

5 Thermochemistry

Visualizing Concepts

- 5.1 The book's potential energy is due to the opposition of gravity by an object of mass m at a distance d above the surface of the earth. Kinetic energy is due to the motion of the book. As the book falls, d decreases and potential energy changes into kinetic energy.

The first law states that the total energy of a system is conserved. At the instant before impact, all potential energy has been converted to kinetic energy, so the book's total kinetic energy is 71 J, assuming no transfer of energy as heat.

For an object under the influence of gravity, both potential ($E_p = mgd$) and kinetic energy ($E_k = \frac{1}{2}mv^2$) are directly proportional to mass of the object. A heavier book falling from the same shelf has greater kinetic energy when it hits the floor.

- 5.2 (a) The caterpillar uses energy produced by its metabolism of food to climb the twig and increase its potential energy.
- (b) Heat, q , is the energy transferred from a hotter to a cooler object. Without knowing the temperature of the caterpillar and its surroundings, we cannot predict the sign of q . It is likely that q is approximately zero, since a small creature like a caterpillar is unlikely to support a body temperature much different from its environmental temperature.
- (c) Work, w , is the energy transferred when a force moves an object. When the caterpillar climbs the twig, it does work as its body moves against the force of gravity.
- (d) No. The amount of work is independent of time, and therefore independent of speed (assuming constant caterpillar speed).
- (e) No. Potential energy depends only on the caterpillar's position, so the change in potential energy depends only on the distance climbed, not on the speed of the climb.
- 5.3 (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.
- 5.4 (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

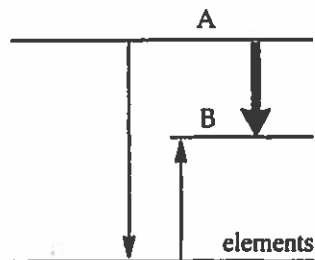
greater than the magnitude of the quantity entering the system. In system (i), the magnitude of the heat leaving the system is less than the magnitude of the work done on the system. In system (iii), the magnitude of the work done by the system is less than the magnitude of the heat entering the system. 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 (a) No. This distance traveled to the top of a mountain depends on the path taken by the hiker. Distance is a path function, not a state function.
- (b) Yes. Change in elevation depends only on the location of the base camp and the height of the mountain, not on the path to the top. Change in elevation is a state function, not a path function.
- 5.6 (a) State B
- (b) ΔE_{AB} = energy difference between State A and State B.
 $\Delta E_{AB} = \Delta E_1 + \Delta E_2$ or $\Delta E_{AB} = \Delta E_3 + \Delta E_4$
- (c) ΔE_{CD} = energy difference between State C and State D.
 $\Delta E_{CD} = \Delta E_2 - \Delta E_4$ or $\Delta E_{DC} = \Delta E_3 - \Delta E_1$
- (Note that the sign of ΔE depends on the definition of initial and final state, but the magnitude is the absolute value of the difference in energy.)
- (d) The energy of State E is $\Delta E_1 + \Delta E_4$, while the energy of State B is $\Delta E_1 + \Delta E_2$. Since $\Delta E_4 > \Delta E_2$, State E is above State B on the diagram; State E would be the highest energy on the diagram.
- 5.7 (a) You, part of the surroundings, do work on the air, part of the system. Energy is transferred to the system via work and the sign of w is (+).
- (b) The body of the pump (the system) is warmer than the surroundings. Heat is transferred from the warmer system to the cooler surroundings and the sign of q is (-).
- (c) The sign of w is positive and the sign of q is negative, so we cannot absolutely determine the sign of ΔE . It is likely that the heat lost is much smaller than the work done on the system, so the sign of ΔE is probably positive.
- 5.8 (a) $w = -P\Delta V$. Since ΔV for the process is (-), the sign of w is (+).
- (b) $\Delta E = q + w$. At constant pressure, $\Delta H = q$. If the reaction is endothermic, the signs of ΔH and q are (+). From (a), 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 5.4.)
- 5.9 (a) The temperature of the system and surroundings will equalize, so the temperature of the hotter system will decrease and the temperature of the colder

surroundings will increase. The system loses heat by decreasing its temperature, so the sign of q_{sys} is (-). The surrounding gains heat by increasing its temperature, so the sign of q_{surr} is (+). From the system's perspective, the process is exothermic because it loses heat.

- (b) If neither volume nor pressure of the system changes, $w = 0$ and $\Delta E = q = \Delta H$. The change in internal energy is equal to the change in enthalpy.
- 5.10 (a) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$. Since $\Delta V = 0$, $w = 0$.
- (b) $\Delta H = \Delta H_f = 90.37 \text{ kJ}$ for production of 1 mol of $\text{NO}(\text{g})$. 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.
- 5.11 (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 diagram shows that the change can be accomplished via reaction A, or via two successive reactions, B then C, with the same net enthalpy change. $\Delta H_A = \Delta H_B + \Delta H_C$ because ΔH is a state function, independent of path.
- (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.
- (c) Hess's law states that the enthalpy change for a net reaction is the sum of the enthalpy changes of the component steps, regardless of whether the reaction actually occurs via this path. The diagrams are a visual statement of Hess's law.
- 5.12 Since mass must be conserved in the reaction $A \rightarrow B$, the component elements of A and B must be the same. Further, if $\Delta H_f^\circ > 0$ for both A and B, the energies of both A and B are above the energies of their component elements on the energy diagram.

- (a) The bold arrow shows the reaction as written; combination of the two thin arrows shows an alternate route from A to B.



- (b) $\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ \text{ B} - \Delta H_f^\circ \text{ A}$. If the overall reaction is exothermic, the sign of ΔH is (-) and $\Delta H_f^\circ \text{ A} > \Delta H_f^\circ \text{ B}$. This means that the enthalpy of A is the highest energy level on the diagram. This is the situation pictured in the diagram above, but nothing in the given information requires this arrangement. If the reaction is endothermic, $\Delta H_f^\circ \text{ B} > \Delta H_f^\circ \text{ A}$ and the enthalpy of B would be the highest energy level on the diagram.

The Nature of Energy (section 5.1)

- 5.13 An object can possess energy by virtue of its motion or position. Kinetic energy, the energy of motion, depends on the mass of the object and its velocity. Potential energy, stored energy, depends on the position of the object relative to the body with which it interacts.

- 5.14 (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 $m g d$, 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 d is half as large.
- 5.15 (a) *Plan.* $E_k = 1/2 mv^2$; $m = 1,200 \text{ kg}$; $v = 18 \text{ m/s}$; $1 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 1 \text{ J}$
Solve. $E_k = 1/2 \times 1,200 \text{ kg} \times (18)^2 \text{ m}^2/\text{s}^2 = 1.944 \times 10^5 = 1.9 \times 10^5 \text{ J}$
- (b) $1 \text{ cal} = 4.184 \text{ J}$; $1.944 \times 10^5 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 4.646 \times 10^4 \text{ cal} = 4.6 \times 10^4 \text{ cal}$
- (c) As the automobile brakes to a stop, its speed (and hence its kinetic energy) drops to zero. Brakes stop a moving vehicle, so the kinetic energy of the automobile is primarily transferred to friction between brakes and wheels, and somewhat to deformation of the tire and friction between the tire and road.
- 5.16 (a) *Analyze.* Given: mass and speed of ball. Find: kinetic energy.
Plan. Since $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$, convert oz \rightarrow kg and mph to m/s to obtain E_k in J.
Solve. $5.13 \text{ oz} \times \frac{1 \text{ lb}}{16 \text{ oz}} \times \frac{1 \text{ kg}}{2.205 \text{ lb}} = 0.14541 = 0.145 \text{ kg}$
 $\frac{95.0 \text{ mi}}{1 \text{ hr}} \times \frac{1.6093 \text{ km}}{1 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ sec}} = 42.468 = 42.5 \text{ m/s}$
 $E_k = 1/2 mv^2 = 1/2 \times 0.14541 \text{ kg} \times \left(\frac{42.468 \text{ m}}{1 \text{ s}}\right)^2 = \frac{131 \text{ kg}\cdot\text{m}^2}{1 \text{ s}^2} = 131 \text{ J}$
Check. $1/2(0.15 \times 1600) \approx 1/2(160+80) \approx 120 \text{ J}$
- (b) Kinetic energy is related to velocity squared (v^2); if the speed of the ball decreases to 55.0 mph, the kinetic energy of the ball will decrease by a factor of $(55.0/95.0)^2$. (The conversion factors to m/s apply to both speeds and will cancel in the ratio.) The numerical multiplier is $(55/95)^2 = 0.335$. The kinetic energy decreases by approximately a factor of 3.
- (c) As the ball hits the catcher's glove, its speed (and hence its kinetic energy) drops to zero. Some of the kinetic energy is transferred to the glove, which deforms when the ball lands. Some is transferred to the catcher's body (mostly the arm), which recoils while catching the ball. As usual, some energy is released as heat through friction between the ball and the glove.
- (d) Assuming that all the kinetic energy is transferred via recoil of the catcher's arm, attach the catcher's mit to a frictionless mechanical arm held a constant distance above the ground. Measure the distance the arm+mit travels and the elapsed time of travel; calculate velocity (distance/time). Knowing the mass of the arm+mit, calculate the kinetic energy ($1/2 mv^2$) transferred to the arm+mit. This

experiment neglects other pathways by which the kinetic energy is transferred. It would be difficult to make enough different careful measurements to completely confirm our answer to (c).

5.17 *Analyze.* Given: heat capacity of water = 1 Btu/lb · °F Find: J/Btu

Plan. heat capacity of water = 4.184 J/g · °C; $\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \rightarrow \frac{\text{J}}{\text{lb} \cdot ^\circ\text{F}} \rightarrow \frac{\text{J}}{\text{Btu}}$

This strategy requires changing °F to °C. Since this involves the magnitude of a degree on each scale, rather than a specific temperature, the 32 in the temperature relationship is not needed. 100 °C = 180 °F; 5 °C = 9 °F

Solve. $\frac{4.184 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times \frac{453.6 \text{ g}}{\text{lb}} \times \frac{5 \text{ }^\circ\text{C}}{9 \text{ }^\circ\text{F}} \times \frac{1 \text{ lb} \cdot ^\circ\text{F}}{1 \text{ Btu}} = 1054 \text{ J/Btu}$

5.18 (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. $1 \text{ kwh} \times \frac{1000 \text{ w}}{1 \text{ kw}} \times \frac{60 \text{ min}}{\text{h}} \times \frac{60 \text{ s}}{\text{min}} \times \frac{1 \text{ J}}{1 \text{ w} \cdot \text{s}} = 3.6 \times 10^6 \text{ J}$

1 kwh = 3.6 × 10⁶ 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 × 10³ 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 × 10³ kcal.

5.19 (a) In thermodynamics, the *system* is the well-defined part of the universe whose energy changes are being studied.

(b) A *closed system* can exchange energy but not mass with its surroundings.

(c) Any part of the universe not part of the system is called the surroundings.

5.20 (a) The system is *open*, because it exchanges both mass and energy with the surroundings. Mass exchange occurs when solution flows into and out of the apparatus. The apparatus is not insulated, so energy exchange also occurs. Closed systems exchange energy but not mass, while isolated systems exchange neither.

(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.

5.21 (a) *Work* is a force applied over a distance.

(b) The amount of work done is the magnitude of the force times the distance over which it is applied. $w = F \times d$.

- 5.22 (a) Heat is the energy transferred from a hotter object to a colder object.
(b) In open or closed systems (but not isolated systems), heat is transferred from one object (system) to another until the two objects (systems) are at the same temperature.
- 5.23 (a) Gravity; work is done because the force of gravity is opposed and the pencil is lifted a distance above the desk.
(b) Mechanical force; work is done because the force of the coiled spring is opposed as the spring is compressed over a distance.
- 5.24 (a) Electrostatic attraction; no work is done because the particles are held apart at a constant distance.
(b) Magnetic attraction; work is done because the nail is moved a distance in opposition to the force of magnetic attraction.

The First Law of Thermodynamics (section 5.2)

- 5.25 (a) In any chemical or physical change, energy can be neither created nor destroyed, but it can be changed in form.
(b) The total *internal energy* (E) of a system is the sum of all the kinetic and potential energies of the system components.
(c) The internal energy of a closed system (where no mass exchange with surroundings occurs) increases when work is done on the system by the surroundings and/or when heat is transferred to the system from the surroundings (the system is heated).
- 5.26 (a) $\Delta E = q + w$
(b) The quantities q and w are negative when the system loses heat to the surroundings (it cools), or does work on the surroundings.
- 5.27 *Analyze.* Given: heat and work. Find: magnitude and sign of ΔE .
Plan. 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. *Solve.*
- (a) $q = 0.763 \text{ kJ}$, $w = -840 \text{ J} = 0.840 \text{ kJ}$. $\Delta E = 0.763 \text{ kJ} - 0.840 \text{ kJ} = -0.077 \text{ kJ}$. The process is endothermic.
- (b) q is negative because the system releases heat, and w is positive because work is done on the system. $\Delta E = -66.1 \text{ kJ} + 44.0 \text{ kJ} = -22.1 \text{ kJ}$. The process is exothermic.
- (c) q is positive because the system absorbs heat. No work is done, since $w = -P\Delta V$ and $\Delta V = 0$ (assuming that only P-V work can be done).
 $\Delta E = 7.25 \text{ kJ} + 0 \text{ kJ} = 7.25 \text{ kJ}$. The process is endothermic.
- 5.28 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 negative and w is positive. $\Delta E = -0.655 \text{ kJ} + 0.382 \text{ kJ} = -0.273 \text{ kJ}$. The process is exothermic.

- (b) q is positive and w is essentially zero. $\Delta E = 322 \text{ J}$. The process is endothermic.
- (c) q is zero (the cylinder is perfectly insulated) and w is positive. $\Delta E = 1.44 \text{ kJ}$. The process is neither endothermic nor exothermic when $q = 0$.

5.29 *Analyze.* How do the different physical situations (cases) affect the changes to heat and work of the system upon addition of 100 J of energy?

Plan. Use the definitions of heat and work and the First Law to answer the questions.

Solve. If the piston is allowed to move, case (1), the heated gas will expand and push the piston up, doing work on the surroundings. If the piston is fixed, case (2), most of the electrical energy will be manifested as an increase in heat of the system.

- (a) Since little or no work is done by the system in case (2), the gas will absorb most of the energy as heat; the case (2) gas will have the higher temperature.
- (b) In case (2), $w = 0$ and $q = 100 \text{ J}$. In case (1), a significant amount of energy will be used to do work on the surroundings ($-w$), but some will be absorbed as heat ($+q$). (The transfer of electrical energy into work is never completely efficient!)
- (c) ΔE is greater for case (2), because the entire 100 J increases the internal energy of the system, rather than a part of the energy doing work on the surroundings.

5.30 $E_{el} = \frac{\kappa Q_1 Q_2}{r^2}$ 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.

5.31 (a) A *state function* is a property of a system that depends only on the physical state (pressure, temperature, etc.) of the system, not on the route used by the system to get to the current state.

(b) Internal energy and enthalpy are state functions; heat is not a state function.

(c) Volume is a state function. The volume of a system depends only on conditions (pressure, temperature, amount of substance), not the route or method used to establish that volume.

5.32 (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.

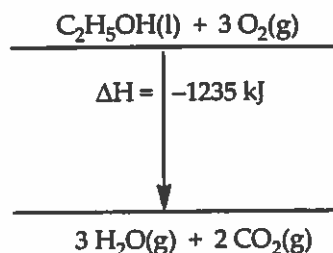
(c) Dependent. The work accomplished depends on whether the gasoline is used in an engine, burned in an open flame, or in some other manner. Work is not a state function.

Enthalpy (sections 5.3 and 5.4)

- 5.33 (a) Change in enthalpy (ΔH) is usually easier to measure than change in internal energy (ΔE) because, at constant pressure, $\Delta H = q_p$. The heat flow associated with a process at constant pressure can easily be measured as a change in temperature. Measuring ΔE requires a means to measure both q and w .
- (b) H describes the enthalpy of a system at a certain set of conditions; the value of H depends only on these conditions. q describes energy transferred as heat, an energy *change* which, in the general case, does depend on how the change occurs. We can equate change in enthalpy, ΔH , with heat, q_p , only for the specific conditions of constant pressure and exclusively P-V work.
- (c) If ΔH is positive, the enthalpy of the system increases and the process is endothermic.
- 5.34 (a) When a process occurs under constant external pressure and only P-V work occurs, the enthalpy change (ΔH) equals the amount of heat transferred. $\Delta H = q_p$.
- (b) $\Delta H = q_p$. If the system releases heat, q and ΔH are negative and the enthalpy of the system decreases.
- (c) If $\Delta H = 0$, $q_p = 0$ and $\Delta E = w$.
- 5.35 At constant pressure, $\Delta E = \Delta H - P\Delta V$. In order to calculate ΔE , more information about the conditions of the reaction must be known. For an ideal gas at constant pressure and temperature, $P\Delta V = RT\Delta n$. The values of either P and ΔV or T and Δn must be known to calculate ΔE from ΔH .
- 5.36 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 .
- 5.37 *Analyze/Plan.* $q = 824 \text{ J} = 0.824 \text{ kJ}$ (heat is absorbed by the system), $w = 0.65 \text{ kJ}$ (work is done on the system). *Solve.*
- $\Delta E = q + w = 0.824 \text{ kJ} + 0.65 \text{ kJ} = 1.47 \text{ kJ}$. $\Delta H = q = 0.824 \text{ kJ}$ (at constant pressure).
- Check.* The reaction is endothermic.
- 5.38 The gas is the system. If 0.49 kJ of heat is added, $q = +0.49 \text{ kJ}$. Work done by the system decreases the overall energy of the system, so $w = -214 \text{ J} = -0.214 \text{ kJ}$.
- $\Delta E = q + w = 0.49 \text{ kJ} - 0.214 \text{ kJ} = 0.276 \text{ kJ}$. $\Delta H = q = 0.49 \text{ kJ}$ (at constant pressure).
- 5.39 (a) $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(g) + 2\text{CO}_2(g)$ $\Delta H = -1235 \text{ kJ}$

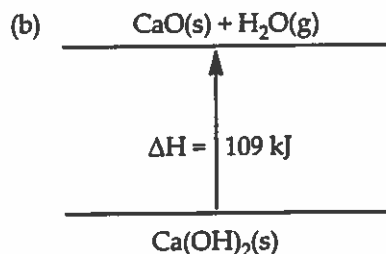
- (b) *Analyze.* How are reactants and products arranged on an enthalpy diagram?

Plan. The substances (reactants or products, collectively) with higher enthalpy are shown on the upper level, and those with lower enthalpy are shown on the lower level.



Solve. For this reaction, ΔH is negative, so the products have lower enthalpy and are shown on the lower level; reactants are on the upper level. The arrow points in the direction of reactants to products and is labeled with the value of ΔH .

- 5.40 (a) $\text{Ca}(\text{OH})_2(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g})$
 $\Delta\text{H} = 109 \text{ kJ}$



- 5.41 *Analyze/Plan.* Consider ΔH for the exothermic reaction as written. *Solve.*

- (a) $\Delta\text{H} = -284.6 \text{ kJ}/2 \text{ mol O}_3(\text{g}) = -142.3 \text{ kJ}/\text{mol O}_3(\text{g})$
(b) Since ΔH is negative, the reactants, $2\text{O}_3(\text{g})$ has the higher enthalpy.

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

- (a) $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$. This change is sublimation, which is endothermic, $+\Delta\text{H}$. $\text{CO}_2(\text{g})$ has the higher enthalpy.
(b) $\text{H}_2 \rightarrow 2\text{H}$. Breaking the H-H bond requires energy, so the process is endothermic, $+\Delta\text{H}$. Two moles of H atoms have higher enthalpy.
(c) $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$. Decomposing H_2O into its elements requires energy and is endothermic, $+\Delta\text{H}$. One mole of $\text{H}_2(\text{g})$ and 0.5 mol $\text{O}_2(\text{g})$ at 25°C have the higher enthalpy.
(d) $\text{N}_2(\text{g})$ at $100^\circ \rightarrow \text{N}_2(\text{g})$ at 300° . An increase in the temperature of the sample requires that heat is added to the system, $+q$ and $+\Delta\text{H}$. $\text{N}_2(\text{g})$ at 300° has the higher enthalpy.

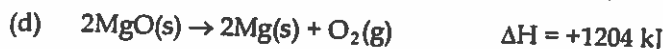
- 5.43 *Analyze/Plan.* Follow the strategy in Sample Exercise 5.4. *Solve.*

- (a) Exothermic (ΔH is negative)
(b) $3.55 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.305 \text{ g Mg}} \times \frac{-1204 \text{ kJ}}{2 \text{ mol Mg}} = -87.9 \text{ kJ}$ heat transferred

Check. The units of kJ are correct for heat. The negative sign indicates heat is evolved.

$$(c) \quad -234 \text{ kJ} \times \frac{2 \text{ mol MgO}}{-1204 \text{ kJ}} \times \frac{40.30 \text{ g MgO}}{1 \text{ mol Mg}} = 15.7 \text{ g MgO produced}$$

Check. Units are correct for mass. $(200 \times 2 \times 40/1200) \approx (16000/1200) > 10 \text{ g}$



This is the reverse of the reaction given above, so the sign of ΔH is reversed.

$$40.3 \text{ g MgO} \times \frac{1 \text{ mol MgO}}{40.30 \text{ g MgO}} \times \frac{1204 \text{ kJ}}{2 \text{ mol MgO}} = +602 \text{ kJ heat absorbed}$$

Check. 40.3 g MgO is just 1 mol MgO, so the calculated value is the heat absorbed per mol of MgO, 1204 kJ/2 mol MgO = 602 kJ.

5.44 (a) The sign of ΔH is positive, so the reaction is endothermic.

$$(b) \quad 24.0 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \times \frac{252.8 \text{ kJ}}{2 \text{ mol CH}_3\text{OH}} = 94.7 \text{ kJ heat absorbed}$$

$$(c) \quad 82.1 \text{ kJ} \times \frac{2 \text{ mol CH}_4}{252.8 \text{ kJ}} \times \frac{16.04 \text{ g CH}_4}{1 \text{ mol CH}_4} = 10.4 \text{ g CH}_4 \text{ produced}$$

(d) The sign of ΔH is reversed for the reverse reaction: $\Delta H = -252.8 \text{ kJ}$

$$38.5 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \times \frac{-252.8 \text{ kJ}}{2 \text{ mol CH}_4} = -303 \text{ kJ heat released}$$

5.45 *Analyze.* Given: balanced thermochemical equation, various quantities of substances and/or enthalpy. *Plan.* Enthalpy is an extensive property; it is "stoichiometric." Use the mole ratios implicit in the balanced thermochemical equation to solve for the desired quantity. Use molar masses to change mass to moles and vice versa where appropriate. *Solve.*

$$(a) \quad 0.450 \text{ mol AgCl} \times \frac{-65.5 \text{ kJ}}{1 \text{ mol AgCl}} = -29.5 \text{ kJ}$$

Check. Units are correct; sign indicates heat evolved.

$$(b) \quad 9.00 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.3 \text{ g AgCl}} \times \frac{-65.5 \text{ kJ}}{1 \text{ mol AgCl}} = -4.11 \text{ kJ}$$

Check. Units correct; sign indicates heat evolved.

$$(c) \quad 9.25 \times 10^{-4} \text{ mol AgCl} \times \frac{+65.5 \text{ kJ}}{1 \text{ mol AgCl}} = 0.0606 \text{ kJ} = 60.6 \text{ J}$$

Check. Units correct; sign of ΔH reversed; sign indicates heat is absorbed during the reverse reaction.

$$5.46 (a) \quad 1.36 \text{ mol O}_2 \times \frac{-89.4 \text{ kJ}}{3 \text{ mol O}_2} = -40.53 = -40.5 \text{ kJ}$$

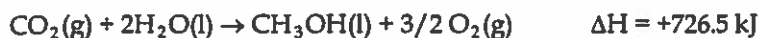
$$(b) \quad 10.4 \text{ g KCl} \times \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} \times \frac{-89.4 \text{ kJ}}{2 \text{ mol KCl}} = -6.2358 = -6.24 \text{ kJ}$$

- (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 $\text{KCl}(s)$ does not spontaneously react with atmospheric $\text{O}_2(g)$, even at elevated temperature.

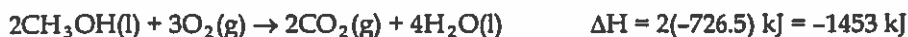
5.47

Analyze. Given: balanced thermochemical equation. *Plan.* Follow the guidelines given in Section 5.4 for evaluating thermochemical equations. *Solve.*

- (a) When a chemical equation is reversed, the sign of ΔH is reversed.



- (b) Enthalpy is extensive. If the coefficients in the chemical equation are multiplied by 2 to obtain all integer coefficients, the enthalpy change is also multiplied by 2.



- (c) The exothermic forward reaction is more likely to be thermodynamically favored.
 (d) Decrease. Vaporization (liquid \rightarrow gas) is endothermic. If the product were $\text{H}_2\text{O}(g)$, the reaction would be more endothermic and would have a smaller negative ΔH . (Depending on temperature, the enthalpy of vaporization for 2 mol H_2O is about +88 kJ, not large enough to cause the overall reaction to be endothermic.)

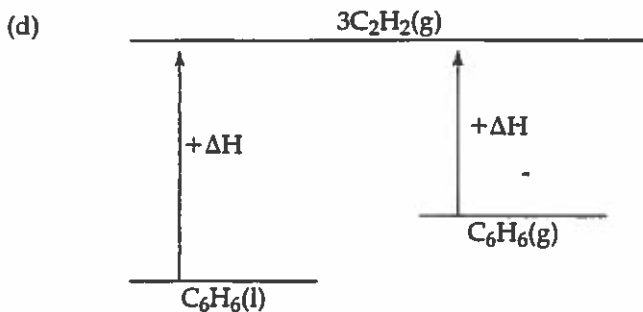
5.48

- (a) $3\text{C}_2\text{H}_2(g) \rightarrow \text{C}_6\text{H}_6(l) \quad \Delta H = -630 \text{ kJ}$

- (b) $\text{C}_6\text{H}_6(l) \rightarrow 3\text{C}_2\text{H}_2(g) \quad \Delta H = +630 \text{ kJ}$

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 $630 \text{ kJ}/3 = 210 \text{ kJ}$.

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



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

Calorimetry (section 5.5)

The specific heat of water to four significant figures, $4.184 \text{ J/g} \cdot \text{K}$, will be used in many of the following exercises; temperature units of K and $^\circ\text{C}$ will be used interchangeably.

5.49

- (a) $\text{J/mol} \cdot \text{K}$ or $\text{J/mol} \cdot ^\circ\text{C}$. Heat capacity is the amount of heat in J required to raise the temperature of an object or a certain amount of substance 1°C or 1 K. Molar heat capacity is the heat capacity of one mole of substance.

- (b) $\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}$ or $\frac{\text{J}}{\text{g} \cdot \text{K}}$ Specific heat is a particular kind of heat capacity where the amount of substance is 1 g.
- (c) To calculate heat capacity from specific heat, the mass of the particular piece of copper pipe must be known.

5.50 *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.

5.51 *Plan.* Manipulate the definition of specific heat to solve for the desired quantity, paying close attention to units. $C_s = q / (m \times \Delta t)$. *Solve.*

(a) $\frac{4.184 \text{ J}}{1 \text{ g} \cdot \text{K}}$ or $\frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}}$

(b) $\frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = \frac{75.40 \text{ J}}{\text{mol} \cdot ^\circ\text{C}}$

(c) $\frac{185 \text{ g H}_2\text{O} \times 4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} = 774 \text{ J}/^\circ\text{C}$

(d) $10.00 \text{ kg H}_2\text{O} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times (46.2^\circ\text{C} - 24.6^\circ\text{C}) = 904 \text{ kJ}$

Check. $(10 \times 4 \times 20) \approx 800 \text{ kJ}$; the units are correct. Note that the conversion factors for $\text{kg} \rightarrow \text{g}$ and $\text{J} \rightarrow \text{kJ}$ cancel. An equally correct form of specific heat would be $\text{kJ}/\text{kg} \cdot ^\circ\text{C}$.

5.52 (a) In Table 5.2, $\text{Hg}(\text{l})$ 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) $50.0 \text{ g Hg}(\text{l}) \times 10 \text{ K} \times \frac{0.14 \text{ J}}{\text{g} \cdot \text{K}} = 70 \text{ J}$

5.53 *Analyze/Plan.* Follow the logic in Sample Exercise 5.5. *Solve.*

(a) $80.0 \text{ g C}_8\text{H}_{18} \times \frac{2.22 \text{ J}}{\text{g} \cdot \text{K}} \times (25.0^\circ\text{C} - 10.0^\circ\text{C}) = 2.66 \times 10^3 \text{ J (or 2.66 kJ)}$

- (b) *Plan.* Calculate the molar heat capacity of octane and compare it with the molar heat capacity of water, $75.40 \text{ J/mol}\cdot^\circ\text{C}$, as calculated in Exercise 5.51(b). *Solve.*

$$\frac{2.22 \text{ J}}{\text{g}\cdot\text{K}} \times \frac{114.2 \text{ g C}_8\text{H}_{18}}{1 \text{ mol C}_8\text{H}_{18}} = \frac{253.58 \text{ J}}{\text{mol}\cdot\text{K}} = \frac{254 \text{ J}}{\text{mol}\cdot\text{K}}$$

The molar heat capacity of $\text{C}_8\text{H}_{18}(\text{l})$, $254 \text{ J/mol}\cdot\text{K}$, is greater than that of $\text{H}_2\text{O}(\text{l})$, so it will require more heat to increase the temperature of octane than to increase the temperature of water.

5.54 (a) $\text{specific heat} = \frac{\text{J}}{\text{g}\cdot^\circ\text{C}} = \frac{322 \text{ J}}{100.0 \text{ g} \times (50^\circ\text{C} - 25^\circ\text{C})} = 0.1288 = \frac{0.13 \text{ J}}{\text{g}\cdot^\circ\text{C}}$

- (b) In general, the greater the heat capacity, the more heat is required to raise the temperature of 1 gram of substance 1°C . The specific heat of gold is $0.13 \text{ J/g}\cdot^\circ\text{C}$, while that of iron is $0.45 \text{ J/g}\cdot^\circ\text{C}$ (Table 5.2). For gold and iron blocks with equal mass, same initial temperature and same amount of heat added, the one with the lower specific heat, gold, will require less heat per $^\circ\text{C}$ and have the higher final temperature.

(c) $\frac{0.1288 \text{ J}}{\text{g}\cdot^\circ\text{C}} \times \frac{196.97 \text{ g Au}}{1 \text{ mol Au}} = 25.37 = \frac{25 \text{ J}}{\text{mol}\cdot^\circ\text{C}}$

- 5.55 *Analyze.* Since the temperature of the water increases, the dissolving process is exothermic and the sign of ΔH is negative. The heat lost by the $\text{NaOH}(\text{s})$ dissolving equals the heat gained by the solution.

Plan/Solve. Calculate the heat gained by the solution. The temperature change is $37.8 - 21.6 = 16.2^\circ\text{C}$. The total mass of solution is $(100.0 \text{ g H}_2\text{O} + 6.50 \text{ g NaOH}) = 106.5 \text{ g}$.

$$106.5 \text{ g solution} \times \frac{4.184 \text{ J}}{\text{g}\cdot^\circ\text{C}} \times 16.2^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 7.2187 = 7.22 \text{ kJ}$$

This is the amount of heat lost when 6.50 g of NaOH dissolves.

The heat loss per mole NaOH is

$$\frac{-7.2187 \text{ kJ}}{6.50 \text{ g NaOH}} \times \frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}} = -44.4 \text{ kJ/mol} \quad \Delta H = q_p = -44.4 \text{ kJ/mol NaOH}$$

Check. $(-7/7 \times 40) \approx -40 \text{ kJ}$; the units and sign are correct.

- 5.56 (a) Follow the logic in Solution 5.55. The total mass of the solution is $(60.0 \text{ g H}_2\text{O} + 4.25 \text{ g NH}_4\text{NO}_3) = 64.25 = 64.3 \text{ g}$. The temperature change of the solution is $22.0 - 16.9 = 5.1^\circ\text{C}$. The heat lost by the surroundings is

$$64.25 \text{ g solution} \times \frac{4.184 \text{ J}}{\text{g}\cdot^\circ\text{C}} \times 5.1^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.371 = 1.4 \text{ kJ}$$

Thus, 1.4 kJ is absorbed when 4.25 g $\text{NH}_4\text{NO}_3(\text{s})$ dissolves.

$$\frac{+1.371 \text{ kJ}}{4.25 \text{ g NH}_4\text{NO}_3} \times \frac{80.04 \text{ g NH}_4\text{NO}_3}{1 \text{ mol NH}_4\text{NO}_3} = +25.82 = +26 \text{ kJ/mol NH}_4\text{NO}_3$$

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

5.57 *Analyze/Plan.* Follow the logic in Sample Exercise 5.7. *Solve.*

$$q_{\text{bomb}} = -q_{\text{rxn}}; \Delta T = 30.57^\circ\text{C} - 23.44^\circ\text{C} = 7.13^\circ\text{C}$$

$$q_{\text{bomb}} = \frac{7.854 \text{ kJ}}{1^\circ\text{C}} \times 7.13^\circ\text{C} = 56.00 = 56.0 \text{ kJ}$$

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

$$\Delta H_{\text{rxn}} \approx \Delta E_{\text{rxn}} = q_{\text{rxn}} = -q_{\text{bomb}} = \frac{-56.0 \text{ kJ}}{2.200 \text{ g C}_6\text{H}_4\text{O}_2} = -25.454 = -25.5 \text{ kJ/g C}_6\text{H}_4\text{O}_2$$

$$\Delta H_{\text{rxn}} = \frac{-25.454 \text{ kJ}}{1 \text{ g C}_6\text{H}_4\text{O}_2} \times \frac{108.1 \text{ g C}_6\text{H}_4\text{O}_2}{1 \text{ mol C}_6\text{H}_4\text{O}_2} = -2.75 \times 10^3 \text{ kJ/mol C}_6\text{H}_4\text{O}_2$$

5.58 (a) $\text{C}_6\text{H}_5\text{OH}(s) + 7\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$

(b) $q_{\text{bomb}} = -q_{\text{rxn}}; \Delta T = 26.37^\circ\text{C} - 21.36^\circ\text{C} = 5.01^\circ\text{C}$

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

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

$$\Delta H_{\text{rxn}} \approx \Delta E_{\text{rxn}} = q_{\text{rxn}} = -q_{\text{bomb}} = \frac{-58.417 \text{ kJ}}{1.800 \text{ g C}_6\text{H}_5\text{OH}} = -32.454 = -32.5 \text{ kJ/g C}_6\text{H}_5\text{OH}$$

$$\Delta H_{\text{rxn}} = \frac{-32.454 \text{ kJ}}{1 \text{ g C}_6\text{H}_5\text{OH}} \times \frac{94.11 \text{ g C}_6\text{H}_5\text{OH}}{1 \text{ mol C}_6\text{H}_5\text{OH}} = \frac{-3.054 \times 10^3 \text{ kJ}}{\text{mol C}_6\text{H}_5\text{OH}}$$

$$= -3.05 \times 10^3 \text{ kJ/mol C}_6\text{H}_5\text{OH}$$

5.59 *Analyze.* Given: specific heat and mass of glucose, ΔT for calorimeter. Find: heat capacity, C , of calorimeter. *Plan.* All heat from the combustion raises the temperature of the calorimeter. Calculate heat from combustion of glucose, divide by ΔT for calorimeter to get $\text{kJ}/^\circ\text{C}$. $\Delta T = 24.72^\circ\text{C} - 20.94^\circ\text{C} = 3.78^\circ\text{C}$ *Solve.*

$$(a) C_{\text{total}} = 3.500 \text{ g glucose} \times \frac{15.57 \text{ kJ}}{1 \text{ g glucose}} \times \frac{1}{3.78^\circ\text{C}} = 14.42 = 14.4 \text{ kJ}/^\circ\text{C}$$

(b) Qualitatively, assuming the same exact initial conditions in the calorimeter, twice as much glucose produces twice as much heat, which raises the calorimeter temperature by twice as many $^\circ\text{C}$. Quantitatively,

$$7.000 \text{ g glucose} \times \frac{15.57 \text{ kJ}}{1 \text{ g glucose}} \times \frac{1^\circ\text{C}}{14.42 \text{ kJ}} = 7.56^\circ\text{C}$$

Check. Units are correct. ΔT is twice as large as in part (a). The result has 3 sig figs, because the heat capacity of the calorimeter is known to 3 sig figs.

5.60 (a) $C = 2.760 \text{ g C}_6\text{H}_5\text{COOH} \times \frac{26.38 \text{ kJ}}{1 \text{ g C}_6\text{H}_5\text{COOH}} \times \frac{1}{8.33^\circ\text{C}} = 8.74055 = 8.74 \text{ kJ}/^\circ\text{C}$

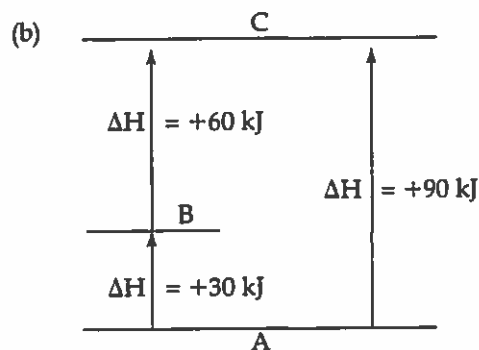
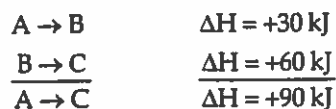
(b) $\frac{8.74055 \text{ kJ}}{^\circ\text{C}} \times 4.95^\circ\text{C} \times \frac{1}{1.440 \text{ g sample}} = 30.046 = 30.0 \text{ kJ/g sample}$

- (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, $\text{kJ}/^\circ\text{C}$, would decrease, because $^\circ\text{C}$ is in the denominator of the expression.

Hess's Law (section 5.6)

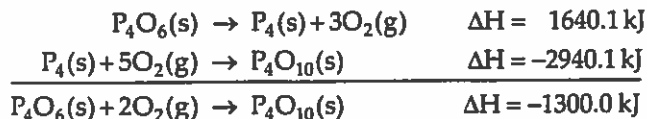
- 5.61 Hess's Law is a consequence of the fact that enthalpy is a state function. Since ΔH is independent of path, we can describe a process by any series of steps that add up to the overall process and ΔH for the process is the sum of the ΔH values for the steps.

- 5.62 (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.*



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

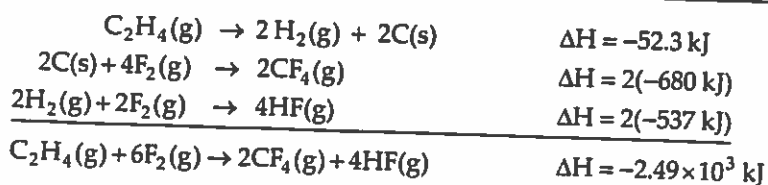
- 5.63 *Analyze/Plan.* Follow the logic in Sample Exercise 5.8. Manipulate the equations so that "unwanted" substances can be canceled from reactants and products. Adjust the corresponding sign and magnitude of ΔH . *Solve.*



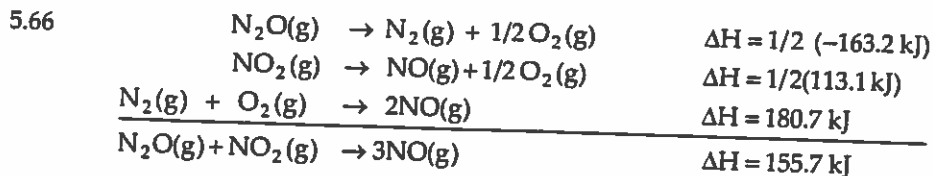
Check. We have obtained the desired reaction.

- 5.64
- $$\begin{array}{l} 2\text{C}(\text{s}) + \text{O}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightarrow 2\text{CH}_3\text{OH}(\text{g}) \quad \Delta H = -402.4 \text{ kJ} \\ 2\text{CO}(\text{g}) \rightarrow \text{O}_2(\text{g}) + 2\text{C}(\text{s}) \quad \Delta H = 221.0 \text{ kJ} \\ \hline 2\text{CO}(\text{g}) + 4\text{H}_2(\text{g}) \rightarrow 2\text{CH}_3\text{OH}(\text{g}) \quad \Delta H = -181.4 \text{ kJ} \\ \text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g}) \quad \Delta H = (-181.4)/2 = -90.7 \text{ kJ} \end{array}$$

- 5.65 *Analyze/Plan.* Follow the logic in Sample Exercise 5.9. Manipulate the equations so that "unwanted" substances can be canceled from reactants and products. Adjust the corresponding sign and magnitude of ΔH . *Solve.*



Check. We have obtained the desired reaction.



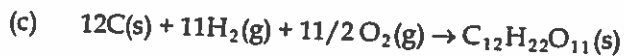
Enthalpies of Formation (section 5.7)

- 5.67 (a) *Standard conditions* for enthalpy changes are usually $P = 1 \text{ atm}$ and $T = 298 \text{ K}$. For the purpose of comparison, standard enthalpy changes, ΔH° , are tabulated for reactions at these conditions.
- (b) *Enthalpy of formation*, ΔH_f° , is the enthalpy change that occurs when a compound is formed from its component elements.
- (c) *Standard enthalpy of formation*, ΔH_f° , is the enthalpy change that accompanies formation of one mole of a substance from elements in their standard states.

- 5.68 (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.



- 5.69 (a) $1/2 \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g})$ $\Delta\text{H}_f^\circ = 33.84 \text{ kJ}$
- (b) $\text{S}(\text{s}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$ $\Delta\text{H}_f^\circ = -395.2 \text{ kJ}$
- (c) $\text{Na}(\text{s}) + 1/2 \text{Br}_2(\text{l}) \rightarrow \text{NaBr}(\text{s})$ $\Delta\text{H}_f^\circ = -361.4 \text{ kJ}$
- (d) $\text{Pb}(\text{s}) + \text{N}_2(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{Pb}(\text{NO}_3)_2(\text{s})$ $\Delta\text{H}_f^\circ = -451.9 \text{ kJ}$
- 5.70 (a) $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{g})$ $\Delta\text{H}_f^\circ = -136.10 \text{ kJ}$
- (b) $\text{Ca}(\text{s}) + \text{C}(\text{s}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s})$ $\Delta\text{H}_f^\circ = -1207.1 \text{ kJ}$
- (c) $1/4 \text{P}_4(\text{s}) + 1/2 \text{O}_2(\text{g}) + 3/2 \text{Cl}_2(\text{g}) \rightarrow \text{POCl}_3(\text{l})$ $\Delta\text{H}_f^\circ = -597.0 \text{ kJ}$
- (d) $2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$ $\Delta\text{H}_f^\circ = -277.7 \text{ kJ}$

5.71 *Plan.* $\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_f^{\circ}(\text{products}) - \sum n\Delta H_f^{\circ}(\text{reactants})$. Be careful with coefficients, states, and signs. *Solve.*

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} \text{Al}_2\text{O}_3(\text{s}) + 2\Delta H_f^{\circ} \text{Fe}(\text{s}) - \Delta H_f^{\circ} \text{Fe}_2\text{O}_3(\text{s}) - 2\Delta H_f^{\circ} \text{Al}(\text{s})$$

$$\Delta H_{\text{rxn}}^{\circ} = (-1669.8 \text{ kJ}) + 2(0) - (-822.16 \text{ kJ}) - 2(0) = -847.6 \text{ kJ}$$

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



$$\Delta H_{\text{rxn}}^{\circ} = 3\Delta H_f^{\circ} \text{CO}_2(\text{g}) + 4\Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_f^{\circ} \text{C}_3\text{H}_8(\text{g}) - 5\Delta H_f^{\circ} \text{O}_2(\text{g})$$

$$\Delta H_{\text{rxn}}^{\circ} = 3(-393.5 \text{ kJ}) + 4(-285.83 \text{ kJ}) - (-103.85 \text{ kJ}) - 5(0) = -2219.97 = -2220.0 \text{ kJ/mol C}_3\text{H}_8$$

$$10.00 \text{ g C}_3\text{H}_8 \times \frac{1 \text{ mol C}_3\text{H}_8}{44.096 \text{ g C}_3\text{H}_8} \times \frac{-2219.97 \text{ kJ}}{1 \text{ mol C}_3\text{H}_8} = -503.4 \text{ kJ}$$

5.73 *Plan.* $\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_f^{\circ}(\text{products}) - \sum n\Delta H_f^{\circ}(\text{reactants})$. Be careful with coefficients, states and signs. *Solve.*

$$(a) \quad \Delta H_{\text{rxn}}^{\circ} = 2\Delta H_f^{\circ} \text{SO}_3(\text{g}) - 2\Delta H_f^{\circ} \text{SO}_2(\text{g}) - \Delta H_f^{\circ} \text{O}_2(\text{g})$$

$$= 2(-395.2 \text{ kJ}) - 2(-296.9 \text{ kJ}) - 0 = -196.6 \text{ kJ}$$

$$(b) \quad \Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} \text{MgO}(\text{s}) + \Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_f^{\circ} \text{Mg}(\text{OH})_2(\text{s})$$

$$= -601.8 \text{ kJ} + (-285.83 \text{ kJ}) - (-924.7 \text{ kJ}) = 37.1 \text{ kJ}$$

$$(c) \quad \Delta H_{\text{rxn}}^{\circ} = 4\Delta H_f^{\circ} \text{H}_2\text{O}(\text{g}) + \Delta H_f^{\circ} \text{N}_2(\text{g}) - \Delta H_f^{\circ} \text{N}_2\text{O}_4(\text{g}) - 4\Delta H_f^{\circ} \text{H}_2(\text{g})$$

$$= 4(-241.82 \text{ kJ}) + 0 - (9.66 \text{ kJ}) - 4(0) = -976.94 \text{ kJ}$$

$$(d) \quad \Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} \text{SiO}_2(\text{s}) + 4\Delta H_f^{\circ} \text{HCl}(\text{g}) - \Delta H_f^{\circ} \text{SiCl}_4(\text{l}) - 2\Delta H_f^{\circ} \text{H}_2\text{O}(\text{l})$$

$$= -910.9 \text{ kJ} + 4(-92.30 \text{ kJ}) - (-640.1 \text{ kJ}) - 2(-285.83 \text{ kJ}) = -68.3 \text{ kJ}$$

5.74 (a) $\Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} \text{CaCl}_2(\text{s}) + \Delta H_f^{\circ} \text{H}_2\text{O}(\text{g}) - \Delta H_f^{\circ} \text{CaO}(\text{s}) - 2\Delta H_f^{\circ} \text{HCl}(\text{g})$

$$= -795.8 \text{ kJ} + (-241.82 \text{ kJ}) - (-635.5 \text{ kJ}) - 2(-92.30 \text{ kJ}) = -217.5 \text{ kJ}$$

$$(b) \quad \Delta H_{\text{rxn}}^{\circ} = 2\Delta H_f^{\circ} \text{Fe}_2\text{O}_3(\text{s}) - 4\Delta H_f^{\circ} \text{FeO}(\text{s}) - \Delta H_f^{\circ} \text{O}_2(\text{g})$$

$$= 2(-822.16 \text{ kJ}) - 4(-271.9 \text{ kJ}) - (0) = -556.7 \text{ kJ}$$

$$(c) \quad \Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} \text{Cu}_2\text{O}(\text{s}) + \Delta H_f^{\circ} \text{NO}_2(\text{g}) - 2\Delta H_f^{\circ} \text{CuO}(\text{s}) - \Delta H_f^{\circ} \text{NO}(\text{g})$$

$$= -170.7 \text{ kJ} + (33.84 \text{ kJ}) - 2(-156.1 \text{ kJ}) - (90.37 \text{ kJ}) = 85.0 \text{ kJ}$$

$$(d) \quad \Delta H_{\text{rxn}}^{\circ} = 2\Delta H_f^{\circ} \text{N}_2\text{H}_4(\text{g}) + 2\Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - 4\Delta H_f^{\circ} \text{NH}_3(\text{g}) - \Delta H_f^{\circ} \text{O}_2(\text{g})$$

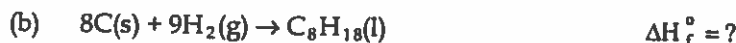
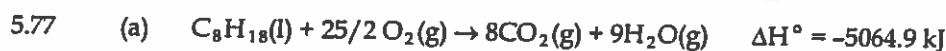
$$= 2(95.40 \text{ kJ}) + 2(-285.83 \text{ kJ}) - 4(-46.19 \text{ kJ}) - (0) = -196.10 \text{ kJ}$$

5.75 *Analyze.* Given: combustion reaction, enthalpy of combustion, enthalpies of formation for most reactants and products. Find: enthalpy of formation for acetone.

Plan. Rearrange the expression for enthalpy of reaction to calculate the desired enthalpy of formation. *Solve.*

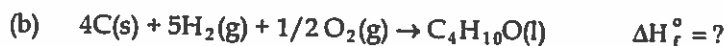
$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= 3\Delta H_f^{\circ} \text{CO}_2(\text{g}) + 3\Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_f^{\circ} \text{C}_3\text{H}_6\text{O}(\text{l}) - 4\Delta H_f^{\circ} \text{O}_2(\text{g}) \\ &= -1790 \text{ kJ} = 3(-393.5 \text{ kJ}) + 3(-285.83 \text{ kJ}) - \Delta H_f^{\circ} \text{C}_3\text{H}_6\text{O}(\text{l}) - 4(0) \\ \Delta H_f^{\circ} \text{C}_3\text{H}_6\text{O}(\text{l}) &= 3(-393.5 \text{ kJ}) + 3(-285.83 \text{ kJ}) + 1790 \text{ kJ} = -248 \text{ kJ}\end{aligned}$$

5.76 $\Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} \text{Ca}(\text{OH})_2(\text{s}) + \Delta H_f^{\circ} \text{C}_2\text{H}_2(\text{g}) - 2\Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_f^{\circ} \text{CaC}_2(\text{s})$
 $-127.2 \text{ kJ} = -986.2 \text{ kJ} + 226.77 \text{ kJ} - 2(-285.83 \text{ kJ}) - \Delta H_f^{\circ} \text{CaC}_2(\text{s})$
 ΔH_f° for $\text{CaC}_2(\text{s}) = -60.6 \text{ kJ}$

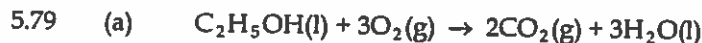


(c) *Plan.* Follow the logic in Solution 5.75 and 5.76. *Solve.*

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= 8\Delta H_f^{\circ} \text{CO}_2(\text{g}) + 9\Delta H_f^{\circ} \text{H}_2\text{O}(\text{g}) - \Delta H_f^{\circ} \text{C}_8\text{H}_{18}(\text{l}) - 25/2 \Delta H_f^{\circ} \text{O}_2(\text{g}) \\ -5064.9 \text{ kJ} &= 8(-393.5 \text{ kJ}) + 9(-241.82 \text{ kJ}) - \Delta H_f^{\circ} \text{C}_8\text{H}_{18}(\text{l}) - 25/2(0) \\ \Delta H_f^{\circ} \text{C}_8\text{H}_{18}(\text{l}) &= 8(-393.5 \text{ kJ}) + 9(-241.82 \text{ kJ}) + 5064.9 \text{ kJ} = -259.5 \text{ kJ}\end{aligned}$$



(c) $\Delta H_{\text{rxn}}^{\circ} = 4\Delta H_f^{\circ} \text{CO}_2(\text{g}) + 5\Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_f^{\circ} \text{C}_4\text{H}_{10}\text{O}(\text{l}) - 6\Delta H_f^{\circ} \text{O}_2(\text{g})$
 $-2723.7 = 4(-393.5 \text{ kJ}) + 5(-285.83 \text{ kJ}) - \Delta H_f^{\circ} \text{C}_4\text{H}_{10}\text{O}(\text{l}) - 6(0)$
 $\Delta H_f^{\circ} \text{C}_4\text{H}_{10}\text{O}(\text{l}) = 4(-393.5 \text{ kJ}) + 5(-285.83 \text{ kJ}) + 2723.7 \text{ kJ} = -279.45 = -279.5 \text{ kJ}$



(b) $\Delta H_{\text{rxn}}^{\circ} = 2\Delta H_f^{\circ} \text{CO}_2(\text{g}) + 3\Delta H_f^{\circ} \text{H}_2\text{O}(\text{g}) - \Delta H_f^{\circ} \text{C}_2\text{H}_5\text{OH}(\text{l}) - 3\Delta H_f^{\circ} \text{O}_2(\text{g})$
 $= 2(-393.5 \text{ kJ}) + 3(-241.82 \text{ kJ}) - (-277.7 \text{ kJ}) - 3(0) = -1234.76 = -1234.8 \text{ kJ}$

(c) *Plan.* The enthalpy of combustion of ethanol [from part (b)] is -1234.8 kJ/mol . Change mol to mass using molar mass, then mass to volume using density. *Solve.*

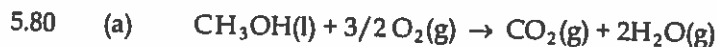
$$\frac{-1234.76 \text{ kJ}}{\text{mol C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.06844 \text{ g}} \times \frac{0.789 \text{ g}}{\text{mL}} \times \frac{1000 \text{ mL}}{\text{L}} = -21,147 = -2.11 \times 10^4 \text{ kJ/L}$$

Check. $(1200/50) \approx 25$; $25 \times 800 \approx 20,000$

(d) *Plan.* The enthalpy of combustion corresponds to any of the molar amounts in the equation as written. Production of -1234.76 kJ also produces 2 mol CO_2 . Use this relationship to calculate mass CO_2/kJ .

$$\frac{2 \text{ mol CO}_2}{-1234.76 \text{ kJ}} \times \frac{44.0095 \text{ g CO}_2}{\text{mol}} = 0.071284 \text{ g CO}_2/\text{kJ emitted}$$

Check. The negative sign associated with enthalpy indicates that energy is emitted.



- (b) $\Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} \text{CO}_2(\text{g}) + 2\Delta H_f^{\circ} \text{H}_2\text{O}(\text{g}) - \Delta H_f^{\circ} \text{CH}_3\text{OH}(\text{l}) - 3/2 \Delta H_f^{\circ} \text{O}_2(\text{g})$
 $= -393.5 \text{ kJ} + 2(-241.82 \text{ kJ}) - (-238.6 \text{ kJ}) - 3/2(0) = -638.54 = -638.5 \text{ kJ}$
- (c) $\frac{-638.54 \text{ kJ}}{\text{mol CH}_3\text{OH}} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g}} \times \frac{0.791 \text{ g}}{\text{mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 1.58 \times 10^4 \text{ kJ/L produced}$
- (d) $\frac{1 \text{ mol CO}_2}{-638.54 \text{ kJ}} \times \frac{44.0095 \text{ g CO}_2}{\text{mol}} = 0.06892 \text{ g CO}_2/\text{kJ emitted}$

Foods and Fuels (Section 5.8)

- 5.81 (a) *Fuel value* is the amount of energy produced when 1 gram of a substance (fuel) is combusted.
- (b) The fuel value of fats is 9 kcal/g and of carbohydrates is 4 kcal/g. Therefore, 5 g of fat produce 45 kcal, while 9 g of carbohydrates produce 36 kcal; 5 g of fat are a greater energy source.
- (c) These products of metabolism are expelled as waste via the alimentary tract, $\text{H}_2\text{O}(\text{l})$ primarily in urine and feces, and $\text{CO}_2(\text{g})$ as gas.

- 5.82 (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.

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

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

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

$$\text{total Cal} = (48.76 + 127.15 + 300.67) = 476.58 = 480 \text{ Cal}$$

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

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

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

- 5.83 (a) *Plan.* Calculate the Cal (kcal) due to each nutritional component of the soup, then sum. *Solve.*

$$2.5 \text{ g fat} \times \frac{38 \text{ kJ}}{1 \text{ g fat}} = 95.0 \text{ or } 0.95 \times 10^2 \text{ kJ}$$

$$14 \text{ g carbohydrates} \times \frac{17 \text{ kJ}}{1 \text{ g carbohydrate}} = 238 \text{ or } 2.4 \times 10^2 \text{ kJ}$$

$$7 \text{ g protein} \times \frac{17 \text{ kJ}}{1 \text{ g protein}} = 119 \text{ or } 1 \times 10^2 \text{ kJ}$$

$$\text{total energy} = 95.0 \text{ kJ} + 238 \text{ kJ} + 119 \text{ kJ} = 452 \text{ or } 5 \times 10^2 \text{ kJ}$$

$$452 \text{ kJ} \times \frac{1 \text{ kcal}}{4.184 \text{ kJ}} \times \frac{1 \text{ Cal}}{1 \text{ kcal}} = 108.03 \text{ or } 1 \times 10^2 \text{ Cal/serving}$$

Check. 100 Cal/serving is a reasonable result; units are correct. The data and the result have 1 sig fig.

(b) Sodium does not contribute to the calorie content of the food, because it is not metabolized by the body; it enters and leaves as Na^+ .

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

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

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

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

$$\text{total fuel value} = 3648 \text{ kJ} + 5440 \text{ kJ} + 357 \text{ kJ} = 9445 \text{ kJ} = 9.4 \times 10^3 \text{ kJ/lb}$$

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

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

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

5.85 *Plan.* g \rightarrow mol \rightarrow kJ \rightarrow Cal *Solve.*

$$16.0 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} \times \frac{2812 \text{ kJ}}{\text{mol C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ Cal}}{4.184 \text{ kJ}} = 59.7 \text{ Cal}$$

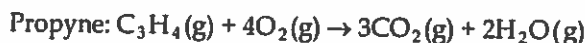
Check. 60 Cal is a reasonable result for most of the food value in an apple.

$$5.86 \quad 177 \text{ mL} \times \frac{1.0 \text{ g wine}}{1 \text{ mL}} \times \frac{0.106 \text{ g ethanol}}{1 \text{ g wine}} \times \frac{1 \text{ mol ethanol}}{46.1 \text{ g ethanol}} \times \frac{1367 \text{ kJ}}{1 \text{ mol ethanol}} \times \frac{1 \text{ Cal}}{4.184 \text{ kJ}}$$

$$= 133 = 1.3 \times 10^2 \text{ Cal}$$

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.

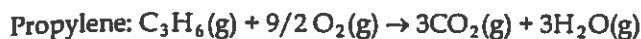
5.87 *Plan.* Use enthalpies of formation to calculate molar heat (enthalpy) of combustion using Hess's Law. Use molar mass to calculate heat of combustion per kg of hydrocarbon. *Solve.*



$$(a) \quad \Delta H_{\text{rxn}}^\circ = 3(-393.5 \text{ kJ}) + 2(-241.82 \text{ kJ}) - (185.4 \text{ kJ}) - 4(0) = -1849.5$$

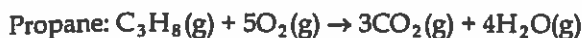
$$= -1850 \text{ kJ/mol C}_3\text{H}_4$$

$$(b) \frac{-1849.5 \text{ kJ}}{1 \text{ mol C}_3\text{H}_4} \times \frac{1 \text{ mol C}_3\text{H}_4}{40.065 \text{ g C}_3\text{H}_4} \times \frac{1000 \text{ g C}_3\text{H}_4}{1 \text{ kg C}_3\text{H}_4} = -4.616 \times 10^4 \text{ kJ/kg C}_3\text{H}_4$$



$$(a) \Delta H_{\text{rxn}}^\circ = 3(-393.5 \text{ kJ}) + 3(-241.82 \text{ kJ}) - (20.4 \text{ kJ}) - 9/2(0) = -1926.4 \\ = -1926 \text{ kJ/mol C}_3\text{H}_6$$

$$(b) \frac{-1926.4 \text{ kJ}}{1 \text{ mol C}_3\text{H}_6} \times \frac{1 \text{ mol C}_3\text{H}_6}{42.080 \text{ g C}_3\text{H}_6} \times \frac{1000 \text{ g C}_3\text{H}_6}{1 \text{ kg C}_3\text{H}_6} = -4.578 \times 10^4 \text{ kJ/kg C}_3\text{H}_6$$



$$(a) \Delta H_{\text{rxn}}^\circ = 3(-393.5 \text{ kJ}) + 4(-241.82 \text{ kJ}) - (-103.8 \text{ kJ}) - 5(0) = -2044.0 \\ = -2044 \text{ kJ/mol C}_3\text{H}_8$$

$$(b) \frac{-2044.0 \text{ kJ}}{1 \text{ mol C}_3\text{H}_8} \times \frac{1 \text{ mol C}_3\text{H}_8}{44.096 \text{ g C}_3\text{H}_8} \times \frac{1000 \text{ g C}_3\text{H}_8}{1 \text{ kg C}_3\text{H}_8} = -4.635 \times 10^4 \text{ kJ/kg C}_3\text{H}_8$$

(c) These three substances yield nearly identical quantities of heat per unit mass, but propane is marginally higher than the other two.

$$5.88 \quad \Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ \text{CO}_2(\text{g}) + 2\Delta H_f^\circ \text{H}_2\text{O}(\text{g}) - \Delta H_f^\circ \text{CH}_4(\text{g}) - 2\Delta H_f^\circ \text{O}_2(\text{g}) \\ = -393.5 \text{ kJ} + 2(-241.82 \text{ kJ}) - (-74.8 \text{ kJ}) - 2(0) \text{ kJ} = -802.3 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ \text{CF}_4(\text{g}) + 4\Delta H_f^\circ \text{HF}(\text{g}) - \Delta H_f^\circ \text{CH}_4(\text{g}) - 4\Delta H_f^\circ \text{F}_2(\text{g}) \\ = -679.9 \text{ kJ} + 4(-268.61 \text{ kJ}) - (-74.8 \text{ kJ}) - 4(0) \text{ kJ} = -1679.5 \text{ kJ}$$

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.

5.89 *Analyze/Plan.* Given population, Cal/person/day and kJ/mol glucose, calculate kg glucose/yr. Calculate kJ/yr, then kg/yr. 1 billion = 1×10^9 . 365 day = 1 yr. 1 Cal = 1 kcal, 4.184 kJ = 1 kcal = 1 Cal. *Solve.*

$$6.8 \times 10^9 \text{ persons} \times \frac{1500 \text{ Cal}}{\text{person} \cdot \text{day}} \times \frac{365 \text{ day}}{1 \text{ yr}} \times \frac{4.184 \text{ kJ}}{1 \text{ Cal}} = 1.5577 \times 10^{16} = 1.6 \times 10^{16} \text{ kJ/yr}$$

$$\frac{1.5577 \times 10^{16} \text{ kJ}}{\text{yr}} \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{2803 \text{ kJ}} \times \frac{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1.0 \times 10^{12} \text{ kg C}_6\text{H}_{12}\text{O}_6 / \text{yr}$$

Check. 1×10^{12} kg is 1 trillion kg of glucose.

5.90 (a) Use density to change L to g, molar mass to change g to mol, heat of combustion to change mol to kJ. Ethanol is $\text{C}_2\text{H}_5\text{OH}$, gasoline is C_8H_{18} . From Exercise 5.79 (c), heat of combustion of ethanol is -1234.8 kJ/mol .

$$1.0 \text{ L C}_2\text{H}_5\text{OH} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.79 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g}} \times \frac{1234.8 \text{ kJ}}{1 \text{ mol C}_2\text{H}_5\text{OH}} \\ = 21,174 = 2.1 \times 10^4 \text{ kJ/L C}_2\text{H}_5\text{OH}$$

$$1.0 \text{ L C}_8\text{H}_{18} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.70 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.23 \text{ g C}_8\text{H}_{18}} \times \frac{5400 \text{ kJ}}{1 \text{ mol C}_8\text{H}_{18}}$$

$$= 33,091 = 3.3 \times 10^4 \text{ kJ/L C}_8\text{H}_{18}$$

- (b) If density and heat of combustion of E85 are weighted averages of the values for the pure substances, then energy per liter E85 is also a weighted average of energy per liter for the two substances.

$$\text{kJ/L E85} = 0.15(\text{kJ/L C}_8\text{H}_{18}) + 0.85(\text{kJ/L C}_2\text{H}_5\text{OH})$$

$$\text{kJ/L E85} = 0.15(33,091 \text{ kJ}) + 0.85(21,174 \text{ kJ}) = 22,962 = 2.3 \times 10^4 \text{ kJ/L E85}$$

- (c) Whether comparing gal of L, all conversion factors for the two fuels cancel, so we can apply the energy ratio directly to the volume under consideration.

The energy ratio for E85 to gasoline is $(22,962/33,091) = 0.6939 = 0.69$

$$10 \text{ gal gas} \times \frac{\text{kJ from E85}}{0.6939 \text{ kJ from gas}} = 14.41 = 14 \text{ gal E85}$$

- (d) If the E85/gasoline energy ratio is 0.69, the the cost ratio must be 0.70 or less in order to "break-even" on price. $0.69(\$3.10) = \$2.14/\text{gal E85}$

Check. $10 \text{ gal gas}(\$3.10/\text{gal}) = \31 ; $14.4 \text{ gal E85}(\$2.14/\text{gal}) = \31

Additional Exercises

- 5.91 (a) mi/hr \rightarrow m/s

$$1050 \frac{\text{mi}}{\text{hr}} \times \frac{1.6093 \text{ km}}{1 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ hr}}{3600 \text{ s}} = 469.38 = 469.4 \text{ m/s}$$

- (b) Find the mass of one N_2 molecule in kg.

$$\frac{28.0134 \text{ g N}_2}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 4.6518 \times 10^{-26}$$

$$= 4.652 \times 10^{-26} \text{ kg}$$

$$E_k = 1/2 mv^2 = 1/2 \times 4.6518 \times 10^{-26} \text{ kg} \times (469.38 \text{ m/s})^2$$

$$= 5.1244 \times 10^{-21} \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = 5.124 \times 10^{-21} \text{ J}$$

- (c) $\frac{5.1244 \times 10^{-21} \text{ J}}{\text{molecule}} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = 3086 \text{ J/mol} = 3.086 \text{ kJ/mol}$

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

(b) $E_k = 1/2 mv^2$; $v = (2E_k/m)^{1/2} = \left(\frac{2 \times 5509.3 \text{ kg} \cdot \text{m}^2/\text{s}^2}{52.0 \text{ kg}} \right)^{1/2} = 14.6 \text{ m/s}$

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

- 5.93 Like the combustion of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ described in Section 5.4, the reaction that inflates airbags is spontaneous after initiation. Spontaneous reactions are usually exothermic, $-\Delta H$. The airbag reaction occurs at constant atmospheric pressure, $\Delta H = q_p$;

both are likely to be large and negative. When the bag inflates, work is done by the system on the surroundings, so the sign of w is negative.

5.94 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.

5.95 (a) It is not surprising that the gas expands when the valve is opened. Gases expand to fill their containers, regardless of other contents. (Nature abhors a vacuum).

(b) No work is done when the gas expands, because the evacuated flask is truly empty. There is no surrounding substance to be "pushed back".

(c) $\Delta E = q + w$. From part (b), no work is done when the gas expands. The flasks are perfectly insulated, so no heat flows. $\Delta E = 0 + 0 = 0$. The answer is a bit surprising, since a definite change occurred that required no work or heat transfer and consequently involved no energy change.

5.96 (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.

Two interpretations of the final state in (b) are possible. If the final state in (b) is identical to the final state in (a), $\Delta E(a) = \Delta E(b)$. If the final volumes are identical, case (b) requires either more (non-PV) work or heat input 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.)

Alternatively, if w is identical in the two cases and q is negative for case (b), then $\Delta E(b) < \Delta E(a)$. Assuming identical final volumes, the final temperature and pressure in (b) are slightly lower than those values in (a).

5.97 $\Delta E = q + w = +38.95 \text{ kJ} - 2.47 \text{ kJ} = +36.48 \text{ kJ}$

$\Delta H = q_p = +38.95 \text{ kJ}$

5.98 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.

5.99 Find the heat capacity of $1.7 \times 10^3 \text{ gal H}_2\text{O}$.

$$C_{\text{H}_2\text{O}} = 1.7 \times 10^3 \text{ gal H}_2\text{O} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{1 \text{ L}}{1.057 \text{ qt}} \times \frac{1 \times 10^3 \text{ cm}^3}{1 \text{ L}} \times \frac{1 \text{ g}}{1 \text{ cm}^3} \times \frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}}$$

$$= 2.692 \times 10^7 \text{ J}/^\circ\text{C} = 2.7 \times 10^4 \text{ kJ}/^\circ\text{C}; \text{ then,}$$

$$\frac{2.692 \times 10^7 \text{ J}}{1^\circ\text{C}} \times \frac{1 \text{ g} \cdot ^\circ\text{C}}{0.85 \text{ J}} \times \frac{1 \text{ kg}}{1 \times 10^3 \text{ g}} \times \frac{1 \text{ brick}}{1.8 \text{ kg}} = 1.8 \times 10^4 \text{ or } 18,000 \text{ bricks}$$

Check. $(1.7 \times 16 \times 10^6) / (1.6 \times 10^3) \approx 17 \times 10^3 \text{ bricks}$; the units are correct.

$$5.100 \quad (a) \quad q_{\text{Cu}} = \frac{0.385 \text{ J}}{\text{g} \cdot \text{K}} \times 121.0 \text{ g Cu} \times (30.1^\circ\text{C} - 100.4^\circ\text{C}) = -3274.9 = -3.27 \times 10^3 \text{ J}$$

The negative sign indicates the $3.27 \times 10^3 \text{ J}$ are lost by the Cu block.

$$(b) \quad q_{\text{H}_2\text{O}} = \frac{4.184 \text{ J}}{\text{g} \cdot \text{K}} \times 150.0 \text{ g H}_2\text{O} \times (30.1^\circ\text{C} - 25.1^\circ\text{C}) = 3138 = 3.1 \times 10^3 \text{ J}$$

The positive sign indicates that $3.14 \times 10^3 \text{ J}$ are gained by the H_2O .

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

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

Since $q_{\text{H}_2\text{O}}$ 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,

$$C_{\text{calorimeter}} = \frac{0.2 \times 10^3 \text{ J}}{5.0^\circ\text{C}} = 4 \times 10^1 \text{ J/K.}$$

$$(d) \quad q_{\text{H}_2\text{O}} = 3.275 \times 10^3 \text{ J} = \frac{4.184 \text{ J}}{\text{g} \cdot \text{K}} \times 150.0 \text{ g} \times (\Delta T)$$

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

- 5.101 (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.



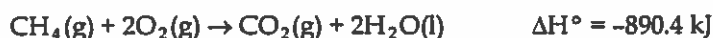
$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Delta H_f^\circ \text{Mg(OH)}_2\text{(s)} + \Delta H_f^\circ \text{H}_2\text{(g)} - 2\Delta H_f^\circ \text{H}_2\text{O(l)} - \Delta H_f^\circ \text{Mg(s)} \\ &= -924.7 \text{ kJ} + 0 - 2(-285.83 \text{ kJ}) - 0 = -353.04 = -353.0 \text{ kJ} \end{aligned}$$

- (b) Use the specific heat of water, $4.184 \text{ J/g}\cdot^\circ\text{C}$, to calculate the energy required to heat the water. Use the density of water at 25°C to calculate the mass of H_2O to be heated. (The change in density of H_2O going from 21°C to 79°C does not substantially affect the strategy of the exercise.) Then use the 'heat stoichiometry' in (a) to calculate mass of Mg(s) needed.

$$75 \text{ mL} \times \frac{0.997 \text{ g H}_2\text{O}}{\text{mL}} \times \frac{4.184 \text{ J}}{\text{g}\cdot^\circ\text{C}} \times 58^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 18.146 \text{ kJ} = 18 \text{ kJ required}$$

$$18.146 \text{ kJ} \times \frac{1 \text{ mol Mg}}{353.04 \text{ kJ}} \times \frac{24.305 \text{ g Mg}}{1 \text{ mol Mg}} = 1.249 \text{ g} = 1.2 \text{ g Mg needed}$$

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



- (b) $\Delta\text{H}_{\text{rxn}}^\circ = \Delta\text{H}_f^\circ \text{C}(\text{s}) + 2\Delta\text{H}_f^\circ \text{H}_2\text{O}(\text{l}) - \Delta\text{H}_f^\circ \text{CH}_4(\text{g}) - \Delta\text{H}_f^\circ \text{O}_2(\text{g})$

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

$$\Delta\text{H}_{\text{rxn}}^\circ = \Delta\text{H}_f^\circ \text{CO}(\text{g}) + 2\Delta\text{H}_f^\circ \text{H}_2\text{O}(\text{l}) - \Delta\text{H}_f^\circ \text{CH}_4(\text{g}) - 3/2 \Delta\text{H}_f^\circ \text{O}_2(\text{g})$$

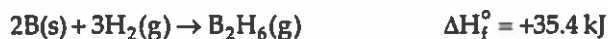
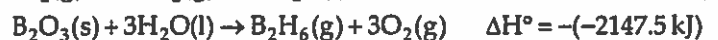
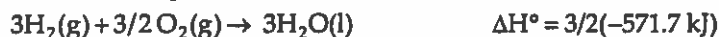
$$= (-110.5 \text{ kJ}) + 2(-285.83 \text{ kJ}) - (-74.8 \text{ kJ}) - 3/2(0) = -607.4 \text{ kJ}$$

$$\Delta\text{H}_{\text{rxn}}^\circ = \Delta\text{H}_f^\circ \text{CO}_2(\text{g}) + 2\Delta\text{H}_f^\circ \text{H}_2\text{O}(\text{l}) - \Delta\text{H}_f^\circ \text{CH}_4(\text{g}) - 2\Delta\text{H}_f^\circ \text{O}_2(\text{g})$$

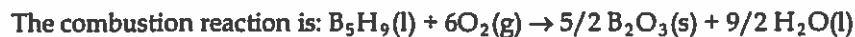
$$= -393.5 \text{ kJ} + 2(-285.83 \text{ kJ}) - (-74.8 \text{ kJ}) - 2(0) = -890.4 \text{ kJ}$$

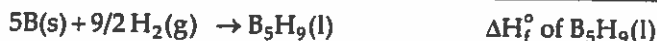
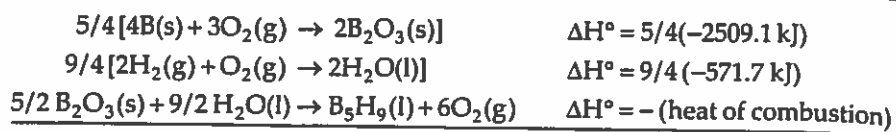
- (c) Assuming that $\text{O}_2(\text{g})$ is present in excess, the reaction that produces $\text{CO}_2(\text{g})$ represents the most negative ΔH per mole of CH_4 burned. More of the potential energy of the reactants is released as heat during the reaction to give products of lower potential energy. The reaction that produces $\text{CO}_2(\text{g})$ is the most "downhill" in enthalpy.

- 5.104 (a) $2\text{B}(\text{s}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta\text{H}^\circ = 1/2(-2509.1 \text{ kJ})$



- (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 .





$$\Delta H_f^\circ \text{ B}_5\text{H}_9(\text{l}) = -[\text{heat of combustion of B}_5\text{H}_9(\text{l})] - 3136.4 \text{ kJ} - 1286 \text{ kJ}$$

We need to measure the heat of combustion of $\text{B}_5\text{H}_9(\text{l})$.

5.105 For nitroethane:

$$\frac{1368 \text{ kJ}}{1 \text{ mol C}_2\text{H}_5\text{NO}_2} \times \frac{1 \text{ mol C}_2\text{H}_5\text{NO}_2}{75.072 \text{ g C}_2\text{H}_5\text{NO}_2} \times \frac{1.052 \text{ g C}_2\text{H}_5\text{NO}_2}{1 \text{ cm}^3} = 19.17 \text{ kJ/cm}^3$$

For ethanol:

$$\frac{1367 \text{ kJ}}{1 \text{ mol C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.069 \text{ g C}_2\text{H}_5\text{OH}} \times \frac{0.789 \text{ g C}_2\text{H}_5\text{OH}}{1 \text{ cm}^3} = 23.4 \text{ kJ/cm}^3$$

For methylhydrazine:

$$\frac{1307 \text{ kJ}}{1 \text{ mol CH}_6\text{N}_2} \times \frac{1 \text{ mol CH}_6\text{N}_2}{46.072 \text{ g CH}_6\text{N}_2} \times \frac{0.874 \text{ g CH}_6\text{N}_2}{1 \text{ cm}^3} = 24.8 \text{ kJ/cm}^3$$

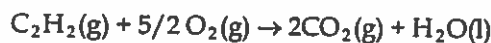
Thus, methylhydrazine would provide the most energy per unit volume, with ethanol a close second.

5.106 (a) $3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ \text{ C}_6\text{H}_6(\text{l}) - 3\Delta H_f^\circ \text{ C}_2\text{H}_2(\text{g}) = 49.0 \text{ kJ} - 3(226.77 \text{ kJ}) = -631.31 = -631.3 \text{ kJ}$$

(b) Since the reaction is exothermic (ΔH is negative), the reactant, 3 moles of $\text{C}_2\text{H}_2(\text{g})$, has more enthalpy than the product, 1 mole of $\text{C}_6\text{H}_6(\text{l})$.

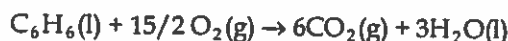
(c) The fuel value of a substance is the amount of heat (kJ) produced when 1 gram of the substance is burned. Calculate the molar heat of combustion (kJ/mol) and use this to find kJ/g of fuel.



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

$$= 2(-393.5 \text{ kJ}) + (-285.83 \text{ kJ}) - 226.77 \text{ kJ} - 5/2(0) = -1299.6 \text{ kJ/mol C}_2\text{H}_2$$

$$\frac{-1299.6 \text{ kJ}}{1 \text{ mol C}_2\text{H}_2} \times \frac{1 \text{ mol C}_2\text{H}_2}{26.036 \text{ g C}_2\text{H}_2} = 49.916 = 50 \text{ kJ/g C}_2\text{H}_2$$



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

$$= 6(-393.5 \text{ kJ}) + 3(-285.83 \text{ kJ}) - 49.0 \text{ kJ} - 15/2(0) = -3267.5 \text{ kJ/mol C}_6\text{H}_6$$

$$\frac{-3267.5 \text{ kJ}}{1 \text{ mol C}_6\text{H}_6} \times \frac{1 \text{ mol C}_6\text{H}_6}{78.114 \text{ g C}_6\text{H}_6} = 41.830 = 42 \text{ kJ/g C}_6\text{H}_6$$

5.107 The reaction for which we want ΔH is:



Before we can calculate ΔH for this reaction, we must calculate ΔH_f for $\text{NH}_3(\text{l})$.

We know that ΔH_f for $\text{NH}_3(\text{g})$ is -46.2 kJ/mol , and that for $\text{NH}_3(\text{l}) \rightarrow \text{NH}_3(\text{g})$, $\Delta H = 23.2 \text{ kJ/mol}$

Thus, $\Delta H_{\text{vap}} = \Delta H_f \text{ NH}_3(\text{g}) - \Delta H_f \text{ NH}_3(\text{l})$.

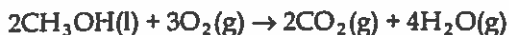
$$23.2 \text{ kJ} = -46.2 \text{ kJ} - \Delta H_f \text{ NH}_3(\text{l}); \Delta H_f \text{ NH}_3(\text{l}) = -69.4 \text{ kJ/mol}$$

Then for the overall reaction, the enthalpy change is:

$$\begin{aligned} \Delta H_{\text{rxn}} &= 6\Delta H_f \text{ H}_2\text{O}(\text{g}) + 2\Delta H_f \text{ N}_2(\text{g}) - 4\Delta H_f \text{ NH}_3(\text{l}) - 3\Delta H_f \text{ O}_2 \\ &= 6(-241.82 \text{ kJ}) + 2(0) - 4(-69.4 \text{ kJ}) - 3(0) = -1173.3 \text{ kJ} \end{aligned}$$

$$\frac{-1173.3 \text{ kJ}}{4 \text{ mol NH}_3} \times \frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} = \frac{0.81 \text{ g NH}_3}{1 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} = \frac{-1.4 \times 10^4 \text{ kJ}}{\text{L NH}_3}$$

(This result has two significant figures because the density is expressed to two figures.)

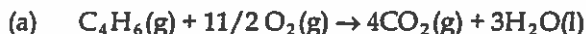


$$\Delta H = 2(-393.5 \text{ kJ}) + 4(-241.82 \text{ kJ}) - 2(-239 \text{ kJ}) - 3(0) = -1276 \text{ kJ}$$

$$\frac{-1276 \text{ kJ}}{2 \text{ mol CH}_3\text{OH}} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \times \frac{0.792 \text{ g CH}_3\text{OH}}{1 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} = \frac{-1.58 \times 10^4 \text{ kJ}}{\text{L CH}_3\text{OH}}$$

In terms of heat obtained per unit volume of fuel, methanol is a slightly better fuel than liquid ammonia.

5.108 1,3-butadiene, C_4H_6 , MM = 54.092 g/mol

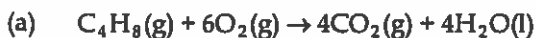


$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 4\Delta H_f^\circ \text{ CO}_2(\text{g}) + 3\Delta H_f^\circ \text{ H}_2\text{O}(\text{l}) - \Delta H_f^\circ \text{ C}_4\text{H}_6(\text{g}) - 11/2 \Delta H_f^\circ \text{ O}_2(\text{g}) \\ &= 4(-393.5 \text{ kJ}) + 3(-285.83 \text{ kJ}) - 111.9 \text{ kJ} + 11/2 (0) = -2543.4 \text{ kJ/mol C}_4\text{H}_6 \end{aligned}$$

(b) $\frac{-2543.4 \text{ kJ}}{1 \text{ mol C}_4\text{H}_6} \times \frac{1 \text{ mol C}_4\text{H}_6}{54.092 \text{ g}} = 47.020 \rightarrow 47 \text{ kJ/g}$

(c) $\% \text{ H} = \frac{6(1.008)}{54.092} \times 100 = 11.18\% \text{ H}$

1-butene, C_4H_8 , MM = 56.108 g/mol

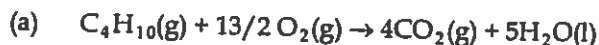


$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 4\Delta H_f^\circ \text{ CO}_2(\text{g}) + 4\Delta H_f^\circ \text{ H}_2\text{O}(\text{l}) - \Delta H_f^\circ \text{ C}_4\text{H}_8(\text{g}) - 6\Delta H_f^\circ \text{ O}_2(\text{g}) \\ &= 4(-393.5 \text{ kJ}) + 4(-285.83 \text{ kJ}) - 1.2 \text{ kJ} - 6(0) = -2718.5 \text{ kJ/mol C}_4\text{H}_8 \end{aligned}$$

(b) $\frac{-2718.5 \text{ kJ}}{1 \text{ mol C}_4\text{H}_8} \times \frac{1 \text{ mol C}_4\text{H}_8}{56.108 \text{ g C}_4\text{H}_8} = 48.451 \rightarrow 48 \text{ kJ/g}$

$$(c) \quad \% \text{H} = \frac{8(1.008)}{56.108} \times 100 = 14.37\% \text{H}$$

n-butane, $\text{C}_4\text{H}_{10}(\text{g})$, MM = 58.124 g/mol

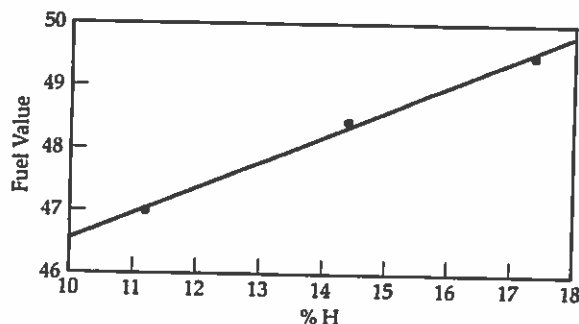


$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 4\Delta H_f^\circ \text{CO}_2(\text{g}) + 5\Delta H_f^\circ \text{H}_2\text{O}(\text{l}) - \Delta H_f^\circ \text{C}_4\text{H}_{10}(\text{g}) - 13/2 \Delta H_f^\circ \text{O}_2(\text{g}) \\ &= 4(-393.5 \text{ kJ}) + 5(-285.83 \text{ kJ}) - (-124.7 \text{ kJ}) - 13/2(0) \\ &= -2878.5 \text{ kJ/mol C}_4\text{H}_{10} \end{aligned}$$

$$(b) \quad \frac{-2878.5 \text{ kJ}}{1 \text{ mol C}_4\text{H}_{10}} \times \frac{1 \text{ mol C}_4\text{H}_{10}}{58.124 \text{ g C}_4\text{H}_{10}} = 49.523 \rightarrow 50 \text{ kJ/g}$$

$$(c) \quad \% \text{H} = \frac{10(1.008)}{58.124} \times 100 = 17.34\% \text{H}$$

- (d) It is certainly true that as the mass % H increases, the fuel value (kJ/g) of the hydrocarbon increases, given the same number of C atoms. A graph of the data in parts (b) and (c) (see below) suggests that mass % H and fuel value are directly proportional when the number of C atoms is constant.



5.109 $\Delta E_p = m g d$. Be careful with units. $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$

$$\begin{aligned} 200 \text{ lb} \times \frac{1 \text{ kg}}{2.205 \text{ lb}} \times \frac{9.81 \text{ m}}{\text{s}^2} \times \frac{45 \text{ ft}}{\text{time}} \times \frac{1 \text{ yd}}{3 \text{ ft}} \times \frac{1 \text{ m}}{1.0936 \text{ yd}} \times 20 \text{ times} \\ = 2.441 \times 10^5 \text{ kg} \cdot \text{m}^2/\text{s}^2 = 2.441 \times 10^5 \text{ J} = 2.4 \times 10^2 \text{ kJ} \end{aligned}$$

$$1 \text{ Cal} = 1 \text{ kcal} = 4.184 \text{ kJ}$$

$$2.441 \times 10^2 \text{ kJ} \times \frac{1 \text{ Cal}}{4.184 \text{ kJ}} = 58.34 = 58 \text{ Cal}$$

No, if all work is used to increase the man's potential energy, 20 rounds of stair-climbing will not compensate for one extra order of 245 Cal fries. In fact, more than 58 Cal of work will be required to climb the stairs, because some energy is required to move limbs and some energy will be lost as heat (see Solution 5.96).

- 5.110 *Plan.* Use dimensional analysis to calculate the amount of solar energy supplied per m^2 in 1 hr. Use stoichiometry to calculate the amount of plant energy used to produce sucrose per m^2 in 1 hr. Calculate the ratio of energy for sucrose to total solar energy, per m^2 per hr.

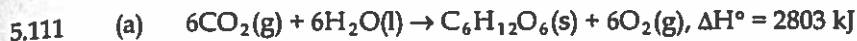
Solve. $1 \text{ W} = 1 \text{ J/s}$, $1 \text{ kW} = 1 \text{ kJ/s}$

$$\frac{1.0 \text{ kW}}{\text{m}^2} = \frac{1.0 \text{ kJ/s}}{\text{m}^2} = \frac{1.0 \text{ kJ}}{\text{m}^2 \cdot \text{s}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ hr}} = \frac{3.6 \times 10^3 \text{ kJ}}{\text{m}^2 \cdot \text{hr}}$$

$$\frac{5645 \text{ kJ}}{\text{mol sucrose}} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}} \times \frac{0.20 \text{ g sucrose}}{\text{m}^2 \cdot \text{hr}} = 3.298 = 3.3 \text{ kJ/m}^2 \cdot \text{hr}$$

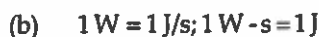
for sucrose production

$$\frac{3.298 \text{ kJ for sucrose}}{3.6 \times 10^3 \text{ kJ total solar}} \times 100 = 0.092\% \text{ sunlight used to produce sucrose}$$



This is the reverse of the combustion of glucose (Section 5.8 and Solution 5.89), so $\Delta H^\circ = -(-2803) \text{ kJ} = +2803 \text{ kJ}$.

$$\frac{5.5 \times 10^{16} \text{ g CO}_2}{\text{yr}} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{2803 \text{ kJ}}{6 \text{ mol CO}_2} = 5.838 \times 10^{17} = 5.8 \times 10^{17} \text{ kJ}$$



$$\frac{5.838 \times 10^{17} \text{ kJ}}{\text{yr}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1 \text{ yr}}{365 \text{ d}} \times \frac{1 \text{ d}}{24 \text{ hr}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ W} \cdot \text{s}}{\text{J}} \\ \times \frac{1 \text{ MW}}{1 \times 10^6 \text{ W}} = 1.851 \times 10^7 \text{ MW} = 1.9 \times 10^7 \text{ MW}$$

$$1.9 \times 10^7 \text{ MW} \times \frac{1 \text{ plant}}{10^3 \text{ MW}} = 1.9 \times 10^4 = 19,000 \text{ nuclear power plants}$$

Integrative Exercises

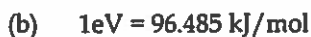


$$\Delta H^\circ = \Delta H_f^\circ \text{CO}_2(\text{g}) + 2\Delta H_f^\circ \text{H}_2\text{O}(\text{l}) - \Delta H_f^\circ \text{CH}_4(\text{g}) - 2\Delta H_f^\circ \text{O}_2(\text{g})$$

$$= -393.5 \text{ kJ} + 2(-285.83 \text{ kJ}) - (-74.8 \text{ kJ}) - 2(0) = -890.36 = -890.4 \text{ kJ/mol CH}_4$$

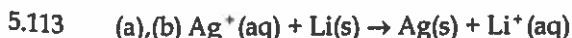
$$\frac{-890.36 \text{ kJ}}{\text{mol CH}_4} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules CH}_4} = 1.4785 \times 10^{-18}$$

$$= 1.479 \times 10^{-18} \text{ J/molecule}$$



$$8 \text{ keV} \times \frac{1000 \text{ eV}}{1 \text{ keV}} \times \frac{96.485 \text{ kJ}}{\text{eV} \cdot \text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} \times \frac{1000 \text{ J}}{\text{kJ}} = 1.282 \times 10^{-15} = 1 \times 10^{-15} \text{ J/X-ray}$$

The X-ray has approximately 1000 times more energy than is produced by the combustion of 1 molecule of $\text{CH}_4(\text{g})$.



$$\Delta H^\circ = \Delta H_f^\circ \text{Li}^+(\text{aq}) - \Delta H_f^\circ \text{Ag}^+(\text{aq})$$

$$= -278.5 \text{ kJ} - 105.90 \text{ kJ} = -384.4 \text{ kJ}$$