) \rightarrow CO(g) + 2H_2O(l)$ $\Delta H^\circ = -607.4$ kJ

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^\circ = -890.4$ kJ

(b) $\Delta H^\circ_{rxn} = \Delta H^\circ_f\ C(s) + 2\Delta H^\circ_f\ H_2O(l) - \Delta H^\circ_f\ CH_4(g) - \Delta H^\circ_f\ O_2(g)$

$= 0 + 2(-285.83\text{ kJ}) - (-74.8) - 0 = -496.9\text{ kJ}$

$\Delta H^\circ_{rxn} = \Delta H^\circ_f\ CO(g) + 2\Delta H^\circ_f\ H_2O(l) - \Delta H^\circ_f\ CH_4(g) - 3/2\,\Delta H^\circ_f\ O_2(g)$

$= (-110.5\text{ kJ}) + 2(-285.83\text{ kJ}) - (-74.8\text{ kJ}) - 3/2(0) = -607.4\text{ kJ}$

$\Delta H^\circ_{rxn} = \Delta H^\circ_f\ CO_2(g) + 2\Delta H^\circ_f\ H_2O(l) - \Delta H^\circ_f\ CH_4(g) - 2\Delta H^\circ_f\ O_2(g)$

$= -393.5\text{ kJ} + 2(-285.83\text{ kJ}) - (-74.8\text{ kJ}) - 2(0) = -890.4\text{ kJ}$

(c) Assuming that $O_2(g)$ is present in excess, the reaction that produces $CO_2(g)$ represents the most negative ΔH per mole of CH_4 burned. More of the potential energy of the reactants is released as heat during the reaction to give products of lower potential energy. The reaction that produces $CO_2(g)$ is the most "downhill" in enthalpy.

5.100 For nitroethane:

$$\frac{1368\text{ kJ}}{1\text{ mol } C_2H_5NO_2} \times \frac{1\text{ mol } C_2H_5NO_2}{75.072\text{ g } C_2H_5NO_2} \times \frac{1.052\text{ g } C_2H_5NO_2}{1\text{ cm}^3} = 19.17\text{ kJ/cm}^3$$

For ethanol:

$$\frac{1367\text{ kJ}}{1\text{ mol } C_2H_5OH} \times \frac{1\text{ mol } C_2H_5OH}{46.069\text{ g } C_2H_5OH} \times \frac{0.789\text{ g } C_2H_5OH}{1\text{ cm}^3} = 23.4\text{ kJ/cm}^3$$

For methylhydrazine:

$$\frac{1305\text{ kJ}}{1\text{ mol } CH_6N_2} \times \frac{1\text{ mol } CH_6N_2}{46.072\text{ g } CH_6N_2} \times \frac{0.874\text{ g } CH_6N_2}{1\text{ cm}^3} = 24.8\text{ kJ/cm}^3$$

Thus, **methylhydrazine** would provide the most energy per unit volume, with ethanol a close second.