

**Figure 1** To stay safe, firefighters rely on insulated suits that protect them from thermal energy.

specific heat capacity (*c*) the quantity of thermal energy required to raise the temperature of 1 g of a substance by 1 °C; SI units J/(g∙°C)

# **5.2** Calorimetry and Enthalpy

Firefighters risk their lives every day when they enter burning buildings. To help reduce this risk, they wear suits that protect them from the high temperatures of fire (**Figure 1**). The temperature inside a protective suit remains in a range that allows the firefighter to continue working. The heat-resistant fibres used to construct these suits protect firefighters from high temperatures while still allowing them to move. Most protective clothing worn by firefighters is constructed with a fabric called Nomex. When Nomex is exposed to high temperatures, the fibres absorb thermal energy and swell, which prevents the firefighter᾽s skin from increasing in temperature and burning. Obviously, fibres such as the cotton in a T-shirt cannot absorb enough thermal energy to protect a person from fire. What chemical property describes the ability of a substance to absorb thermal energy? WEB LINK

# Heat Capacity

Have you ever dashed across hot beach sand so you could stand comfortably in the cool water? Both the water and the sand are heated by the same energy source the Sun—and yet the sand feels so much hotter. Both substances have been heated by the Sun for the same amount of time, so why is the temperature of the sand so much higher? This difference in temperature is caused by a difference in the specific heat capacity of water and sand. Specific heat capacity (*c*) is the quantity of thermal energy required to raise the temperature of 1 g of a substance by 1 °C. The SI units for specific heat capacity are J/g∙°C. It takes a lot of thermal energy to raise the temperature of a substance with a high specific heat capacity, such as water, but relatively little to raise the temperature of a substance with a low specific heat capacity, such as sand.

**Table 1** shows the specific heat capacities of some common substances. Note that water's specific heat capacity is more than five times that of sand. This means that the amount of thermal energy required to raise the temperature of water by 1 °C is five times the amount of thermal energy required to raise the temperature of sand. The high specific heat capacity of water is the reason the temperature of a lake remains cool well into the summer while the surrounding land is warm. Substances with a high specific heat capacity also take longer to cool. A lake, for example, remains warm into autumn, long after the land temperature has decreased. It will also remain cool in the spring longer than the surrounding land.

Table 1 Specific Heat Capacities of Some Common Substances



# Calorimetry and Thermal Energy Transfer

Heating water on a gas stove transfers thermal energy from the natural gas to the water. This energy transfer increases the kinetic energy of the water molecules, which makes them move faster. As a result, the average kinetic energy, or temperature, of the water increases. One way that scientists can study thermal energy transfers is by calorimetry. Calorimetry is the process of measuring energy changes during a physical or chemical change.

A calorimeter is a device used to measure energy changes during a physical or chemical change. The design of calorimeters varies (**Figure 2** shows three examples of calorimeters). In general, a calorimeter consists of a well-insulated reaction chamber, a tight-fitting cover with insulated holes for a thermometer, and some mechanism to stir the calorimeter contents. Using an insulated chamber minimizes energy losses to the surroundings. A tight lid prevents matter from leaving or entering the calorimeter. A simple calorimeter can be made from two nested polystyrene foam cups and a lid to hold a stirrer and thermometer, as shown in Figure 2(a). The inner cup is where the chemical system being studied (for example, a chemical reaction) is placed. The inner cup also holds a liquid, usually water. Any change in the thermal energy of the system is detected as a temperature change of the water. The outer cup provides additional insulation. If you have ever kept a hot or cold liquid in a foam cup for a long time, you know that thermal energy eventually escapes. That is why more elaborate calorimeters are used, such as the model in Figure 2(b), when precise measurements are required.

Reactions carried out in calorimeters like those in Figure 2(a) or 2(b) take place under constant pressure, since a small amount of gas will always escape. As a result, the volume of the contents will change, which keeps the pressure constant. Therefore, to study a physical or chemical change involving a gas or gases, chemists use a bomb calorimeter (Figure 2(c)). A bomb calorimeter is a very rigid, tightly sealed vessel that prevents almost all gas from escaping while maintaining a constant volume. If a physical or chemical change produces gas(es), the pressure in the bomb calorimeter will increase. If a change consumes gas(es), the pressure will decrease. A bomb calorimeter is particularly useful for studying the energy changes of combustion reactions, since one reactant is always oxygen gas and the products always include one or more gases.

calorimetry the experimental process of measuring the thermal energy change in a chemical or physical change

calorimeter a device that is used to measure thermal energy changes in a chemical or physical change



Figure 2 (a) A coffee-cup calorimeter can provide reasonably accurate data. (b) A laboratory calorimeter can provide precise data for changes of state or chemical reactions that do not involve gases. (c) A bomb calorimeter can provide precise data for changes of state or chemical reactions that involve gases.

# Calorimetry Calculations

For the investigations provided in this text, you will use a coffee-cup calorimeter. When analyzing data obtained using a coffee-cup calorimeter, make these assumptions:

- Any thermal energy transferred from the calorimeter to the outside environment is negligible.
- Any thermal energy absorbed by the calorimeter itself is negligible.
- All dilute, aqueous solutions have the same density  $(1.00 \text{ g/mL})$  and specific heat capacity  $(4.18 \text{ J/(g} \cdot {}^{\circ}C))$  as water.

These assumptions are valid only for physical or chemical changes that take place in water or a dilute aqueous solution.

In calorimetry, the total amount of thermal energy absorbed or released by a chemical system is given the symbol  $q$ . The magnitude of  $q$  depends on three factors:

- the mass of the substance
- the specific heat capacity of the substance
- the temperature change experienced by the substance as it warms or cools

The value of  $q$  is calculated using the equation

 $q = mc\Delta T$ 

where *m* is the mass of the substance, *c* is the specific heat capacity of the substance, and  $\Delta T$  is the change in temperature of that substance. The change in temperature is the difference between the final temperature,  $T_{\text{final}}$ , and the initial temperature,  $T_{\text{initial}}$ , which can be written as

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

The value of  $q$  has two parts: the magnitude of  $q$  tells you how much energy is involved, and the sign tells you the direction of energy transfer.

The transfer of energy from a system to the surroundings in a coffee-cup calorimeter is illustrated in **Figure 3**. The system is composed only of the components of the physical or chemical change that occurs. The water in a coffee-cup calorimeter is the surroundings, and all energy transfers are assumed to take place between the system and the water. The calorimeter itself is assumed not to be involved in these energy transfers. You can use the value of  $q$  for the surroundings (the water) to predict whether a change will be exothermic or endothermic.



**Figure 3** The chemical system undergoes either a physical change or a chemical change. Energy is either absorbed from, or released to, the surroundings (the water in the calorimeter). An increase in the temperature of the water indicates an exothermic reaction, whereas a decrease in the temperature of the water indicates an endothermic reaction.

If  $q$  has a negative value, the system transfers thermal energy to its surroundings and the change is exothermic. The temperature of the water (the surroundings) in the calorimeter increases. If  $q$  has a positive value, the system absorbs thermal energy from its surroundings and the change is endothermic. The temperature of the water in the calorimeter decreases.

Since energy cannot be destroyed, the total thermal energy of the system and its surroundings remains constant. Therefore, the sum of  $q_{\text{system}}$  plus  $q_{\text{surroundings}}$  should equal zero, since these symbols represent equal quantities but with opposite signs:

 $q_{\text{system}} + q_{\text{surroundings}} = 0$  or  $q_{\text{system}} = -q_{\text{surroundings}}$ 

# Tutorial 1 Calculations Involving Thermal Energy Transfer

In this tutorial, you will use calorimetry data to determine the quantity of thermal energy released or absorbed during a reaction when the specific heat capacity of a substance is known, and to determine the specific heat capacity of a substance.

### Sample Problem 1: Thermal Energy Transfer Involving a Metal in Water

A student places 50.0 mL of liquid water at 21.00 °C into a coffee-cup calorimeter. She places a sample of gold at 100.00 °C into the calorimeter. The final temperature of the water is 21.33 °C. The specific heat capacity of water is 4.18 J/g∙°C and the density of water, *d*, is 1.00 g/mL. Calculate the quantity of thermal energy, *q*, absorbed by the water in the calorimeter.

Given:  $V_{H_20(1)} = 50.0$  mL;  $c = 4.18$  J/(g⋅°C);  $d_{H_20(1)} = 1.00$  g/mL;  $T_{initial} = 21.00$  °C;

 $T_{\text{final}} = 21.33 \text{ °C}$ 

Required: quantity of thermal energy absorbed, *q*

**Analysis:**  $m = Vd$ ;  $\Delta T = T_{final} - T_{initial}$ ;  $q = mc\Delta T$ 

#### Solution:

Step 1. Determine the mass of water, *m*, in the calorimeter.

$$
m = Vd
$$
  
= 50.0 mE ×  $\frac{1.00 g}{1 mE}$   

$$
m = 50.0 g
$$

**Step 2.** Determine the change in temperature,  $\Delta T$ , of the water in the calorimeter.

$$
\Delta T = \Delta T_{\text{final}} - T_{\text{initial}}
$$
  
= 21.33 °C - 21.00 °C  

$$
\Delta T = 0.33 °C
$$

Step 3. Calculate the quantity of thermal energy, *q*, transferred to the water in the calorimeter.

$$
q = mc\Delta T
$$
  
= (50.0 g)  $\bigg(4.18 \frac{J}{g \cdot \mathcal{Q}}\bigg)(0.33 \cdot \mathcal{Q})$   

$$
q = 69 J
$$

Step 4. Check that the sign of *q* makes sense.

Since the temperature in the water increased, water absorbed energy. Therefore, *q* should be positive.

Statement: The quantity of thermal energy absorbed by the water was 69 J.

# Sample Problem 2: Determining Specific Heat Capacity of a Substance from Calorimetric Data

Using the value for *q* that you calculated in Sample Problem 1, calculate the specific heat capacity, *c*, of the sample of gold if its mass is 6.77 g. Assume that the final temperature of the gold sample was the same as the final temperature of the water in the calorimeter.

**Given:**  $m_{Au} = 6.77$  g;  $q = 69$  J;  $T_{initial} = 100.00$  °C;  $T_{final} = 21.33$  °C

Required: specific heat capacity of the gold sample, *c*

Analysis:  $\Delta T = T_{\text{final}} - T_{\text{initial}}$ ;  $q = mc\Delta T$ 

# Solution

**Step 1.** Determine the change in temperature,  $\Delta T$ , of the gold sample.

 $\Delta T = \Delta T_{\text{final}} - T_{\text{initial}}$  $= 21.33 °C - 100.00 °C$  $\Delta T = -78.67$  °C

Step 2. Determine if *q* should be positive or negative.

You know from Sample Problem 1 that 69 J of thermal energy was absorbed by the water (the surroundings). The quantity of thermal energy lost by the gold sample (the system) must be of the same magnitude but opposite in sign:

 $q = -69$  J

**Step 3.** Rearrange  $q = mc\Delta T$  to solve for *c*.

$$
q = mc\Delta T
$$
  
\n
$$
c = \frac{q}{m\Delta T}
$$
  
\n
$$
= \frac{-69 \text{ J}}{(6.77 \text{ g})(-78.67 \text{ °C})}
$$
  
\n
$$
c = 0.13 \text{ J/(g·°C)}
$$

**Statement:** The specific heat capacity of the sample of gold is 0.13 J/(g  $\cdot$  °C).

# Sample Problem 3: Calculating the Thermal Energy Transfer during a Neutralization Reaction

A 50.0 mL sample of a 1.0 mol/L aqueous solution of hydrochloric acid, HCl(aq), was mixed with 50.0 mL of a 1.0 mol/L aqueous solution of sodium hydroxide, NaOH(aq), at 25.0 °C in a calorimeter. After the solutions were mixed by stirring, the temperature was 31.9 °C. (a) Determine the quantity of thermal energy transferred by the reaction to the water, *q*, and state whether the reaction was endothermic or exothermic. Assume that the specific heat capacity and density of both solutions is the same as that of liquid water  $(c_{H_20(1)} = 4.18 \text{ J/(g·°C)}$  and  $d_{H_20(1)} = 1.00 \text{ g/mL})$ .

(b) State if the reaction is exothermic or endothermic.

**Given:**  $V_{\text{NaOH(aq)}} = 50.0 \text{ mL}$ ;  $V_{\text{HCl(aq)}} = 50.0 \text{ mL}$ ;

$$
d_{H_20(l)} = 1.00
$$
 g/mL;  $T_{initial} = 25.0$  °C;

 $T_{\text{final}} = 31.9 \text{ °C};$   $c_{H_20(l)} = 4.18 \text{ J/(g·°C)}$ 

Required: *q*

**Analysis:**  $m = Vd$ ;  $q = mc\Delta T$ ;  $m_{total} = m_{NaOH(aa)} + m_{HCl(aa)}$ ;  $\Delta T = T_{final} - T_{initial}$ 

#### **Solution**

Step 1. Determine the mass of the solution, *m*.

Since 50.0 mL of the first solution was combined with 50.0 mL of the second solution, the total volume in the calorimeter is 100.0 mL. Assuming these solutions have the same density as liquid water, then use the equation

$$
m = Vd
$$
  
= (100.0 mL)  $\left(1.00 \frac{g}{mL}\right)$ 

 $m = 100$  g

**Step 2.** Calculate the change in temperature,  $\Delta T$ .

$$
\Delta T = T_{\text{final}} - T_{\text{initial}}
$$
  
= 31.9 °C - 25.0 °C  

$$
\Delta T = 6.9 °C
$$

Step 3. Calculate the quantity of thermal energy absorbed by the water, *q*, and determine if the reaction is exothermic or endothermic.

$$
q = mc\Delta T
$$
  
= (100 g) $\left(4.18 \frac{J}{g \cdot 2C}\right)$ (6.9.32)  
= 2.9 × 10<sup>3</sup> J  

$$
q = 2.9 \text{ kJ}
$$

 Therefore, the thermal energy transferred by the reaction to the water is  $-2.9$  kJ. Since the value of *q* is negative, the reaction is exothermic.

**Statement:** The quantity of thermal energy transferred was  $-2.9$  kJ, and the reaction was exothermic.

# **Practice**

- 1. How much thermal energy is required to raise the temperature of 6.0 mL of water from 25 °C to 75 °C in a calorimeter or other closed system? TM [ans: 1.3 kJ]
- 2. Aqueous ethylene glycol is commonly used in car radiators as an antifreeze and coolant. A 50 % ethylene glycol solution in a radiator has a specific heat capacity, *c*, of 3.5 J/(g ⋅  $\degree$ C). If a 4.0 kg quantity of ethylene glycol absorbs 250 kJ of thermal energy, what was the temperature change, ∆*T*, of the solution? Assume the radiator is a closed system. The [ans: 18 °C]
- 3. When 50.0 mL of 1.0 mol/L hydrochloric acid is neutralized completely by 75.0 mL of 1.0 mol/L sodium hydroxide in a coffee-cup calorimeter, the temperature of the total solution changes from 20.2 °C to 25.6 °C. Determine the quantity of energy transferred, *q*, and state whether the reaction was endothermic or exothermic. The fans: 2800 J; exothermic]

# Mini **Investigation**

# Thermal Energy Transfer in a Coffee-Cup Calorimeter

**Skills:** Performing, Observing, Analyzing, Evaluating, Communicating

In this activity, you will place a heated piece of metal into water in a coffee-cup calorimeter. You will then calculate the quantity of thermal energy, *q*, that is transferred for both the system and the surroundings.

Equipment and Materials: balance; coffee-cup calorimeter; graduated cylinder; thermometer; 250 mL beaker; kettle; tongs; glass rod; sample of metal; hot water

- 1. Using the balance, determine and record the mass of your assigned metal.
- 2. Use the tongs to place your metal in a hot water bath for a minimum of 2 minutes.
- 3. Use the graduated cylinder to measure out 100 mL of tap water. Pour the measured tap water into the calorimeter.
- 4. Measure and record the initial temperature of the water in the calorimeter using the thermometer.
- 5. Use the thermometer to measure the temperature of the hot water in the hot water bath.

 6. Use the tongs to carefully transfer the hot metal into the calorimeter containing the 100 mL of tap water. Close the lid of the calorimeter.

SKILLS **A1, A2.1, A3** 

- 7. Insert the glass rod into the calorimeter lid and stir the water in the calorimeter. Do not open the calorimeter.
- 8. Remove the glass rod. Insert the thermometer into the calorimeter, taking care not to strike the metal with the thermometer. Measure and record the final temperature of the water.
- A. Calculate the quantity of thermal energy gained by the water.  $\Box$ III
- B. Assume that the initial temperature of the metal was the temperature of the hot water bath and the final temperature was the temperature of the warm water in the calorimeter. Calculate the quantity of thermal energy lost by the metal, using the specific heat capacity given in Table 1 (page 292).  $\Pi$
- C. Compare your answers to A and B. Explain any differences. The
- D. What were some sources of experimental error? How would you improve this investigation? TAI

# Enthalpy Change

enthalpy (*H*) the total amount of thermal energy in a substance

enthalpy change (Δ*H*) the energy released to or absorbed from the surroundings during a chemical or physical change

Every substance undergoing a chemical or physical change contains a certain amount of thermal energy. The total amount of thermal energy is sometimes called enthalpy (*H*). Chemists have yet to find a way of measuring the enthalpy of a given substance. However, the energy change that occurs in a system during a reaction, called the **enthalpy change**  $(\Delta H)$ , can be measured using calorimetry data. Let us examine why this is possible.

Chemists have found that as long as pressure remains constant, the enthalpy change of the chemical system is equal to the flow of thermal energy in and out of the system, or

 $\Delta H_{\text{system}} = |q_{\text{system}}|$ 

For a chemical reaction, the enthalpy change, ∆*H*, is given by the equation

 $\Delta H = H_{\text{products}} - H_{\text{reactants}}$ 

When the products of a reaction have a greater enthalpy than the reactants, ∆*H*  will be positive. The system absorbs thermal energy from its surroundings and the reaction is endothermic. On the other hand, if the enthalpy of the products is less than that of the reactants, ∆*H* will be negative. In this case, the system releases thermal energy to its surroundings and the reaction is exothermic.

> $ΔH > 0$ , endothermic reaction ∆*H* < 0, exothermic reaction

For example, suppose we use a bomb calorimeter to determine the enthalpy of the reaction in which magnesium metal, Mg(s), reacts with an aqueous solution of hydrochloric acid, HCl(aq), according to the net ionic equation

 $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$ 

The chemical system consists of solid magnesium, aqueous hydrochloric acid, magnesium ions, and hydrogen gas. The surroundings are the liquid water in the calorimeter. During the reaction, the water temperature increases. You can infer from the temperature increase that energy is transferred from the chemical system to the surroundings (**Figure 4**). Therefore, the products have a lower enthalpy than the reactants, so  $\Delta H$  < 0 and this is an exothermic reaction.



#### Changes in Kinetic and Potential Energy during the Exothermic Reaction  $Mg(s) + 2 H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_{2}(g)$

#### Reaction progress

Figure 4 As this exothermic reaction progresses, the quantity of energy in the chemical system,  $q<sub>system</sub>$ , decreases as the system releases energy to the surroundings. Consistent with the law of

# Molar Enthalpy Change

The **molar enthalpy change (** $\Delta H$ **)** of reaction for a substance is the energy change that occurs when 1 mol of that substance undergoes a physical, chemical, or nuclear change. The SI unit for molar enthalpy change is joules per mole (J/mol). In the symbol  $\Delta H_r$ , the subscript "r" indicates the chemical reaction type. **Table 2** shows how the symbol for molar enthalpy change is written for various types of chemical reactions and gives examples of balanced equations for each. Notice that when you write the balanced equation for the molar enthalpy change of *formation* of a product, the coefficient of that product must always be 1. Other substances in the equation may have fractional coefficients as a result (see the equation for the formation of methanol, CH<sub>3</sub>OH).

molar enthalpy change  $(\Delta H_r)$  the enthalpy change associated with a physical, chemical, or nuclear change involving 1 mol of a substance; SI units J/mol

Table 2 Molar Enthalpies of Reaction



Investigation  $5.2.1$ 

Molar Enthalpy of a Chemical Change (page 333) In this investigation, you will use a calorimeter to determine an experimental value for the molar enthalpy change of the neutralization of a base by an acid, ∆*H*neut.

\*Enthalpy of neutralization can be written per mole of base or acid.

The quantity of energy involved in a change (the enthalpy change, ∆*H*, expressed in kJ) depends on the quantity of matter that undergoes the change. For example, it takes twice the quantity of energy to convert 1 L of liquid water to water vapour as it does to convert 500 mL. To calculate an enthalpy change, ∆*H*, for some amount of substance other than 1 mol, you need to obtain the molar enthalpy value, ∆*H*r, from a reference source, and then use the formula

 $\Delta H = n \Delta H_r$ 

where *n* is the amount and  $\Delta H_r$  is the molar enthalpy change of the reaction.

# Tutorial 2 Molar Enthalpy Calculations

In this tutorial, you will use molar enthalpy change of a reaction, ∆*H*r, data to predict the enthalpy change for a physical or chemical change.

# Sample Problem 1: Calculate ∆*H* for Vaporization Reactions

Ethanol,  $CH<sub>3</sub>OH<sub>2</sub>OH<sub>1</sub>$ , is used to disinfect the skin prior to an injection. If a 1.00 g sample of ethanol is spread across the skin and evaporated, what is the expected enthalpy change? The molar enthalpy of vaporization of ethanol is 38.6 kJ/mol.

**Given:**  $m_{\text{ethanol}} = 1.00 \text{ g}$ ;  $\Delta H_{\text{van}} = 38.6 \text{ kJ/mol}$ 

### Required: ∆*H*

Analysis:  $\Delta H = n \Delta H_{\text{van}}$ 

Solution:

Step 1. Calculate the amount of ethanol in 1.00 g.

$$
M_{\text{CH}_3\text{CH}_2\text{OH}(I)} = 46.08 \text{ g/mol}
$$
  

$$
n_{\text{CH}_3\text{CH}_2\text{OH}(I)} = \frac{m_{\text{CH}_3\text{CH}_2\text{OH}(I)}}{M_{\text{CH}_3\text{CH}_2\text{OH}(I)}}
$$

 $= \frac{1.00 \text{ g}}{46.08 \text{ g/mol}}$ 

 $n_{\text{CH}_3\text{CH}_2\text{OH}(l)} = 0.021701$  mol (2 extra digits carried)

**Step 2.** Solve for the change in enthalpy using  $\Delta H = n \Delta H_{\text{van}}$ .

$$
\Delta H = n \Delta H_{\text{vap}}
$$
  
= 0.021701 m\text{e}t \times \frac{38.6 \text{ kJ}}{1 \text{ m}\text{e}t}  
= 0.838 \text{ kJ}  

$$
\Delta H = 838 \text{ J}
$$

**Step 3.** Determine whether the enthalpy change is positive or negative.

In this case, ethanol must absorb energy to evaporate. Therefore, evaporation is endothermic and  $\Delta H > 0$ .

**Statement:** The enthalpy change for the evaporation of 1.00 g of ethanol is  $+838$  J.

#### Sample Problem 2: Calculate ∆*H* for Dissolution Reactions

An energy change called enthalpy of solution,  $\Delta H_{\text{sol}}$ , occurs when a substance dissolves in water. A student places 125 g of liquid water,  $H_2O(1)$ , at 24.2 °C into a coffee-cup calorimeter, and then adds 10.5 g of solid potassium bromide, KBr(s), also at 24.2 °C. He stirs the liquid until the potassium bromide dissolves, and then determines that the temperature has changed to 21.1 °C. Calculate the molar enthalpy change for this dissolution reaction,  $\Delta H_{sol}$ . Assume that the specific heat capacity, *c*, of the liquid in the calorimeter is the same as the specific heat capacity of water, 4.18 J/(g∙°C).

**Given:**  $m_{H_2O(1)} = 125$  g;  $m_{KBr(s)} = 10.5$  g;  $T_{initial} = 24.2$  °C;  $T_{final} = 21.1$  °C

#### **Required:**  $\Delta H_{\text{sol}}$

Analysis:  $q = mc\Delta T$ ;  $\Delta T = T_{\text{final}} - T_{\text{initial}}$ 

#### Solution:

Step 1. Calculate  $q_{\text{surroundings}}$ .

 $q_{\text{surrou}}$ 

$$
q_{\text{surroundings}} = mc\Delta T
$$
  
=  $(m_{\text{H}_20(1)}) (c) (T_{\text{final}} - T_{\text{initial}})$   
=  $(125 \text{ g}) \left( 4.18 \frac{\text{J}}{\text{g} \cdot ^0\text{C}} \right) (21.1 - 24.2 \text{ } ^0\text{C})$   
=  $(125 \text{ g}) \left( 4.18 \frac{\text{J}}{\text{g} \cdot ^0\text{C}} \right) (-3.1 \text{ } ^0\text{C})$ 

 $q_{\text{surroundings}} = -1.620 \times 10^3$  J (2 extra digits carried)

Step 2. Determine ∆*H*<sub>system</sub>.

Since the final temperature is lower than the initial temperature, the surroundings lose thermal energy to the system. Therefore, the system absorbs energy and so the reaction is endothermic.

 $\Delta H_{\text{system}} = 1.620 \times 10^3 \text{ J}$ 

Step 3. Convert enthalpy change to molar enthalpy change using the molar mass, *M*. Use the periodic table to determine the molar mass of potassium bromide,  $M_{KBr(s)}$ , and then convert the mass of potassium bromide,  $m_{KBr(s)}$ , to amount,  $n_{KBr(s)}$ . Then, use this amount to convert the enthalpy change to the molar enthalpy change.

$$
M_{KBr(s)} = 119.00 \text{ g/mol}
$$

$$
\eta_{KBr(s)} = \frac{m_{KBr(s)}}{M_{KBr(s)}}
$$

$$
= \frac{10.5 \text{ g}}{119.00 \text{ g/mol}}
$$
  
\n
$$
n_{KBr(s)} = 0.088235 \text{ mol (two extra digits carried)}
$$
  
\n
$$
\Delta H = n \Delta H_{sol}
$$
  
\n
$$
\Delta H_{sol} = \frac{\Delta H}{n}
$$
  
\n
$$
= \frac{1.620 \times 10^3 \text{ J}}{0.088235 \text{ mol}}
$$
  
\n
$$
\Delta H_{sol} = 18 \text{ kJ/mol}
$$

Statement: The molar enthalpy change of the dissolution reaction of potassium bromide in water is 18 kJ/mol.

#### **Practice**

- 1. Calculate the enthalpy change expected when 50.0 g of water vaporizes, if the molar enthalpy of vaporization of water is  $44.0 \text{ kJ/mol}$ . The [ans: 122 kJ]
- 2. Some ionic compounds are hydrates—solid compounds to which is bound a specific percentage of water. Some hydrates melt when heated and release energy when they solidify. For example, at 32 °C, liquid Glauber's salt—sodium sulfate decahydrate, Na<sub>2</sub>SO<sub>4</sub>⋅10 H<sub>2</sub>O(I)—solidifies and releases 78.0 kJ/mol of energy. Calculate the enthalpy change when 2.50 kg of Glauber's salt enters the solid state?  $\blacksquare$  $[ans: -605 kJ]$
- 3. Propane,  $C_3H_8$ , is a liquid in a pressurized barbecue tank but vaporizes instantly as it flows out of the tank. Calculate the mass of propane that would vaporize as a result of absorbing 100.0 kJ of energy. The molar enthalpy of vaporization of propane is 15.7 kJ/mol. **T/I** [ans: 281 g]
- 4. Sodium hydroxide, NaOH, is the active ingredient in some brands of drain openers. A temperature increase of 10.6 °C is observed when 4.00 g of sodium hydroxide is dissolved in 100.0 mL of water. Calculate the molar enthalpy of dissolution of sodium hydroxide.  $\blacksquare$  [ans:  $-44.3 \times 10^3$  J/mol or  $-44.3$  kJ/mol]

# Representing Molar Enthalpy Changes

All chemical reactions undergo a change in enthalpy. Spectacular reactions such as the combustion of the highly flammable liquid ethanol are obviously exothermic (**Figure 5**). In most chemical reactions, however, the enthalpy change is more subtle. In fact, it is often difficult to tell whether a reaction is exothermic or endothermic. Therefore, it is important to have a clear way of communicating this information in the chemical equation for the reaction. A chemical equation that describes the enthalpy change of a reaction is called a thermochemical equation.

For example, the synthesis of water from its elements is an exothermic reaction and can be represented by the two thermochemical equations

$$
H_2(g) + \frac{1}{2}O_2(g) \to H_2O(l) + 285 \text{ kJ}
$$
  

$$
H_2(g) + \frac{1}{2}O_2(g) \to H_2O(l) \quad \Delta H = -285 \text{ kJ}
$$

In the first thermochemical equation, an energy term is on the product side to indicate that energy is released by the chemical system. In the second thermochemical equation, the enthalpy change, ∆*H*, is written after the balanced chemical equation. In this example, the enthalpy change is negative, indicating that the process is exothermic. Notice that both equations indicate that 1 mol of hydrogen reacts to release 285 kJ of thermal energy. The only difference is how this energy change is communicated.



Figure 5 A flambé involves burning an alcoholic beverage, such as brandy, mixed with food.

Now consider the reverse of this synthesis reaction. Electricity can be used to decompose water into its elements. For this reaction to occur, water must absorb 285 kJ/mol of energy. This reaction can be represented by the following two thermochemical equations:

$$
H_2O(l) + 285 \text{ kJ} \rightarrow H_2(g) + \frac{1}{2}O_2(g)
$$
  

$$
H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H = 285 \text{ kJ}
$$

In the first equation, the energy term is on the reactant side, indicating that energy is absorbed by the system. In the second equation, the molar enthalpy term has a positive sign, indicating that the decomposition reaction is endothermic.

You can also represent the enthalpy change of a reaction using a potential energy diagram. In a chemical reaction, both reactants and products have potential energy. In a **potential energy diagram**, you express the potential energy  $(y\text{-axis})$  as a function of the reaction progress  $(x-axis)$ . For an exothermic reaction, the reactants have more potential energy than the products. Therefore, you will draw the line for the potential energy of the reactants higher than the line drawn for the products (**Figure 6(a)**). In an endothermic reaction, the products have more potential energy than the reactants, as the system absorbs energy (**Figure 6(b)**). Neither of the axes have numerical values, since you are only describing the enthalpy change,  $\Delta H$ , of the reaction. CAREER LINK



Figure 6 (a) The condensation reaction of 1 mol of water vapour is exothermic. The reactant has a higher potential energy than the product. (b) The vaporization reaction of liquid water to water vapour is endothermic. The reactant has a lower potential energy than the product.

#### Tutorial 3 Representing Thermochemical Enthalpy Changes

This tutorial provides an opportunity to gain experience in representing enthalpy changes in three ways: as a thermochemical equation with an energy term, as a thermochemical equation with a ∆*H* value, and in potential energy diagrams.

#### Sample Problem 1: Thermochemical Equations with Energy Terms

The combustion of methane gas,  $CH<sub>4</sub>(g)$ , is an exothermic reaction. When 1 mol of methane burns, 802.3 kJ of energy is released. Write the thermochemical equation both by representing the energy change as a ∆*H* value, and by representing the energy change as an energy term in the equation.

potential energy diagram a graphical representation of the energy transferred during a physical or a chemical change

# Solution

**Step 1.** Write the balanced chemical equation without the energy term.

 $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$ 

Step 2. To write the thermochemical equation with the energy included, decide whether the energy term should be on the reactant or product side. Since an exothermic reaction releases energy, place the energy term on the right, or product, side of the equation.

 $CH<sub>4</sub>(g) + 2 O<sub>2</sub>(g) \rightarrow CO<sub>2</sub>(g) + 2 H<sub>2</sub>O(l) + 802.3 kJ$ 

 Notice that in this type of equation, you do not change the sign of the thermal energy term.

Step 3. To write the thermochemical equation with the ∆*H* to the side, determine the sign of the enthalpy change.

> Since combustion reactions are exothermic, the enthalpy change has a negative value.

 $CH<sub>4</sub>(q) + 2 O<sub>2</sub>(q) \rightarrow CO<sub>2</sub>(q) + 2 H<sub>2</sub>O(l) \Delta H<sub>c</sub> = -802.3 kJ$ 

# **Sample Problem 2: Drawing Potential Energy Diagrams**

Draw potential energy diagrams for the following reactions:

(a)  $CO_2(s) + 20.3 \text{ kJ} \rightarrow CO_2(g)$ 

- (b) CaCl<sub>2</sub>(s)  $\rightarrow$  CaCl<sub>2</sub>(aq)  $\Delta H_{\text{sol}} = -82.8$  kJ
- (c)  $2 \text{ Ag}(s) + \text{Cl}_2(g) \rightarrow 2 \text{ AgCl}(s) + 254 \text{ kJ}$

### Solution

(a)  $CO_2(s) + 20.3 \text{ kJ} \rightarrow CO_2(g)$ 

Since the energy term is on the reactant side of the equation, it is endothermic. Draw the reaction coordinates with the *x*-axis labelled "Reaction progress" and the *y*-axis labelled "Potential energy,  $E_p$  (kJ)." Since the product will have greater potential energy than the reactant, point the arrow from the reactant upward to the product. Write the reactant on the lower left-hand side of the graph and the product on the upper right-hand side of the graph. Include the ∆*H* of the reaction. This process is sublimation, so  $\Delta H$  is  $\Delta H_{sub}$ .



(b) CaCl<sub>2</sub>(s)  $\rightarrow$  CaCl<sub>2</sub>(aq)  $\Delta H_{sol} = -82.8$  kJ

Since ∆*H* is negative, this reaction is exothermic. In an exothermic reaction, the reactants will have greater energy than the products, so the arrow will point downward from the reactant to the product.



(c)  $2 \text{ Ag}(s) + \text{Cl}_2(q) \rightarrow 2 \text{ AgCl}(s) + 254 \text{ kJ}$ 

Since the energy term is on the side of the product, the reaction is exothermic. The equation is for the formation of 2 mol AgCl(s), so divide reactants, product, and enthalpy in half. Draw the potential energy diagram, per mole of AgCl(s) formed.



#### **Practice**

1. The molar enthalpy of combustion of ethyne,  $C_2H_2(q)$ , is  $-1300$  kJ/mol. The contact of combustion of ethyne,  $C_2H_2(q)$ , is  $-1300$  kJ/mol. (a) Write a thermochemical equation for the combustion of 1 mol of ethyne.

[ans:  $C_2H_2(g) + \frac{5}{2}$  $\frac{3}{2}$  O<sub>2</sub>(g)  $\rightarrow$  2 CO<sub>2</sub>(g) + H<sub>2</sub>O(g) + 1300 kJ]

- (b) Draw a potential energy diagram for the reaction.
- 2. A cold pack consists of an inner pouch containing ammonium nitrate,  $NH<sub>A</sub>NO<sub>3</sub>(s)$ , and an outer pouch of water. Twisting the pack breaks the inner pouch and allows the water and ammonium nitrate to mix. As the ammonium nitrate dissolves, the temperature of the surroundings decreases. The energy change per mole of ammonium nitrate dissociated is 25.7 kJ. T/I C
	- (a) Classify the reaction as endothermic or exothermic. [ans: endothermic]
	- (b) Draw a potential energy diagram for the reaction. Label the change in enthalpy.
	- (c) Write a thermochemical equation for this reaction.

[ans:  $NH_4NO_3(s) + 25.7 \text{ kJ} \xrightarrow{H_2O} NH_4NO_3(aq)$ ]

3. Write out the corresponding thermochemical equation for the reaction depicted by each of the following potential energy diagrams:  $\Box$ 



 $\text{[ans: } C_8H_{18}(l) + \frac{25}{2} O_2(g) \rightarrow 8 CO_2(g) + 9 H_2O(l) \Delta H_c = -5074 \text{ kJ}$ 

4. In a coffee-cup calorimeter, 50.0 mL of 0.100 mol/L AgNO<sub>3</sub>(aq) and 50.0 mL of 0.100 mol/L HCl(aq) are mixed. The following equation represents the reaction that occurs:

 $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ 

The two solutions were initially at 22.6 °C, and the final temperature is 23.4 °C. Calculate the thermal energy that accompanies this reaction in kJ/mol of AgCl formed. Assume that the combined solution has a mass of 100.0 g and a specific heat capacity of 4.18 J/(g  $\cdot$ °C). K/U T/I [ans: -70 kJ]

# 5.2 Review

# Summary

- Specific heat capacity, *c*, is the quantity of thermal energy required to raise the temperature of 1 g of a substance by 1 °C. The units for specific heat capacity are  $J/(g·°C)$ .
- The quantity of thermal energy required to raise the temperature of a substance depends on the substance's mass, its specific heat capacity, and the temperature change.
- Calorimeters are devices that are used to determine the amount of thermal energy transferred during a chemical or physical change.
- Under constant pressure, the enthalpy change of a reaction, Δ*H*, equals the thermal energy released or absorbed by a system, *q*.
- The molar enthalpy of a reaction can be determined using  $\Delta H = n \Delta H_r$ .
- Exothermic reactions release energy and have a negative Δ*H*.
- Endothermic reactions absorb energy and have a positive Δ*H*.
- The enthalpy change of a reaction can be written as an energy term in a chemical equation or a  $\Delta H$  value written after the chemical equation.

# **Questions**

- 1. A potato is wrapped in aluminum foil and cooked in a campfire. The wrapped potato is then removed from the fire and allowed to cool for 1 min. The aluminum foil can be safely removed using your fingers, but touching the inside of the potato results in a serious burn. Use Table 1 on page 292 to explain these observations. (*Hint*: A potato contains a great deal of water.)  $K/U$   $T/I$  A
- 2. Assuming gasoline is pure  $C_8H_{18}(l)$ , predict the sign of  $q_{\text{system}}$   $\Delta H$ , and  $q_{\text{surroundings}}$  for the process of burning gasoline into  $CO<sub>2</sub>(g)$  and  $H<sub>2</sub>O(g)$ . K/U T/I
- 3. The enthalpy change for the chemical reaction represented by the chemical equation  $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$  $is -891$  kJ. K/U T/I
	- (a) What is the enthalpy change for each mole of water formed?
	- (b) What is the enthalpy change for each mole of carbon dioxide formed?
	- (c) What is the enthalpy change for each mole of oxygen reacted?
- 4. The molar enthalpy of solution for ammonium chloride is  $+14.8$  kJ/mol. What is the final temperature observed when 20.0 g of ammonium chloride is added to 125 mL water at 20.0 °C? K/U T/I
- 5. Draw a potential energy diagram for the reactions represented by the following equations: K/U T/I C
	- (a)  $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$  $\Delta H = 26$  kJ
- (b) The combustion reaction of ethane,  $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)$  $\Delta H_c = -1423 \text{ kJ}$
- 6. Rewrite each of the following using a thermochemical equation with a  $\Delta H$  value: KU TA C
	- (a) The standard molar enthalpy of combustion for propane is  $-2220$  kJ/mol.
	- (b) The molar enthalpy for the separation of the atoms in the chlorine molecule is 243 kJ /mol of chlorine.
	- (c) The molar enthalpy of the formation of iron(III) oxide from its elements is  $-824$  kJ/mol of iron(III) oxide.
	- (d) The molar enthalpy for the decomposition of hydrogen chloride into its elements is  $+93$  kJ/mol.
- 7. For each of the following, write a thermochemical equation that includes an energy term within the equation. K/U T/I c
	- (a) The formation of 1 mol of copper(II) chloride from its elements releases 220.1 kJ of energy.
	- (b) The energy absorbed when graphite is converted to diamond is 2.0 kJ/mol of graphite.
	- (c) The decomposition of silver chloride into its elements requires 127.1 kJ/mol of silver chloride.