

5 Thermochemistry

Nature of Energy

5.1 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.

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

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

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

5.3 (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 g \rightarrow kg to obtain E_k in joules.

$$\text{Solve. } E_k = 1/2 mv^2 = 1/2 \times 45 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left(\frac{61 \text{ m}}{1 \text{ s}} \right)^2 = \frac{84 \text{ kg} \cdot \text{m}^2}{1 \text{ s}^2} = 84 \text{ J}$$

$$\text{Check. } 1/2(45 \times 3600/1000) \approx 1/2(40 \times 4) \approx 80 \text{ J}$$

(b) $83.72 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 20 \text{ cal}$

(c) As the ball hits the sand, its speed (and hence its kinetic energy) drops to zero. Most of the kinetic energy is transferred to the sand, which deforms when the ball lands. Some energy is released as heat through friction between the ball and the sand.

5.4 (a) *Plan.* Convert lb \rightarrow kg, mi/hr \rightarrow m/s.

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

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

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

- (b) E_k is proportional to v^2 , so if speed decreases by a factor of 2, kinetic energy decreases by a factor of 4.
- (c) Brakes stop a moving vehicle, so the kinetic energy of the motorcycle is primarily transferred to friction between brakes and wheels, and somewhat to deformation of the tire and friction between the tire and road.

5.5 *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.

$$100^\circ\text{C} = 180^\circ\text{F}; \quad 5^\circ\text{C} = 9^\circ\text{F}$$

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

5.6 *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

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

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

5.7 *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.



5.8 The energy source of a 100 watt light bulb is electrical current from household wiring. Current passes through and heats a tungsten filament (thin wire) in the bulb. The energy is radiated in the form of heat and visible light.

The energy source for an adult person is food. When a person eats, the food undergoes a complex series of chemical reactions that release the potential energy stored in chemical bonds. Some of this energy is transferred as electrical impulses that trigger muscle action and become kinetic energy. Some is released as heat.

In both cases, the energy must travel through a network (house wiring and lamp or human body) and undergo several changes in form before it is in the correct location and form to accomplish the desired task. In both cases, the energy given off as heat is wasted; it cannot be applied to the tasks of producing light or motion.

5.9

5.10

5.11



(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 heat but not mass with its surroundings.

5.12



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

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

5.13



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

(b)

5.14



(a) If energy is the capacity to do work or transfer heat, then heat is energy because it can do work. For example, heat causes a gas to expand inside a cylinder and move a piston, doing work.

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

5.15



(a) Gravity; work is done because the force of gravity is opposed and the pencil is lifted.

5.15 (b) Mechanical force; work is done because the force of the coiled spring is opposed as the spring is compressed over a distance.

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

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

The First Law of Thermodynamics

5.17 (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 system 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).

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

(b) In applying the first law, we need only to measure changes in internal energy, not absolute values of E . This is because doing work or transferring heat involves changes in energy, not absolute values. This is convenient, since it is almost impossible to measure the internal energy of a system because it has so many components.

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

5.19 *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

(a) q is negative because the system loses heat and w is negative because the system does work. $\Delta E = -113 \text{ kJ} - 39 \text{ kJ} = -152 \text{ kJ}$. The process is exothermic.

(b) $\Delta E = +1.62 \text{ kJ} - 847 \text{ J} = +1.62 \text{ kJ} - 0.847 \text{ kJ} = +0.773 \text{ kJ} \approx +0.77 \text{ kJ}$. The process is endothermic.

(c) q is positive because the system gains heat and w is negative because the system does work. $\Delta E = +77.5 \text{ kJ} - 63.5 \text{ kJ} = +14.0 \text{ kJ}$. The process is endothermic.

5.20

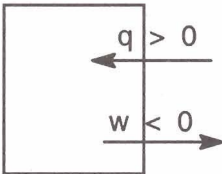


(a) $\Delta E = +3140 \text{ J}$. The process is endothermic.

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

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

- 5.21 (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 greater than the magnitude of the heat entering the system. $\Delta E < 0$ for system (iii) only.
- (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. $\Delta E > 0$ for systems (i) and (ii).

- 5.22 (a)  (b) ΔE will be positive for this process if the magnitude of w is greater than the magnitude of q .
- (c) ΔE will be negative for this process if the magnitude of q is greater than the magnitude of w .

- 5.23 *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), $w \approx 0$ and $q \approx 100 \text{ J}$. 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.

- 5.24  $E_{\text{el}} = \frac{kQ_1Q_2}{r^2}$ 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.

5.25 (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; work is not a state function.
- (c) Temperature is a state function; regardless of how hot or cold the sample has been, the temperature depends only on its present condition.

- 5.26 (a) Independent. Potential energy is a state function.
- (b) Dependent. Some of the energy released could be employed in performing work, as is done in the body when sugar is metabolized; heat is not a state function.
- (c) Dependent. The work accomplished depends on whether the gasoline is used in an engine, burned in an open flame, or in some other manner. Work is not a state function.

Enthalpy


5.27 (a) For the many laboratory and real world processes that occur at constant atmospheric pressure, the enthalpy change is a meaningful measure of the energy change associated with the process. At constant pressure, most of the energy change is transferred as heat ($\Delta H = q_p$), even if gases are involved in the process.



- (b) Only under conditions of constant pressure is ΔH for a process equal to the heat transferred during the process.
- (c) If ΔH is negative, the enthalpy of the system decreases and the process is exothermic.

5.28



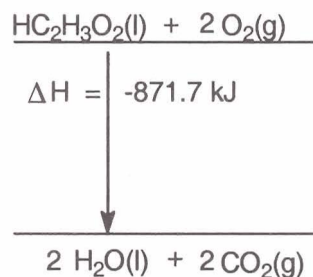
- (a) 
- (b) State functions are particularly useful because they are totally defined by the current conditions (state) of the system, not the history of how the system arrived at its current state. Changes to state functions, like ΔH can be calculated from knowledge of initial and final states, without details of how the change takes place.
- (c) $\Delta H = q_p$. If the system absorbs heat, q and ΔH are positive and the enthalpy of the system increases.



$$\Delta H = -871.7 \text{ kJ}$$

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

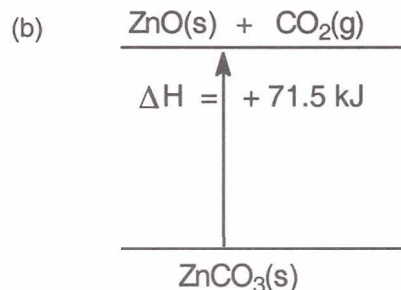
Plan. The substances (reactants or products, collectively) with higher enthalpy are shown on the upper level, and those with lower enthalpy are shown on the lower level.



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 .



$$\Delta H = 71.5 \text{ kJ}$$



- 5.31 *Plan.* Consider the sign of ΔH . *Solve:*

Since ΔH is negative, the reactants, $2\text{Cl}(\text{g})$ have the higher enthalpy.

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

- (a) $\text{H}_2\text{O}(\text{g})$ has the higher enthalpy.

- (b) $\text{H}_2 \rightarrow 2\text{H}$. Breaking the H–H bond requires energy, so the process is endothermic, $+\Delta H$. 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, $+\Delta H$. 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 $+\Delta H$. $\text{N}_2(\text{g})$ at 300° has the higher enthalpy.

- 5.33 *Analyze/Plan.* Follow the strategy in Sample Exercise 5.5. *Solve:*

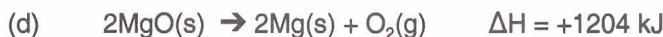


- (a) Exothermic (ΔH is negative)

$$(b) \quad 2.4 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.305 \text{ g Mg}} \times \frac{-1204 \text{ kJ}}{2 \text{ mol Mg}} = -59 \text{ kJ heat transferred}$$

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

$$(c) \quad -96.0 \text{ kJ} \times \frac{2 \text{ mol MgO}}{-1204 \text{ kJ}} \times \frac{40.30 \text{ g MgO}}{1 \text{ mol Mg}} = 6.43 \text{ g MgO produced}$$



$$7.50 \text{ g MgO} \times \frac{1 \text{ mol MgO}}{40.30 \text{ g MgO}} \times \frac{1204 \text{ kJ}}{2 \text{ mol MgO}} = +112 \text{ kJ heat absorbed}$$

Check. The units are correct for energy. $(\sim 9000/80) \approx 110 \text{ kJ}$

5.34



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

$$(b) \quad 1.60 \text{ kg CH}_3\text{OH} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \times \frac{90.7 \text{ kJ}}{1 \text{ mol CH}_3\text{OH}} = +4.53 \times 10^3 \text{ kJ heat transferred (absorbed)}$$

$$(c) \quad 64.7 \text{ kJ} \times \frac{2 \text{ mol H}_2}{90.7 \text{ kJ}} \times \frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} = 2.88 \text{ g H}_2 \text{ produced}$$

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

$$32.0 \text{ g CO} \times \frac{1 \text{ mol CO}}{28.01 \text{ g CO}} \times \frac{-90.7 \text{ kJ}}{1 \text{ mol CO}} = -104 \text{ kJ heat transferred (evolved)}$$

5.35

$$(a) \quad 0.540 \text{ mol AgCl} \times \frac{-65.5 \text{ kJ}}{1 \text{ mol AgCl}} = -35.4 \text{ kJ}$$

Check. Units are correct; sign indicates heat evolved.

$$(b) \quad 1.66 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.3 \text{ g AgCl}} \times \frac{-65.5 \text{ kJ}}{1 \text{ mol AgCl}} = -0.759 \text{ kJ}$$

Check. Units correct; sign indicates heat evolved.

$$(c) \quad 0.188 \text{ mmol AgCl} \times \frac{1 \times 10^{-3} \text{ mol}}{1 \text{ mmol}} \times \frac{+65.5 \text{ kJ}}{1 \text{ mol AgCl}} = +0.0123 \text{ kJ} = +12.3 \text{ J}$$

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

5.36

$$(a) \quad 4.34 \text{ mol O}_2 \times \frac{-89.4 \text{ kJ}}{3 \text{ mol O}_2} = -129.33 = -129 \text{ kJ}$$

$$(b) \quad 200.8 \text{ g KCl} \times \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} \times \frac{-89.4 \text{ kJ}}{2 \text{ mol KCl}} = -120.40 = -120 \text{ kJ}$$

- (c) Since the sign of ΔH is reversed for the reverse reaction, it seems reasonable that other characteristics would be reversed, as well. If the forward reaction proceeds spontaneously, the reverse reaction is probably not spontaneous. Also, we know from experience that KCl(s) does not spontaneously react with atmospheric $\text{O}_2(\text{g})$, even at elevated temperature.

5.37 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 .

5.38 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 .

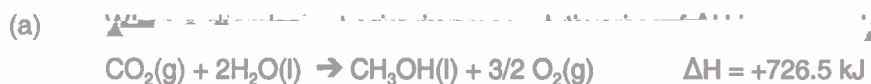
5.39 *Analyze/Plan.* $q = -89 \text{ kJ}$ (heat is given off by the system), $w = -36 \text{ kJ}$ (work is done by the system). *Solve:*

$$\Delta E = q + w = -89 \text{ kJ} - 36 \text{ kJ} = -125 \text{ kJ}. \quad \Delta H = q = -89 \text{ kJ} \text{ (at constant pressure).}$$

Check. The reaction is exothermic.

5.40 The gas is the system. If 518 J of heat is added, $q = +518 \text{ J}$. Work done by the system decreases the overall energy of the system, so $w = -127 \text{ J}$.

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

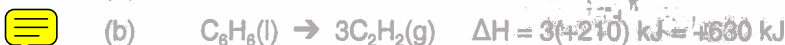


(b) Enthalpy is extensive. If the coefficients in the chemical equation are multiplied by 2 to obtain all integer coefficients, the enthalpy change is also multiplied by 2.

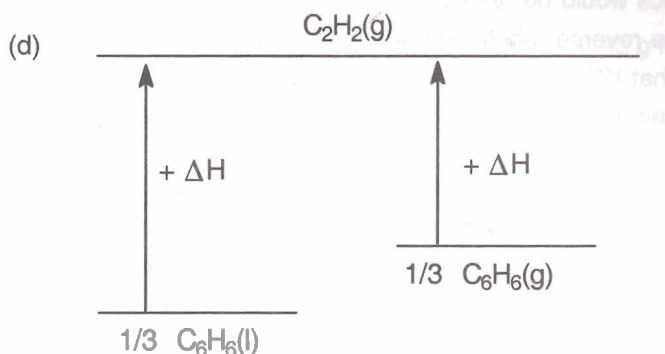


(c) The exothermic forward reaction is more likely to be thermodynamically favored.

(d) Vaporization (liquid \rightarrow gas) is endothermic. If the product were $\text{H}_2\text{O}(\text{g})$, 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.)



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



Calorimetry

5.43 (a) $\text{J}/^\circ\text{C}$ or J/K . Heat capacity is the amount of heat in J required to raise the temperature of an object or a certain amount of a substance 1°C or 1 K. Since the amount is defined, units of amount are not included.

(b) $\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}$ or $\frac{\text{J}}{\text{g} \cdot ^\circ\text{K}}$ Specific heat is a particular kind of heat capacity where the amount of substance is 1 g.

5.44 *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.

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

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

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

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 $\text{kJ/kg} \cdot ^\circ\text{C}$.

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

$$(b) \quad 8.42 \text{ mol H}_2\text{O} \times \frac{75.40 \text{ J}}{\text{mol} \cdot ^\circ\text{C}} = 635 \text{ J}/^\circ\text{C}$$

$$(c) \quad 2.56 \text{ kg H}_2\text{O} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{4.84 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times (92.0^\circ\text{C} - 44.8^\circ\text{C}) = 505.56 = 506 \text{ kJ}$$

$$1.42 \text{ kg Cu} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{0.385 \text{ J}}{\text{g} \cdot \text{K}} \times (88.5^\circ\text{C} - 25.0^\circ\text{C}) = 3.47 \times 10^4 \text{ J (or } 34.7 \text{ kJ)}$$

5.48 $62.0 \text{ g C}_7\text{H}_8 \times \frac{1.13 \text{ J}}{\text{g} \cdot \text{K}} \times (38.8^\circ\text{C} - 16.3^\circ\text{C}) = 1.58 \times 10^3 \text{ J}$

- 5.49 *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 NaOH(s) dissolving equals the heat gained by the solution.

Plan/Solve. Calculate the heat gained by the solution. The temperature change is $47.4 - 23.6 = 23.8^\circ\text{C}$. The total mass of solution is $(100.0 \text{ g H}_2\text{O} + 9.55 \text{ g NaOH}) = 109.55 = 109.6 \text{ g}$.

$$109.55 \text{ g solution} \times \frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} \times 23.8^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 10.909 = 10.9 \text{ kJ}$$

This is the amount of heat lost when 9.55 g of NaOH dissolves.

The heat loss per mole NaOH is

$$\frac{-10.909 \text{ kJ}}{9.55 \text{ g NaOH}} \times \frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}} = -45.7 \text{ kJ/mol} \quad \Delta H = q_p = -45.7 \text{ kJ/mol NaOH}$$

Check. $(-11/9 \times 40) \approx -45 \text{ kJ}$; the units and sign are correct.

- 5.50 Following the logic in Solution 5.49, the dissolving process is endothermic, ΔH is positive. The total mass of the solution is $(60.0 \text{ g H}_2\text{O} + 3.88 \text{ g NH}_4\text{NO}_3) = 63.88 = 63.9 \text{ g}$. The temperature change of the solution is $23.0 - 18.4 = 4.6^\circ\text{C}$. The heat lost by the water is

$$63.88 \text{ g H}_2\text{O} \times \frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} \times 4.6^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.229 = 1.2 \text{ kJ}$$

Thus, 1.2 kJ is absorbed when 3.88 g $\text{NH}_4\text{NO}_3(\text{s})$ dissolves.

$$\frac{+ 1.229 \text{ kJ}}{3.88 \text{ NH}_4\text{NO}_3} \times \frac{80.05 \text{ g NH}_4\text{NO}_3}{1 \text{ mol NH}_4\text{NO}_3} = +25.36 = +25 \text{ kJ/mol NH}_4\text{NO}_3$$

5.51



Analyze/Plan. Follow the logic in Sample Exercise 5.8. *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.

$$\Delta H_{\text{rxn}} \approx \Delta E_{\text{rxn}} = q_{\text{rxn}} = -q_{\text{bomb}} = \frac{-56.0 \text{ kJ}}{2.20 \text{ g C}_6\text{H}_4\text{O}_2} = -25.454 = -25.5 \text{ kJ/g C}_6\text{H}_4\text{O}_2$$

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

(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.

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

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

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

5.53

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 $\text{kJ}/^\circ\text{C}$. *Solve:*

(a) $C_{\text{total}} = 2.500 \text{ g glucose} \times \frac{15.57 \text{ kJ}}{1 \text{ g glucose}} \times \frac{1}{2.70^\circ\text{C}} = 14.42 = 14.4 \text{ kJ}/^\circ\text{C}$

(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,

$$5.000 \text{ g glucose} \times \frac{15.57 \text{ kJ}}{1 \text{ g glucose}} \times \frac{1^\circ\text{C}}{14.42 \text{ kJ}} = 5.40^\circ\text{C}$$

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.

5.54 (a) $C = 1.640 \text{ g HC}_7\text{H}_5\text{O}_2 \times \frac{26.38 \text{ kJ}}{1 \text{ g HC}_7\text{H}_5\text{O}_2} \times \frac{1}{4.95^\circ\text{C}} = 8.740 = 8.74 \text{ kJ/}^\circ\text{C}$

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

(c)

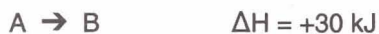
Hess's Law

5.55

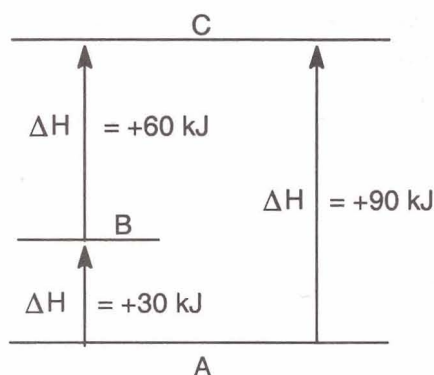


5.56 Hess's Law is a consequence of the fact that enthalpy is a state function. Since ΔH is independent of path, we can describe a process by any series of steps that add up to the overall process and ΔH for the process is the sum of the ΔH values for the steps.

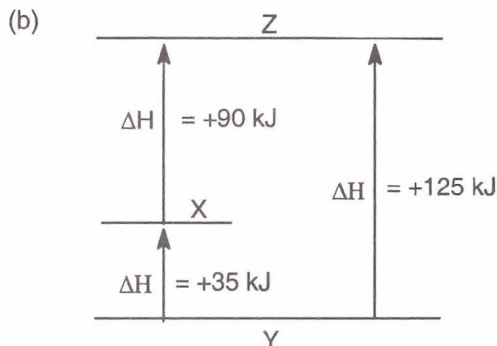
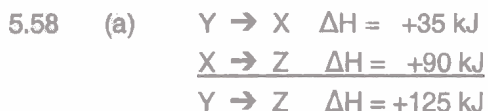
5.57 (a) *Analyze/Plan.* Arrange the reactions so that in the overall sum, B appears in both reactants and products and can be canceled. This is a general technique for using Hess's Law. *Solve:*



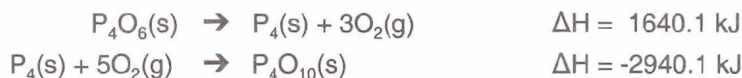
(b)



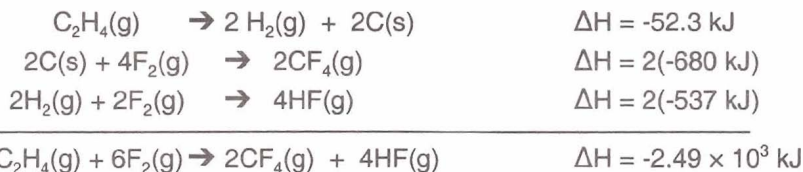
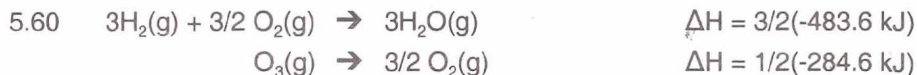
Check. The process of A forming C can be described as A forming B and B forming C.



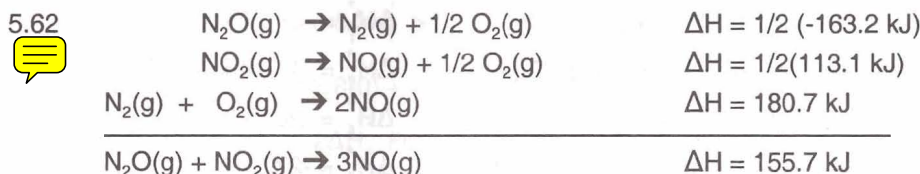
- (c) No. Any temperature change is accompanied by a change in heat. Comparing reactions and enthalpies of reaction at different temperatures doesn't take into account the change in heat to go from one temperature to the other.



Check. We have obtained the desired reaction.



Check. We have obtained the desired reaction.



Enthalpies of Formation

5.63 (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.

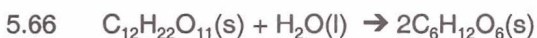
(c) Standard enthalpy of formation, ΔH_f° , is the enthalpy change that accompanies formation of one mole of a substance from elements in their standard states.

5.64 (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.

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

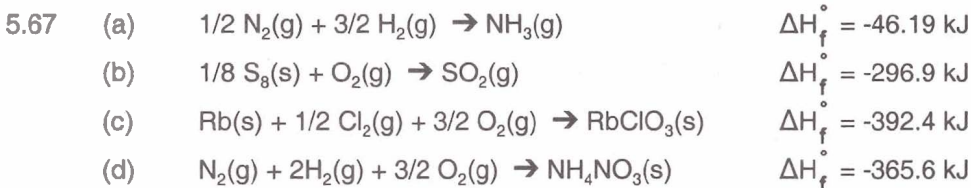
(b) The standard enthalpy of formation for any element in its standard state is zero. Elements in their standard states are the reference point for the enthalpy of formation scale.

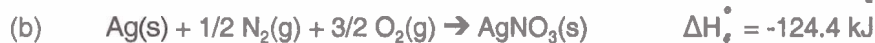
5.65 Yes, it would still be possible to have tables of standard enthalpies of formation like Table 5.3. Standard enthalpies of formation are the overall **enthalpy difference** between a compound and its component elements in their standard states. Regardless of the value of the enthalpy of formation of the elements, the magnitude of the difference in enthalpies should be the same (assuming the same reaction stoichiometry).



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 2\Delta H_f^\circ \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) - \Delta H_f^\circ \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) - \Delta H_f^\circ \text{H}_2\text{O}(\text{l}) \\ &= 2(-1273) - (-2221) - (-285.83) = -39 \text{ kJ} \end{aligned}$$

The reaction is slightly exothermic.





- 5.69 *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:*

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

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

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



$$\Delta H_{\text{rxn}}^\circ = 4\Delta H_f^\circ \text{CO}_2\text{(g)} + 5\Delta H_f^\circ \text{H}_2\text{O(l)} - \Delta H_f^\circ \text{C}_4\text{H}_{10}\text{(l)} - 13/2 \Delta H_f^\circ \text{O}_2\text{(g)}$$

$$\Delta H_{\text{rxn}}^\circ = 4(-393.5 \text{ kJ}) + 5(-285.83 \text{ kJ}) - (-147.6 \text{ kJ}) - 13/2(0) = -2855.6 = -2856 \text{ kJ/mol C}_4\text{H}_{10}$$

$$1.0 \text{ g C}_4\text{H}_{10} \times \frac{1 \text{ mol C}_4\text{H}_{10}}{58.123 \text{ g C}_4\text{H}_{10}} \times \frac{-2855.6 \text{ kJ}}{1 \text{ mol C}_4\text{H}_{10}} = -49 \text{ kJ}$$

- 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:*

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

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

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

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

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

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

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

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

- 5.72 (a) $\Delta H_{\text{rxn}}^\circ = 2\Delta H_f^\circ \text{H}_2\text{O(g)} + \Delta H_f^\circ \text{N}_2\text{(g)} - \Delta H_f^\circ \text{N}_2\text{O}_4\text{(g)} - \Delta H_f^\circ \text{H}_2\text{(g)}$

$$= 2(-241.82) + 0 - (9.66) - 0 = -493.30 \text{ kJ}$$

(b) $\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ \text{K}_2\text{CO}_3\text{(s)} + \Delta H_f^\circ \text{H}_2\text{O(g)} - 2\Delta H_f^\circ \text{KOH(s)} - \Delta H_f^\circ \text{CO}_2\text{(g)}$

$$= -1150.18 \text{ kJ} - 241.82 \text{ kJ} - 2(-424.7) \text{ kJ} - (-393.5 \text{ kJ}) = -149.1 \text{ kJ}$$

$$\begin{aligned}
 \text{(c)} \quad \Delta H_{\text{rxn}}^{\circ} &= 3/8\Delta H_{\text{f}}^{\circ} \text{S}_8(\text{s}) + 2\Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}(\text{g}) - \Delta H_{\text{f}}^{\circ} \text{SO}_2(\text{g}) - 2\Delta H_{\text{f}}^{\circ} \text{H}_2\text{S}(\text{g}) \\
 &= 3/8(0) + 2(-241.82) - (-269.9) - 2(-20.17) = -173.4 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \text{(d)} \quad \Delta H_{\text{rxn}}^{\circ} &= 2\Delta H_{\text{f}}^{\circ} \text{FeCl}_3(\text{s}) + 3\Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}(\text{g}) - \Delta H_{\text{f}}^{\circ} \text{Fe}_2\text{O}_3(\text{s}) - 6\Delta H_{\text{f}}^{\circ} \text{HCl}(\text{g}) \\
 &= 2(-400 \text{ kJ}) + 3(-241.82 \text{ kJ}) - (-822.16 \text{ kJ}) - 6(-92.30 \text{ kJ}) = -149.5 \text{ kJ}
 \end{aligned}$$

5.73



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:**

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

$$\Delta H_{\text{f}}^{\circ} \text{C}_3\text{H}_6\text{O}(\text{l}) = -248 \text{ kJ}$$

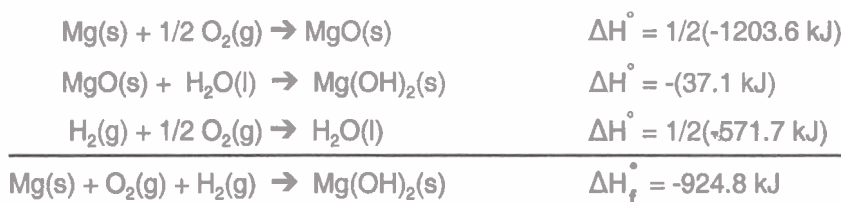
5.74

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ} \text{Ca}(\text{OH})_2(\text{s}) + \Delta H_{\text{f}}^{\circ} \text{C}_2\text{H}_2(\text{g}) - 2\Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_{\text{f}}^{\circ} \text{CaC}_2(\text{s})$$



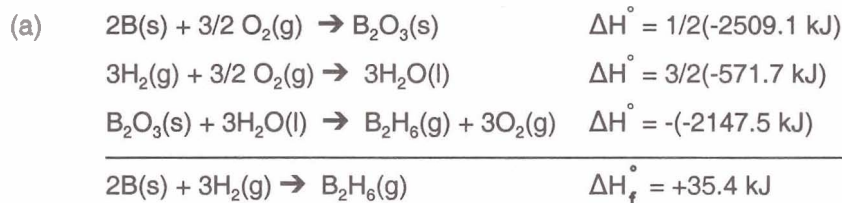
5.75

Plan. Use Hess's Law to arrange the given reactions so the overall sum is the formation reaction for $\text{Mg}(\text{OH})_2(\text{s})$. Adjust the corresponding ΔH values and calculate $\Delta H_{\text{f}}^{\circ}$ for $\text{Mg}(\text{OH})_2(\text{s})$. **Solve:**



Check. The overall reaction is correct.

5.76



(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 .