# 1 7 Thermochemistry

## **INSIDE:**

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- 17.2 Measuring and Expressing Enthalpy Changes
- 17.3 Heat in Changes of State
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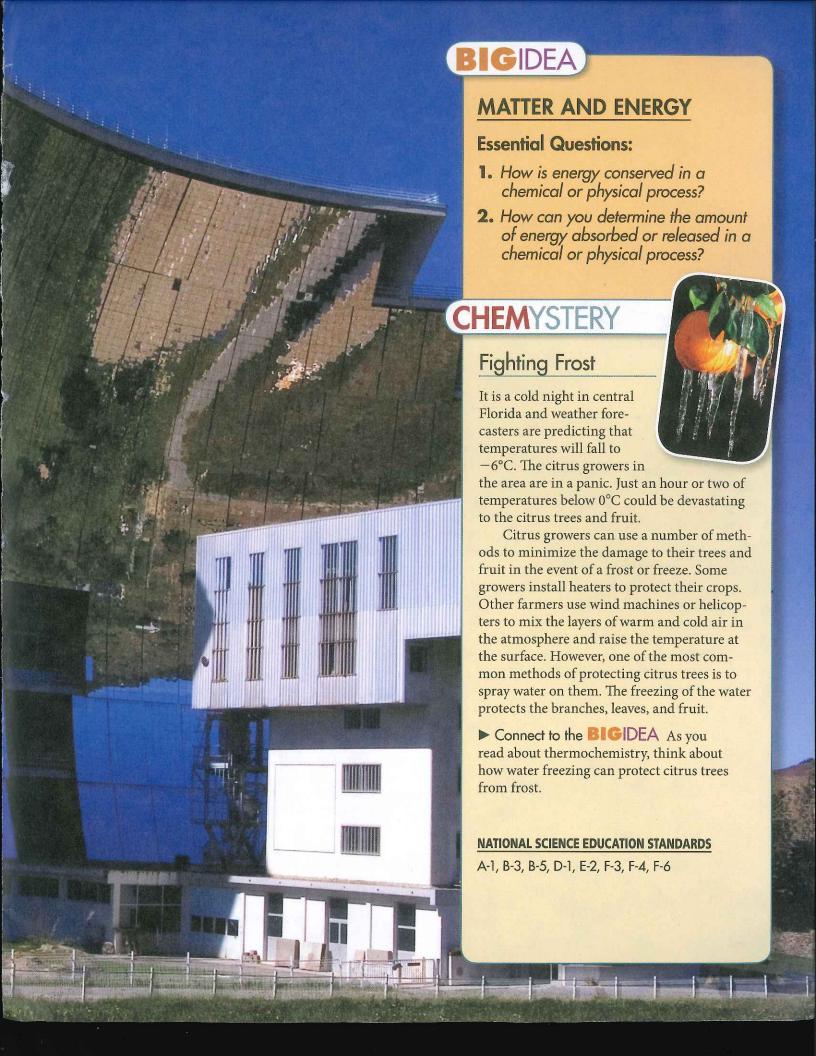












# 7. The Flow of Energy



# CHEMISTRY YOU

Q: Why does lava cool faster in water than in air? Lava flowing out of an erupting volcano is very hot. Its temperature ranges from 550°C to 1400°C. As lava flows down the side of a volcano, it loses heat and begins to cool slowly. In some instances, the lava may flow into the ocean, where it cools more rapidly. In this lesson, you will learn about heat flow.

#### **Key Questions**

What are the ways in which energy changes can occur?

What happens to the energy of the universe during a chemical or physical process?

On what factors does the heat capacity of an object depend?

#### Vocabulary

- thermochemistry
- chemical potential energy
- heat system
- surroundings
- · law of conservation of energy
- endothermic process
- exothermic process
- heat capacity
- specific heat

## **Energy Transformations**

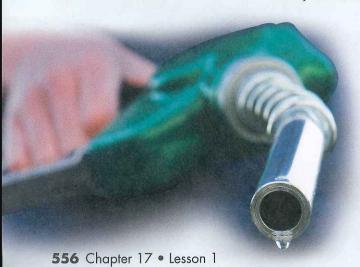
What are the ways in which energy changes can occur?

Energy is the capacity for doing work or supplying heat. Unlike matter, energy has neither mass nor volume. Energy is detected only because of its effects. For example, a car moves because of the energy supplied by the fuel. **Thermochemistry** is the study of energy changes that occur during chemical reactions and changes in state. Every substance has a certain amount of energy stored inside it. The energy stored in the chemical bonds of a substance is called **chemical potential energy.** The kinds of atoms and the arrangement of the atoms in a substance determine the amount of energy stored in the substance.

During a chemical reaction, a substance is transformed into another substance with a different amount of chemical potential energy. When you buy gasoline, shown in Figure 17.1, you are actually buying the stored potential energy it contains. The controlled explosions of the gasoline in a car's engine transform the potential energy into useful work, which can be used to propel the car. At the same time, however, heat is also produced, making the car's engine extremely hot. Energy changes occur as either heat transfer or work, or a combination of both.

**Heat,** represented by *q*, is energy that transfers from one object to another because of a temperature difference between the objects. One of the effects of adding heat to an object is an increase in its temperature. Heat flows spontaneously from a warmer object to a cooler object. If two objects remain in contact, heat will flow from the warmer object to the cooler object until the temperature of both objects is the same.

Figure 17.1 Chemical Potential Energy Chemical potential energy is stored within the bonds of the molecules in gasoline.



#### **Endothermic and Exothermic Processes**

What happens to the energy of the universe during a chemical or physical process?

Chemical reactions and changes in physical state generally involve either the absorption or the release of heat. In studying energy changes, you can define a **system** as the part of the universe on which you focus your attention. Everything else in the universe makes up the **surroundings**. In thermochemical experiments, you can consider the region in the immediate vicinity of the system as the surroundings. Together, the system and its surroundings make up the universe.

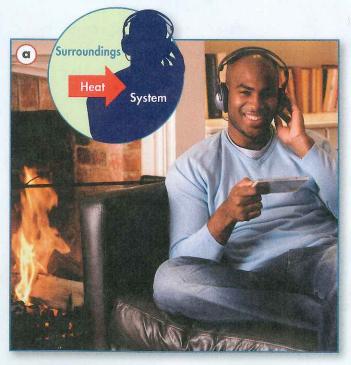
A major goal of thermochemistry is to examine the flow of heat between the system and its surroundings. The law of conservation of energy states that in any chemical or physical process, energy is neither created nor destroyed. During any chemical or physical process, the energy of the universe remains unchanged. If the energy of the system increases during that process, the energy of the surroundings must decrease by the same amount. Likewise, if the energy of the system decreases during that process, the energy of the surroundings must increase by the same amount.

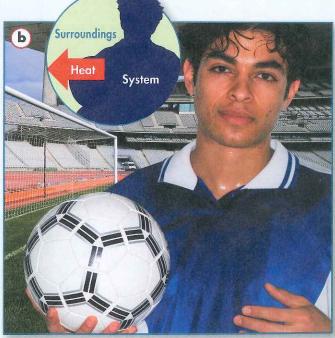
**Direction of Heat Flow** In thermochemical calculations, the direction of heat flow is given from the point of view of the system. Heat is absorbed from the surroundings in an **endothermic process**. In an endothermic process, the system gains heat as the surroundings lose heat. In Figure 17.2a, the system (the body) gains heat from its surroundings (the fire). Heat flowing into a system from its surroundings is defined as positive; q has a positive value. An **exothermic process** is one that releases heat to its surroundings. In an exothermic process, the system loses heat as the surroundings gain heat. In Figure 17.2b, the system (the body) loses heat to the surroundings (the perspiration on the skin, and the air). Heat flowing out of a system into its surroundings is defined as negative; q has a negative value.

Learn about temperature and heat online.

Figure 17.2 Heat Flow
Heat flow is defined from the point
of view of the system. a. In an
endothermic process, heat flows into
the system from the surroundings.
b. In an exothermic process,
heat flows from the system to the
surroundings. In both cases, energy
is conserved.

Apply Concepts In which process does a have a negative value?





# Sample Problem 17.1

#### Recognizing Endothermic and Exothermic Processes

On a sunny winter day, the snow on a rooftop begins to melt. As the melted water drips from the roof, it refreezes into icicles. Describe the direction of heat flow as the water freezes. Is this process endothermic or exothermic?

**1** Analyze Identify the relevant concepts. Heat flows from a warmer object to a cooler object. An endothermic process absorbs heat from the surroundings. An exothermic process releases heat to the surroundings.

2 Solve Apply the concepts to this problem.

First, identify the system and the surroundings.

Determine the direction of heat flow.

Determine if the process is endothermic or exothermic.

System: water Surroundings: air

In order for water to freeze, its temperature must decrease. Heat flows out of the water and into the air.

Heat is released from the system to the surroundings. The process is exothermic.

**1.** A container of melted wax stands at room temperature. What is the direction of heat flow as the liquid wax solidifies? Is the process endothermic or exothermic?

First, identify the system and surroundings in each situation. Then, determine the direction of heat flow.



2. When barium hydroxide octahydrate, Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O is mixed in a beaker with ammonium thiocyanate, NH<sub>4</sub>SCN, a reaction occurs. The beaker becomes very cold. Is the reaction endothermic or exothermic?

Units for Measuring Heat Flow Describing the amount of heat flow requires units different than those used to describe temperature. Heat flow is measured in two common units, the calorie and the joule. You have probably heard of someone exercising to "burn calories." During exercise, your body breaks down sugars and fats in a process that releases heat. Although there is not an actual fire burning the sugars and fats within your body, chemical reactions accomplish the same result. For example, in breaking down 10 g of sugar, your body releases the same amount of heat that would be released if 10 g of sugar were completely burned in a fire.

A calorie (cal) is defined as the quantity of heat needed to raise the temperature of 1 g of pure water 1°C. The word *calorie* is written with a small *c* except when referring to the energy contained in food. The dietary Calorie, written with a capital *C*, always refers to the energy in food. One dietary Calorie is equal to one kilocalorie, or 1000 calories.

1 Calorie = 1 kilocalorie = 1000 calories

The joule (J) is the SI unit of energy. One joule of heat raises the temperature of 1 g of pure water 0.2390°C. You can convert between calories and joules using the following relationships:

1 J = 0.2390 cal 4.184 J = 1 cal

# **Heat Capacity and Specific Heat**

On what factors does the heat capacity of an object depend?

The amount of heat needed to increase the temperature of an object exactly 1°C is the **heat capacity** of that object. The heat capacity of an object depends on both its mass and its chemical composition. The greater the mass of the object, the greater its heat capacity. One of the massive steel cables on the bridge in Figure 17.3, for example, requires much more heat to raise its temperature 1°C than a small steel nail does.

Different substances with the same mass may have different heat capacities. On a sunny day, a 20-kg puddle of water may be cool, while a nearby 20-kg iron sewer cover may be too hot to touch. This situation illustrates how different heat capacities affect the temperature of objects. Assuming that both the water and the iron absorb the same amount of radiant energy from the sun, the temperature of the water changes less than the temperature of the iron in the same amount of time because the specific heat capacity of water is larger than the specific heat capacity of iron.

The specific heat capacity, or simply the **specific heat**, of a substance is the amount of heat it takes to raise the temperature of 1 g of the substance 1°C. Table 17.1 gives specific heats for some common substances. Water has a very high specific heat compared with the other substances in the table. Metals generally have low specific heats. The same amount of heat affects the temperature of objects of the same mass with a high specific heat much less than the temperature of those with a low specific heat.



Figure 17.3 Heat Capacity
A massive steel cable has a higher heat capacity than a steel nail.
Compare Which has a greater heat capacity: a cup of water or a drop of water?

#### **Interpret** Data

Specific Heat	s of Some Commo	on Substances				
Substance	Specific heat					
Substance	J/(g·°C)	cal/(g·°C)				
Liquid water	4.18	1.00				
Ethanol	2.4	0.58				
Ice	2.1	0.50				
Steam	1.9	0.45				
Chloroform	0.96	0.23				
Aluminum	0.90	0.21				
Iron	0.46	0.11				
Silver	0.24	0.057				
Mercury	0.14	0.033				

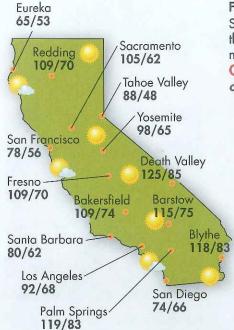
**Table 17.1** The specific heat of a substance can be expressed in  $J/(g^{\circ}C)$  or cal/ $(g^{\circ}C)$ .

**a. Read Tables** What is the specific heat of chloroform in cal/(g·°C)?

**b.** Compare Which metal in the table has the highest specific heat?

**c.** Calculate Show how to convert the specific heat of liquid water from J/(g·°C) to cal/(g·°C).

Hint: For part c, use the relationship 1 J = 0.2390 cal to write the appropriate conversion factor.



#### CHEMISTRY YOU

Q: Heat will flow from the lava to the surroundings until the lava and surroundings are at the same temperature. Air has a smaller specific heat than water. Why would lava then cool more quickly in water than in air?

Figure 17.5 Cooling of Water
The filling of a hot apple pie is mostly water, so it is much more likely to burn your tongue than the crust.

Figure 17.4 Temperature Moderation

San Francisco is located on the Pacific coast. The high specific heat of the water in the ocean helps keep the temperature in San Francisco much more moderate than that of the towns and cities farther inland.

Compare Describe how the ocean affects the temperature of coastal areas in the summer and in the winter.

Specific Heat of Water Just as it takes a lot of heat to raise the temperature of water, water also releases a lot of heat as it cools. Water in lakes and oceans absorbs heat from the air on hot days and releases it back into the air on cool days. As illustrated in Figure 17.4, this property of water is responsible for moderate climates in coastal areas. Citrus farmers often spray their trees with water to protect the fruit from frost damage during icy weather. As the water freezes, it releases heat, which helps prevent the fruit from freezing. When a freshly baked apple pie, such as the one shown in Figure 17.5, comes out of the oven, both the filling and crust are at the same temperature. However, the filling, which is mostly water, has a higher specific heat than the crust. In order to cool down, the filling must give off a lot of heat. This release of heat is why you have to be careful not to burn your tongue when eating hot apple pie.

**Calculating Specific Heat** To calculate the specific heat (*C*) of a substance, you divide the heat input by the mass of the substance times the temperature change.

$$C = \frac{q}{m \times \Delta T} = \frac{\text{heat (J or cal)}}{\text{mass (g)} \times \text{change in temperature (°C)}}$$

In the equation above, q is heat and m is mass. The symbol  $\Delta T$  (read "delta T") represents the change in temperature.  $\Delta T$  is calculated from the equation  $\Delta T = T_{\rm f} - T_{\rm i}$ , where  $T_{\rm f}$  is the final temperature and  $T_{\rm i}$  is the initial temperature. As you can see from the equation and in Table 17.1 on the previous page, heat may be expressed in terms of joules or calories. Therefore, the units of specific heat are either J/(g·°C) or cal/(g·°C).



#### Calculating the Specific Heat of a Substance

The temperature of a 95.4-g piece of copper increases from 25.0°C to 48.0°C when the copper absorbs 849 J of heat. What is the specific heat of copper?

- **1** Analyze List the knowns and the unknown. Use the known values and the definition of specific heat.
- 2 Calculate Solve for the unknown.

KNOWNS

 $m_{Cu} = 95.4 g$   $\Delta T = 48.0^{\circ}\text{C} - 25.0^{\circ}\text{C} = 23.0^{\circ}\text{C}$ q = 849 J

UNKNOWN

 $C_{Cu} = ? J/(g \cdot {}^{\circ}C)$ 

Start with the equation for specific heat.

Substitute the known quantities into the equation to calculate the unknown value  $C_{Cu}$ .

$$C_{Cu} = \frac{q}{m_{Cu} \times \Delta T}$$

$$C_{\text{Cu}} = \frac{849 \text{ J}}{95.4 \text{ g} \times 23.0^{\circ}\text{C}} = \frac{0.387 \text{ J/(g} \cdot ^{\circ}\text{C})}{2.387 \text{ J/(g} \cdot ^{\circ}\text{C})}$$

- **3 Evaluate** Does the result make sense? Remember that liquid water has a specific heat of 4.18 J/( $g \cdot {}^{\circ}C$ ). Metals have specific heats lower than water. Thus the calculated value of 0.387 J/( $g \cdot {}^{\circ}C$ ) seems reasonable.
- **3.** When 435 J of heat is added to 3.4 g of olive oil at 21°C, the temperature increases to 85°C. What is the specific heat of the olive oil?



**4.** How much heat is required to raise the temperature of 250.0 g of mercury 52°C?

You can find the specific heat of mercury on Table 17.1.

#### ONLINE ORIENO

# 17.1 LessonCheck

- **5.** Review What are the ways that energy conversion can occur?
- **6.** Describe What happens to the energy of the universe during a physical or chemical process?
- 7. Capacity On what two factors does the heat capacity of an object depend?
- **8.** Classify On a cold night you use an electric blanket to warm your body. Describe the direction of heat flow. Is this process endothermic or exothermic?
- **9. Calculate** A chunk of silver has a heat capacity of 42.8 J/°C and a mass of 181 g. Calculate the specific heat of silver.
- **10.** Calculate Using calories, calculate how much heat 32.0 g of water absorbs when it is heated from 25.0°C to 80.0°C. How many joules is this?

#### **BIGIDEA** MATTER AND ENERGY

**11.** How is the energy of the universe conserved during the combustion of gasoline in a car engine?

# Measuring and Expressing Enthalpy Changes



# CHEMISTRY (YOU)

Q: How can you measure the amount of heat released when a match burns? When you strike a match, heat is released to the surroundings. In addition to describing the direction of heat flow, you may also want to determine the quantity of heat that is transferred. The concept of specific heat allows you to measure heat flow in chemical and physical processes.

#### **Key Questions**

How can you measure the change in enthalpy of a reaction?

How can you express the enthalpy change for a reaction in a chemical equation?

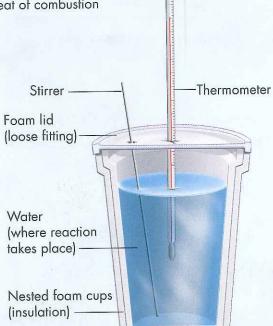
#### Vocabulary

- calorimetry
- calorimeter

enthalpy thermochemical equation

heat of reaction

heat of combustion



### Calorimetry

How can you measure the change in enthalpy of a reaction?

Heat that is absorbed or released during many chemical reactions can be measured by a technique called calorimetry. Calorimetry is the measurement of the heat flow into or out of a system for chemical and physical processes. In a calorimetry experiment involving an endothermic process, the heat absorbed by the system is equal to the heat released by its surroundings. In an exothermic process, the heat released by a system is equal to the heat absorbed by its surroundings. The insulated device used to measure the absorption or release of heat in chemical or physical processes is called a colorimeter.

> Constant-Pressure Calorimeters Foam cups can be used as simple calorimeters because they do not let much heat in or out. The heat flows for many chemical reactions can be measured in a constant-pressure calorimeter similar to the one shown in Figure 17.6. Most chemical reactions and physical changes carried out in the laboratory are open to the atmosphere and, thus, occur at constant pressure. The enthalpy (H) of a system accounts for the heat flow of the system at constant pressure.

Figure 17.6 Constant-Pressure Calorimeter

In a simple constant-pressure calorimeter, a thermometer records the temperature change as chemicals react in water. The reacting substances constitute the system. The water constitutes the surroundings.

Relate Cause and Effect What happens to the temperature of the water if heat is released by the reaction in the calorimeter?

The heat absorbed or released by a reaction at constant pressure is the same as the change in enthalpy, symbolized as  $\Delta H$ . The value of  $\Delta H$  of a reaction can be determined by measuring the heat flow of the reaction at constant pressure. In this textbook, the terms heat and enthalpy change are used interchangeably because the reactions presented occur at constant pressure. In other words,  $q = \Delta H$ .

To measure the enthalpy change for a reaction in aqueous solution in a foam cup calorimeter, dissolve the reacting chemicals (the system) in known volumes of water (the surroundings). Measure the initial temperature of each solution, and mix the solutions in the foam cup. After the reaction is complete, measure the final temperature of the mixed solutions. You can calculate the heat absorbed or released by the surroundings ( $q_{\rm surr}$ ) using the formula for specific heat, the initial and final temperatures, and the heat capacity of water.

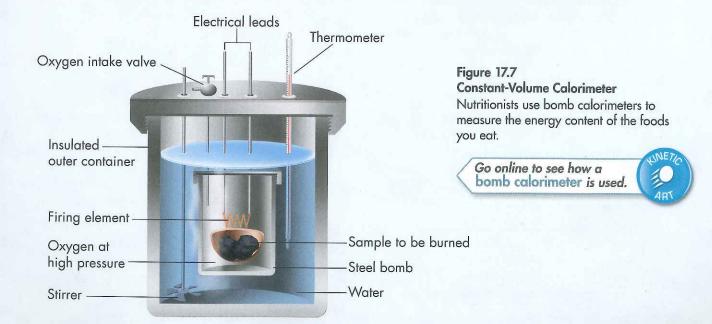
$$q_{\text{surr}} = m \times C \times \Delta T$$

In this expression, m is the mass of the water, C is the specific heat of water, and  $\Delta T = T_{\rm f} - T_{\rm i}$ . The heat absorbed by the surroundings is equal to, but has the opposite sign of, the heat released by the system. Conversely, the heat released by the surroundings is equal to, but has the opposite sign of, the heat absorbed by the system. Therefore, the enthalpy change for the reaction  $(\Delta H)$  can be written as follows:

$$q_{\rm sys} = \Delta H = -q_{\rm surr} = -m \times C \times \Delta T$$

The sign of  $\Delta H$  is positive for an endothermic reaction and negative for an exothermic reaction.

**Constant-Volume Calorimeters** Calorimetry experiments can also be performed at constant volume using a device called a bomb calorimeter. In a bomb calorimeter, which is shown in Figure 17.7, a sample of a compound is burned in a constant-volume chamber in the presence of oxygen at high pressure. The heat that is released warms the water surrounding the chamber. By measuring the temperature increase of the water, it is possible to calculate the quantity of heat released during the combustion reaction.



**Q:** What type of calorimeter would you use to measure the heat released when a match burns? Describe the experiment and how you would calculate the heat released.

#### **Enthalpy Change in a Calorimetry Experiment**

When 25.0 mL of water containing 0.025 mol HCl at 25.0°C is added to 25.0 mL of water containing 0.025 mol NaOH at 25.0°C in a foam cup calorimeter, a reaction occurs. Calculate the enthalpy change (in kJ) during this reaction if the highest temperature observed is 32.0°C. Assume the densities of the solutions are 1.00 g/mL and that the volume of the final solution is equal to the sum of the volumes of the reacting solutions.

- **1** Analyze List the knowns and the unknown. Use dimensional analysis to determine the mass of the water. You must also calculate  $\Delta T$ . Use  $\Delta H = -q_{\rm surr} = -m \times C \times \Delta T$  to solve for  $\Delta H$ .
- Calculate Solve for the unknown.

KNOWNS

UNKNOWN  $\Delta H = ? kJ$ 

$$C_{\text{water}} = 4.18 \text{ J/(g-°C)}$$

 $V_{\text{final}} = V_{\text{HCI}} + V_{\text{NaOH}}$ 

 $= 25.0 \, \text{mL} + 25.0 \, \text{mL} = 50.0 \, \text{mL}$ 

T<sub>f</sub> = 32.0°C

$$density_{solution} = 1.00 g/mL$$

First, calculate the total mass of the water.

Now, calculate  $\Delta T$ .

Use the values for  $m_{\text{water}}$ ,  $C_{\text{water}}$  and  $\Delta T$  to calculate  $\Delta H$ .

 $m_{\text{water}} = 50.0 \,\text{mH} \times \frac{1.00 \,\text{g}}{1 \,\text{mH}} = 50.0 \,\text{g}$ 

 $\Delta T = T_f - T_i = 32.0^{\circ}\text{C} - 25.0^{\circ}\text{C} = 7.0^{\circ}\text{C}$ 

 $\Delta H = -q_{\text{surr}} = -m_{\text{water}} \times C_{\text{water}} \times \Delta T$ 

 $= -(50.0 g)(4.18 J/(g \cdot \mathcal{L}))(7.0 \mathcal{L})$ 

= -1500 J = -1.5 kJ

Use the relationship 1 kJ = 1000 Jto convert your answer from J to kJ.

- **3 Evaluate** Does the result make sense? The temperature of the solution increases, which means that the reaction is exothermic, and thus the sign of  $\Delta H$  should be negative. About 4 J of heat raises the temperature of 1 g of water 1°C, so 200 J of heat is required to raise 50 g of water 1°C. Raising the temperature of 50 g of water 7°C requires about 1400 J, or 1.4 kJ. This estimated answer is very close to the calculated value of  $\Delta H$ .
- 12. When 50.0 mL of water containing 0.50 mol HCl at 22.5°C is mixed with 50.0 mL of water containing 0.50 mol NaOH at 22.5°C in a calorimeter, the temperature of the solution increases to 26.0°C. How much heat (in kJ) is released by this reaction?

Assume that the densities of the solutions are 1.00 g/mL to find the total mass of the water.



13. A small pebble is heated and placed in a foam cup calorimeter containing 25.0 mL of water at 25.0°C. The water reaches a maximum temperature of 26.4°C. How many joules of heat are released by the pebble?

# **Thermochemical Equations**

How can you express the enthalpy change for a reaction in a chemical equation?

If you mix calcium oxide with water, the water in the mixture becomes warm. This exothermic reaction occurs when cement, which contains calcium oxide, is mixed with water to make concrete. When 1 mol of calcium oxide reacts with 1 mol of water, 1 mol of calcium hydroxide forms and 65.2 kJ of heat is released. In a chemical equation, the enthalpy change for the reaction can be written as either a reactant or a product. In the equation describing the exothermic reaction of calcium oxide and water, the enthalpy change can be considered a product.

$$CaO(s) + H2O(l) \longrightarrow Ca(OH)2(s) + 65.2 kJ$$

This equation is presented visually in Figure 17.8. A chemical equation that includes the enthalpy change is called a **thermochemical equation**.

**Heats of Reaction** The **heat of reaction** is the enthalpy change for the chemical equation exactly as it is written. You will usually see heats of reaction reported as  $\Delta H$ , which is equal to the heat flow at constant pressure. The physical state of the reactants and products must also be given. The standard conditions are that the reaction is carried out at 101.3 kPa (1 atm) and that the reactants and products are in their usual physical states at 25°C. The heat of reaction, or  $\Delta H$ , in the above example is -65.2 kJ. Each mole of calcium oxide and water that reacts to form calcium hydroxide produces 65.2 kJ of heat.

# $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$ $\Delta H = -65.2 \text{ kJ}$

In this and other exothermic processes, the chemical potential energy of the reactants is higher than the chemical potential energy of the products.

#### **READING SUPPORT**

**Build Comprehension:** Use Prior Knowledge Thermochemical equations are just like other balanced equations. If heat is absorbed in the reaction, it is written as a reactant. If heat is released, it is written as a product. Recall chemical reactions from Chapter 11. For the combustion of methane, on which side of the reaction arrow would you write the heat absorbed or released by the reaction?

Figure 17.8 Exothermic Process
Calcium oxide is one of the
components of cement. The reaction
of calcium oxide and water is an
exothermic process.



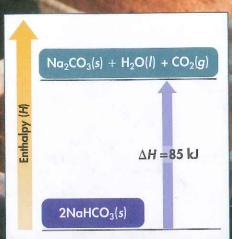




Figure 17.9 Endothermic Process
Muffin batter often contains
baking soda, also known
as sodium bicarbonate. The
decomposition of sodium
bicarbonate is an endothermic
process.

Other reactions absorb heat from the surroundings. For example, baking soda (sodium bicarbonate) decomposes when it is heated. The carbon dioxide released in the reaction causes muffins to rise while baking. This process is endothermic.

$$2\text{NaHCO}_3(s) + 85 \text{ kJ} \longrightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$$

Remember that  $\Delta H$  is positive for endothermic reactions. Therefore, you can write the reaction as follows:

$$2\text{NaHCO}_3(s) \longrightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$$
  $\Delta H = 85 \text{ kJ}$ 

Figure 17.9 shows the enthalpy diagram for this reaction.

Chemistry problems involving enthalpy changes are similar to stoichiometry problems. The amount of heat released or absorbed during a reaction depends on the number of moles of the reactants involved. The decomposition of 2 mol of sodium bicarbonate, for example, requires 85 kJ of heat. Therefore, the decomposition of 4 mol of the same substance would require twice as much heat, or 170 kJ. In this and other endothermic processes, the chemical potential energy of the products is higher than the chemical potential energy of the reactants.

To see why the physical state of the reactants and products in a thermochemical reaction must be stated, compare the following two equations for the decomposition of 1 mol  $\rm H_2O$ :

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$
  $\Delta H = 285.8 \text{ kJ}$   
 $H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$   $\Delta H = 241.8 \text{ kJ}$   
difference = 44.0 kJ

Although the two equations are very similar, the different physical states of  $\rm H_2O$  result in different  $\Delta H$  values. In one case, the reactant is a liquid; in the other case, the reactant is a gas. The vaporization of 1 mol of liquid water to water vapor at 25°C requires 44.0 kJ of heat.

$$H_2O(l) \longrightarrow H_2O(g)$$
  $\Delta H = 44.0 \text{ kJ}$ 

# Sample Problem 17.4

#### Using the Heat of Reaction to Calculate Enthalpy Change

Calculate the amount of heat (in kJ) required to decompose 2.24 mol NaHCO<sub>3</sub>(s).

$$2NaHCO_3(s) + 85 kJ \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

**1** Analyze List the knowns and the unknown. Use the thermochemical equation above to write a conversion factor relating kilojoules of heat and moles of NaHCO<sub>3</sub>. Then use the conversion factor to determine  $\Delta H$  for 2.24 mol NaHCO<sub>3</sub>.

#### KNOWNS

amount of NaHCO $_3(s)$  that decomposes = 2.24 mol  $\Delta H = 85$  kJ for 2 mol NaHCO $_3$ 

#### UNKNOWN

 $\Delta H = ? kJ \text{ for } 2.24 \text{ mol NaHCO}_3$ 

2 Calculate Solve for the unknown.

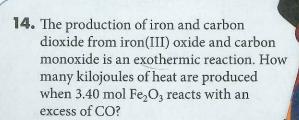
Write the conversion factor relating kJ of heat and moles of NaHCO<sub>3</sub>.

Using dimensional analysis, solve for ∆H.

85 kJ 2 mol NaHCO<sub>3</sub>(s) The thermochemical equation indicates that  $85\,\mathrm{kJ}$  are needed to decompose 2 mol NaHCO $_3$ (s).

 $\Delta H = 2.24 \frac{\text{mol NaHCO}_3(s)}{2 \frac{\text{mol N$ 

**3 Evaluate** Does the result make sense? The 85 kJ in the thermochemical equation refers to the decomposition of 2 mol NaHCO<sub>3</sub>(s). Therefore, the decomposition of 2.24 mol should absorb more heat than 85 kJ. The answer of 95 kJ is consistent with this estimate.



Fe<sub>2</sub>O<sub>3</sub>(s) + 3CO(g) 
$$\longrightarrow$$
 2Fe(s) + 3CO<sub>2</sub>(g) + 26.3 kJ

To do Problem 15, first convert from mass of  $CS_2$  to moles of  $CS_2$ .

15. When carbon disulfide is formed from its elements, heat is absorbed. Calculate the amount of heat (in kJ) absorbed when 5.66 g of carbon disulfide is formed.

$$C(s) + 2S(s) \longrightarrow CS_2(l)$$
$$\Delta H = 89.3 \text{ kJ}$$

#### Figure 17.10 Combustion

The combustion of natural gas is an exothermic reaction. As bonds in methane (the main component of natural gas) and oxygen are broken and bonds in carbon dioxide and water are formed, large amounts of energy are released.



#### **Table 17.2**

Heats of Combustion at 25°C						
Substance	Formula	ΔH (kJ/mol)				
Hydrogen	H <sub>2</sub> (g)	-286				
Carbon	C(s, graphite)	-394				
Methane	CH₄(g)	-890				
Acetylene	C <sub>2</sub> H <sub>2</sub> (g)	-1300				
Ethanol	C <sub>2</sub> H <sub>6</sub> O(/)	-1368				
Propane	C <sub>3</sub> H <sub>8</sub> (g)	-2220				
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)	-2808				
Octane	C <sub>8</sub> H <sub>18</sub> ( <i>I</i> )	-5471				
Sucrose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (s)	-5645				

Heats of Combustion Table 17.2 lists heats of combustion for some common substances. The heat of combustion is the heat of reaction for the complete burning of one mole of a substance. Figure 17.10 shows the combustion of natural gas, which is mostly methane. Small amounts of natural gas within crude oil are burned off at oil refineries. This is an exothermic reaction.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) + 890 \text{ kJ}$$

You can also write this equation as follows:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
  $\Delta H = -890 \text{ kJ}$ 

Burning 1 mol of methane releases 890 kJ of heat. The heat of combustion  $(\Delta H)$  for this reaction is -890 kJ per mole of methane burned.

Like other heats of reaction, heats of combustion are reported as the enthalpy changes when the reactions are carried out at 101.3 kPa of pressure and the reactants and products are in their physical states at 25°C.

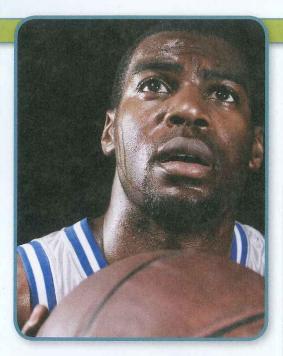


# 17.2 LessonCheck

- **16.** Describe How can you determine the value of  $\Delta H$  of a reaction?
- **17.** Review How are enthalpy changes expressed in chemical equations?
- **18.** Calculate A lead mass is heated and placed in a foam cup calorimeter containing 40.0 mL of water at 17.0°C. The water reaches a temperature of 20.0°C. How many joules of heat were released by the lead?
- **19. Explain** What does the term *heat of combustion* refer to?
- **20.** Describe When 2 mol of solid magnesium (Mg) combines with 1 mol of oxygen gas (O<sub>2</sub>), 2 mol of solid magnesium oxide (MgO) is formed and 1204 kJ of heat is released. Write the thermochemical equation for this combustion reaction.
- **21.** Calculate Gasohol contains ethanol,  $C_2H_6O(l)$ . When ethanol burns, it reacts with  $O_2(g)$  to produce  $CO_2(g)$  and  $H_2O(l)$ . How much heat is released when 12.5 g of ethanol burns?

$$C_2H_6O(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$
  
$$\Delta H = -1368 \text{ kJ}$$

# 17.3 Heat in Changes of State



#### **Key Questions**

What is the relationship between molar heat of fusion and molar heat of solidification?

What is the relationship between molar heat of vaporization and molar heat of condensation?

What thermochemical changes can occur when a solution forms?

#### Vocabulary

- molar heat of fusion
- molar heat of solidification
- molar heat of vaporization
- molar heat of condensation
- molar heat of solution

# CHEMISTRY YOU

Q: Why does sweating help cool you off? An athlete can burn a lot of calories during a game. These calories are either used to do work or are released as heat. When your body heats up, you start to sweat. The evaporation of sweat is your body's way of cooling itself to a normal temperature.

# Heats of Fusion and Solidification

What is the relationship between molar heat of fusion and molar heat of solidification?

What happens if you place an ice cube on a table in a warm room? The ice cube is the system, and the table and air around it are the surroundings. The ice absorbs heat from its surroundings and begins to melt. The temperature of the ice and the liquid water produced remains at 0°C until all of the ice has melted.

Like ice cubes, all solids absorb heat as they melt to become liquids. The gain of heat causes a change of state instead of a change in temperature. Whenever a change of state occurs by a gain or loss of heat, the temperature of the substance undergoing the change remains constant. The heat absorbed by one mole of a solid substance as it melts to a liquid at a constant temperature is the **molar heat of fusion** ( $\Delta H_{\rm fus}$ ). The **molar heat of solidification** ( $\Delta H_{\rm solid}$ ) is the heat lost when one mole of a liquid substance solidifies at a constant temperature. The **quantity of heat absorbed** by a melting solid is exactly the same as the quantity of heat released when the liquid solidifies; that is,  $\Delta H_{\rm fus} = -\Delta H_{\rm solid}$ .

The melting of 1 mol of ice at 0°C to 1 mol of liquid water at 0°C requires the absorption of 6.01 kJ of heat. This quantity of heat is the molar heat of fusion of water. Likewise, the conversion of 1 mol of liquid water at 0°C to 1 mol of ice at 0°C releases 6.01 kJ of heat. This quantity of heat is the molar heat of solidification of water.

$$H_2O(s) \longrightarrow H_2O(l)$$
  $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$   $H_2O(l) \longrightarrow H_2O(s)$   $\Delta H_{\text{solid}} = -6.01 \text{ kJ/mol}$ 



#### Using the Heat of Fusion in Phase-Change Calculations

How many grams of ice at 0°C will melt if 2.25 kJ of heat are added?

1 Analyze List the knowns and the unknown. Find the number of moles of ice that can be melted by the addition of 2.25 kJ of heat. Convert moles of ice to grams of ice.

#### KNOWNS

Initial and final temperatures are O°C

 $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$ 

 $\Delta H = 2.25 \,\mathrm{kJ}$ 

#### UNKNOWN

 $m_{ice} = ? g$ 

2 Calculate Solve for the unknown.

Start by expressing  $\Delta H_{\text{fus}}$  as a conversion factor.

Express the molar mass of ice as a conversion factor.

Multiply the known enthalpy change by the conversion factors.

1 mol H<sub>2</sub>O(s) 6.01 kJ Use the thermochemical equation  $H_2O(s) + 6.01 \text{ kJ} \xrightarrow{} H_2O(s)$ 

 $\frac{18.0 \text{ g H}_2 O(s)}{1 \text{ mol H}_2 O(s)}$ 

 $m_{\rm lce} = 2.25 \,\mathrm{kJ} \times \frac{1 \,\mathrm{mol} \,\mathrm{H}_2 \,\mathrm{O(s)}}{6.01 \,\mathrm{kJ}} \times \frac{18.0 \,\mathrm{g} \,\mathrm{H}_2 \,\mathrm{O(s)}}{1 \,\mathrm{mol} \,\mathrm{H}_2 \,\mathrm{O(s)}}$ 

 $= 6.74 g H_2 O(s)$ 

- **3** Evaluate Does the result make sense? To melt 1 mol of ice, 6.01 kJ of energy is required. Only about one third of this amount of heat (roughly 2 kJ) is available, so only about one-third mol of ice, or 18.0 g/3 = 6 g, should melt. This estimate is close to the calculated answer.
- **22.** How many grams of ice at 0°C could be melted by the addition of 0.400 kJ of heat?



**23.** How many kilojoules of heat are required to melt a 50.0-g popsicle at 0°C? Assume the popsicle has the same molar mass and heat of fusion as water.

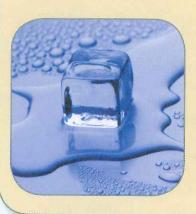
To do Problem 23, first convert from mass to moles. Then, express  $\Delta H_{\rm fus}$  as a conversion factor to convert from moles of ice to kJ of heat.

#### Quick Lab

**Purpose** To estimate the heat of fusion of ice

#### Materials

- 100-ml graduated cylinder
- hot tap water
- foam cup
- thermometer
- ice



#### Heat of Fusion of Ice

## Procedure BAR

- **1.** Fill the graduated cylinder with hot tap water and let stand for 1 minute. Pour the water into the sink.
- **2.** Measure 70 mL of hot water. Pour the water into the foam cup. Measure the temperature of the water.
- **3.** Add an ice cube to the cup of water. Gently swirl the cup. Measure the temperature of the water as soon as the ice cube has completely melted.
- **4.** Pour the water into the graduated cylinder and measure the volume.

#### **Analyze and Conclude**

- **1.** Calculate Determine the mass of the ice. (*Hint:* Use the increase in the volume of water and the density of water.) Convert this mass into moles.
- **2.** Calculate Determine the heat transferred from the water to the ice using the mass of the hot water, the specific heat of liquid water, and the change in temperature.
- **3.** Calculate Determine  $\Delta H_{\text{fus}}$  of ice (kJ/mol) by dividing the heat transferred from the water by the moles of ice melted.
- **4.** Perform Error Analysis Compare your experimental value of  $\Delta H_{\rm fus}$  of ice with the accepted value of 6.01 kJ/mol. Account for any error.

# Heats of Vaporization and Condensation

What is the relationship between molar heat of vaporization and molar heat of condensation?

A liquid that absorbs heat at its boiling point becomes a vapor. The amount of heat required to vaporize one mole of a given liquid at a constant temperature is called its **molar heat of vaporization** ( $\Delta H_{\rm vap}$ ). Table 17.3 lists the molar heats of vaporization for several substances at their normal boiling points.

The molar heat of vaporization of water is 40.7 kJ/mol. This means that it takes 40.7 kJ of energy to convert 1 mol of liquid water to 1 mol of water vapor at the normal boiling point of water (100°C at 101.3 kPa).

$$H_2O(l) \longrightarrow H_2O(g)$$
  $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$ 

Diethyl ether ( $C_4H_{10}O$ ) has a boiling point of 34.6°C and a molar heat of vaporization ( $\Delta H_{\rm vap}$ ) of 26.5 kJ/mol. If liquid diethyl ether is poured into a beaker on a warm, humid day, the ether will absorb heat from the beaker walls and evaporate rapidly. If the beaker loses enough heat, the water vapor in the air may condense and freeze on the beaker walls, forming a coating of frost on the outside of the beaker.

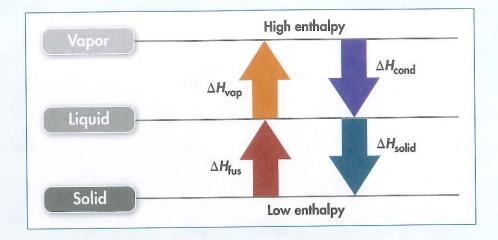
$$C_4H_{10}O(l) \longrightarrow C_4H_{10}O(g)$$
  $\Delta H_{\text{vap}} = 26.5 \text{ kJ/mol}$ 

#### Table 17.3

Substance	ΔH <sub>fus</sub> (kJ/mol)	∆H <sub>vap</sub> (kJ/mol)
Ammonia (NH <sub>3</sub> )	5.66	23.3
Ethanol (C <sub>2</sub> H <sub>6</sub> O)	4.93	38.6
Hydrogen (H <sub>2</sub> )	0.12	0.90
Methanol (CH <sub>4</sub> O)	3.22	35.2
Oxygen (O <sub>2</sub> )	0.44	6.82
Water (H <sub>2</sub> O)	6.01	40.7

Figure 17.11 Changes in State Enthalpy changes accompany changes in state. Fusion and vaporization are endothermic processes. Solidification and condensation are exothermic processes.

Interpret Diagrams Which arrows represent processes that release heat to the surroundings?



CHEMISTRY (YOU)

**Q:** Explain why the evaporation of sweat off your body helps to cool you off.

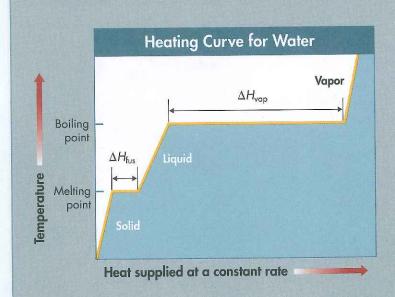
Condensation is the exact opposite of vaporization. When a vapor condenses, heat is released. The **molar heat of condensation** ( $\Delta H_{\rm cond}$ ) is the amount of heat released when one mole of a vapor condenses at its normal boiling point. The quantity of heat absorbed by a vaporizing liquid is exactly the same as the quantity of heat released when the vapor condenses; that is,  $\Delta H_{\rm vap} = -\Delta H_{\rm cond}$ . Figure 17.11 shows the relationships between the molar heat of fusion and molar heat of solidification and between the molar heat of vaporization and molar heat of condensation.

Figure 17.12 summarizes the enthalpy changes that occur as ice is heated to a liquid and then to a vapor. You should be able to identify certain trends regarding the temperature during changes of state and the energy requirements that accompany these changes from the graph. The large values for  $\Delta H_{\rm vap}$  and  $\Delta H_{\rm cond}$  are the reason hot vapors such as steam can be very dangerous. You can receive a scalding burn from steam when the heat of condensation is released as the steam touches your skin.

$$H_2O(g) \longrightarrow H_2O(l)$$

$$\Delta H_{\rm cond} = -40.7 \, \text{kJ/mol}$$

# **Interpret** Graphs



**Figure 17.12** A heating curve graphically describes the enthalpy changes that take place during phase changes.

**a.** Identify In which region(s) of the graph is temperature constant?

**b.** Compare How does the amount of energy required to melt a given mass of ice compare to the energy required to vaporize the same mass of liquid water? Explain.

**c.** Apply Concepts Which region of the graph represents the coexistence of solid and liquid? Liquid and vapor?

Remember: The temperature of a substance remains constant during a change in state.



#### Using the Heat of Vaporization in Phase-Change Calculations

How much heat (in kJ) is absorbed when 24.8 g  $H_2O(l)$  at 100°C and 101.3 kPa is converted to  $H_2O(g)$  at 100°C?

**1** Analyze List the knowns and the unknown. First, convert grams of water to moles of water. Then, find the amount of heat that is absorbed when the liquid water is converted to steam.

#### KNOWNS

Initial and final conditions are  $100^{\circ}$ C and 101.3 kPa mass of liquid water converted to steam = 24.8 g  $\Delta H_{\rm vap} = 40.7$  kJ/mol

UNKNOWN

 $\Delta H = ? kJ$ 

2 Calculate Solve for the unknown.

Start by expressing the molar mass of water as a conversion factor.

Express  $\Delta H_{\text{vap}}$  as a conversion factor.

Multiply the mass of water in grams by the conversion factors.

1 mol H<sub>2</sub>O(I) 18.0 g H<sub>2</sub>O(I)

40.7 kJ 1 mol H<sub>2</sub>O(I) Use the thermochemical equation  $H_2O(1) + 40.7 \text{ kJ} \longrightarrow H_2O(g)$ 

 $\Delta H = 24.8 \text{ gH}_2 \Theta(\hat{t}) \times \frac{1 \text{ molH}_2 \Theta(\hat{t})}{18.0 \text{ gH}_2 \Theta(\hat{t})} \times \frac{40.7 \text{ kJ}}{1 \text{ molH}_2 \Theta(\hat{t})}$ = 56.1 kJ

**3 Evaluate** Does the result make sense? Knowing the molar mass of water is 18.0 g/mol, 24.8 g  $H_2O(l)$  can be estimated to be somewhat less than 1.5 mol  $H_2O$ . The calculated enthalpy change should be a little less than 1.5 mol  $\times$  40 kJ/mol = 60 kJ, and it is.

**24.** How much heat is absorbed when 63.7 g  $H_2O(l)$  at 100°C and 101.3 kPa is converted to  $H_2O(g)$  at 100°C? Express your answer in kJ.



**25.** How many kilojoules of heat are absorbed when 0.46 g of chloroethane (C<sub>2</sub>H<sub>5</sub>Cl, bp 12.3°C) vaporizes at its normal boiling point? The molar heat of vaporization of chloroethane is 24.7 kJ/mol.

For Problem 25, start by writing the thermochemical equation for the vaporization of chloroethane.

#### **Heat of Solution**

#### What thermochemical changes can occur when a solution forms?

If you've ever used a hot pack or a cold pack, then you have felt the enthalpy changes that occur when a solute dissolves in a solvent. During the formation of a solution, heat is either released or absorbed. The enthalpy change caused by the dissolution of one mole of substance is the molar heat of solution ( $\Delta H_{\rm soln}$ ). For example, when 1 mol of sodium hydroxide, NaOH(s), is dissolved in water, the solution can become so hot that it steams. The heat from this process is released as the sodium ions and the hydroxide ions interact with the water. The temperature of the solution increases, releasing 44.5 kJ of heat as the molar heat of solution.

NaOH(s) 
$$\longrightarrow$$
 Na<sup>+</sup>(aq) + OH<sup>-</sup>(aq)  
 $\Delta H_{\text{soln}} = -44.5 \text{ kJ/mol}$ 

A practical application of an exothermic dissolution process is a hot pack. In a hot pack, calcium chloride,  $CaCl_2(s)$ , mixes with water, producing heat.

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^{-}(aq)$$
  
 $\Delta H_{soln} = -82.8 \text{ kJ/mol}$ 

The dissolution of ammonium nitrate,  $NH_4NO_3(s)$ , is an example of an endothermic process. When ammonium nitrate dissolves in water, the solution becomes so cold that frost may form on the outside of the container. The cold pack in Figure 17.13 contains solid ammonium nitrate crystals and water. Once the solute dissolves in the solvent, the pack becomes cold. In this case, the solution process absorbs energy from the surroundings.

$$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$$
  
 $\Delta H_{soln} = 25.7 \text{ kJ/mol}$ 



#### Figure 17.13 Cold Pack

The cold pack shown has two sealed plastic bags, one inside the other. The outer bag contains ammonium nitrate crystals. The inner bag contains liquid water. When the pack is squeezed, the inner bag breaks, allowing the ammonium nitrate and water to mix.

Infer How would you define the system and the surroundings in this process?

# Sample Problem 17.7

#### Calculating the Enthalpy Change in Solution Formation

How much heat (in kJ) is released when 2.50 mol NaOH(s) is dissolved in water?

- **1** Analyze List the knowns and the unknown. Use the heat of solution for the dissolution of NaOH(s) in water to solve for the amount of heat released ( $\Delta H$ ).
- 2 Calculate Solve for the unknown.

KNOWNS

 $\Delta H_{\rm soln} = -44.5 \, \text{kJ/mol}$ amount of NaOH(s) dissolved = 2.50 mol

UNKNOWN

 $\Delta H = ? kJ$ 

Start by expressing  $\Delta H_{\text{soin}}$  as a conversion factor.

Use the thermochemical equation

$$NaOH(s) \longrightarrow Na^{+}(aq) + OH^{-}(aq) + 44.5 \text{ kJ/mol}$$

Multiply the number of moles by the conversion factor.

$$\Delta H = 2.50 \text{ mol NaOH(s)} \times \frac{-44.5 \text{ kJ}}{1 \text{ mol NaOH(s)}} = -111 \text{ kJ}$$

- **3** Evaluate Does the result make sense?  $\Delta H$  is 2.5 times greater than  $\Delta H_{\rm soln}$ , as it should be. Also,  $\Delta H$  should be negative, as the dissolution of NaOH(s) in water is exothermic.
- **26.** How much heat (in kJ) is released when 0.677 mol NaOH(s) is dissolved in water?



**27.** How many moles of NH<sub>4</sub>NO<sub>3</sub>(s) must be dissolved in water so that 88.0 kJ of heat is absorbed from the water?

 $\Delta H_{\rm soln}$  for the dissolution of NH<sub>4</sub>NO<sub>3</sub>(s) in water is 25.7 kJ/mol.



# 17.3 LessonCheck

- **28.** Describe How does the molar heat of fusion of a substance compare to its molar heat of solidification?
- **29.** Describe How does the molar heat of vaporization of a substance compare to its molar heat of condensation?
- **30.** Called Identify What enthalpy changes occur when a solute dissolves in a solvent?
- **31.** Calculate How much heat must be removed to freeze a tray of ice cubes at 0°C if the water has a mass of 225 g?
- **32.** Calculate How many kilojoules of heat are required to vaporize 50.0 g of ethanol,  $C_2H_6O$ ? The boiling point of ethanol is 78.3°C. Its molar heat of vaporization is 38.6 kJ/mol.
- **33.** Calculate How many kilojoules of heat are released when 25.0 g of NaOH(s) is dissolved in water?

#### **BIGIDEA** MATTER AND ENERGY

**34.** Use what you know about hydrogen bonding to explain why water has such a large heat of vaporization.

# Geothermal Energy

Deep within Earth lies a powerful source of clean, renewable energy—the heat of Earth's interior. This energy, known as geothermal energy, is contained in the molten rock (magma), hot water, and steam of Earth's subsurface. Underground pockets of hot steam or heated water can be harnessed to generate heat and electricity, which can then be used to heat, cool, and provide electrical power to buildings.

The three main ways to tap into Earth's geothermal energy supply is through direct heating systems, heat pumps, and power plants. Using direct geothermal energy involves piping hot water from hot springs on Earth's surface directly into a building's heat system. Geothermal heat pumps are systems that make use of the relatively constant temperatures near Earth's surface. In the winter, the temperature below Earth's surface is warmer than the temperature of the air. Heat pumps are used to move heat from the ground to the surface through a series of pipes containing fluid. In the summer, the temperature below Earth's surface is cooler than the temperature of the air. Therefore, heat pumps can also be used to cool buildings by drawing heat away from a building and transferring it to the ground outside. Geothermal power plants tap into hot water and steam buried deep beneath Earth's surface. Hot steam or water can then be piped or pumped under high pressures from geothermal reservoirs into generators in the power plants on the surface. These power plants provide electricity to homes and businesses.



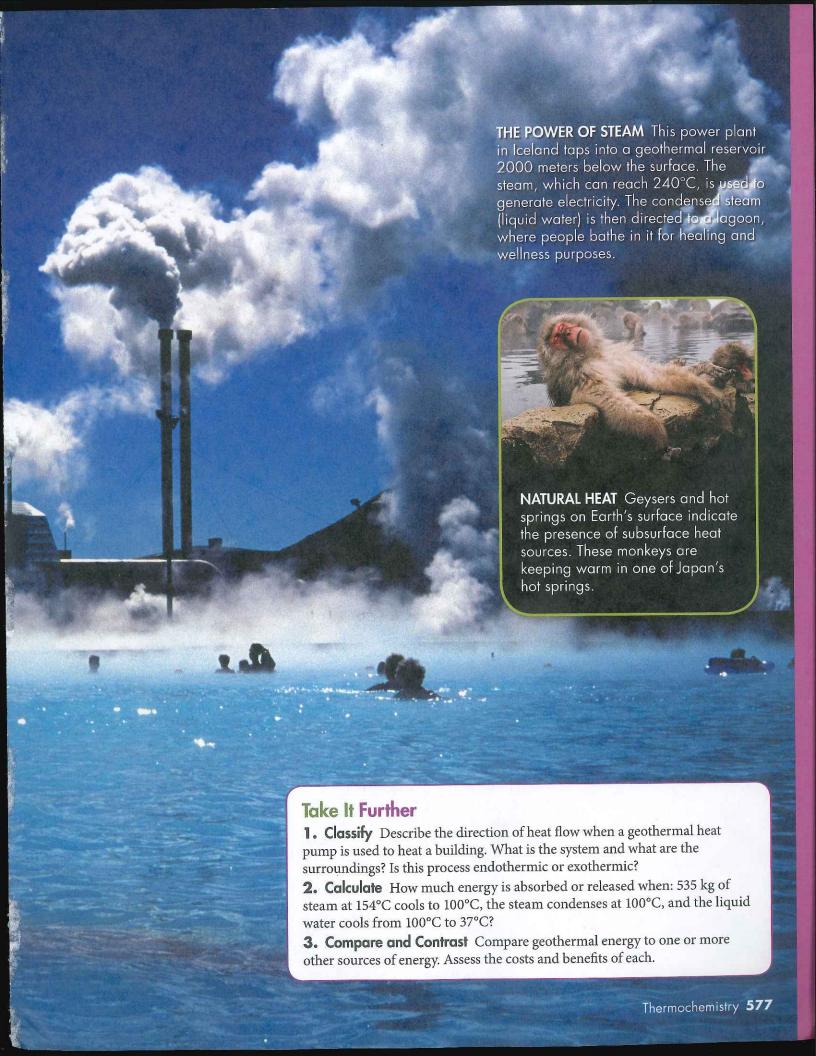
#### **Pros & Cons**

#### **Advantages of Using Geothermal Energy**

- Low operating costs Once the initial cost of constructing a geothermal energy facility has been paid for, there are no additional fuel costs.
- ✓ Clean Energy Direct geothermal heating systems, geothermal heat pumps, and geothermal power plants emit little or no greenhouse gases.
- ✓ Sustainable Energy Source Unlike fossil fuels, heat from beneath Earth's surface is a renewable resource.

#### Disadvantages of Using Geothermal Energy

- **X** Large initial expense The initial cost of drilling wells to reach geothermal reservoirs and installing geothermal power plants is millions of dollars.
- **X** Large space requirements Geothermal heat pumps and power plants require large expanses of land for pipes and wells.
- X Disruptive to the environment Deep drilling can cause small earthquakes and hot water and steam can bring contaminants to Earth's surface.



# 17.4 Calculating Heats of Reaction



# CHEMISTRY YOU

Q: How much heat is released when a diamond changes into graphite? Diamonds are gemstones composed of carbon. Over a time period of millions and millions of years, diamond will break down into graphite, which is another form of carbon. How then can you determine the enthalpy change for the reaction?

#### **Key Question**

How can you calculate the heat of reaction when it cannot be directly measured?

#### Vocabulary

- Hess's law of heat summation
- standard heat of formation

#### Hess's Law

# How can you calculate the heat of reaction when it cannot be directly measured?

Sometimes it is hard to measure the enthalpy change for a reaction. The reaction might take place too slowly to measure the enthalpy change, or the reaction might be an intermediate step in a series of reactions. Fortunately, it is possible to determine a heat of reaction indirectly using Hess's law of heat summation. Hess's law of heat summation states that if you add two or more thermochemical equations to give a final equation, then you can also add the heats of reaction to give the final heat of reaction. Hess's law allows you to determine the heat of reaction indirectly by using the known heats of reaction of two or more thermochemical equations.

Consider the conversion of diamond to graphite, discussed above.

$$C(s, diamond) \longrightarrow C(s, graphite)$$

Although the enthalpy change for this reaction cannot be measured directly, you can use Hess's law to find the enthalpy change for the conversion of diamond to graphite by using the following combustion reactions and Figure 17.14:

**a.** 
$$C(s, graphite) + O_2(g) \longrightarrow CO_2(g)$$
  $\Delta H = -393.5 \text{ kJ}$   
**b.**  $C(s, diamond) + O_2(g) \longrightarrow CO_2(g)$   $\Delta H = -395.4 \text{ kJ}$ 

Write equation **a** in reverse to give:

**c.** 
$$CO_2(g) \longrightarrow C(s, \text{ graphite}) + O_2(g)$$
  $\Delta H = 393.5 \text{ kJ}$ 

When you write a reverse reaction, you must also change the sign of  $\Delta H$ . If you add equations **b** and **c**, you get the equation for the conversion of diamond to graphite. The  $CO_2(g)$  and  $O_2(g)$  terms on both sides of the summed equations cancel. If you also add the values of  $\Delta H$  for equations **b** and **c**, you get the heat of reaction for this conversion.

$$C(s, diamond) + O_2(g) \longrightarrow CO_2(g)$$
  $\Delta H = -395.4 \text{ kJ}$   
 $CO_2(g) \longrightarrow C(s, graphite) + O_2(g)$   $\Delta H = 393.5 \text{ kJ}$   
 $C(s, diamond) \longrightarrow C(s, graphite)$   $\Delta H = -1.9 \text{ kJ}$ 

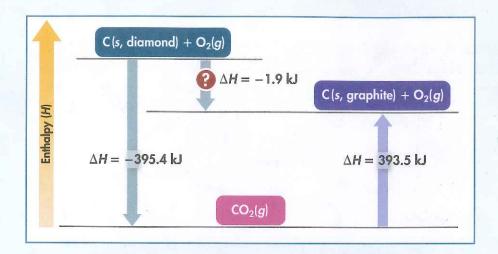


Figure 17.14 Conversion of Diamond to Graphite

Hess's law is used to determine the enthalpy change for the conversion of diamond to graphite.

Go online to see how Hess's law is used.



Another case where Hess's law is useful is when reactions yield products in addition to the product of interest. Suppose you want to determine the enthalpy change for the formation of carbon monoxide from its elements. You can write the following equation for this reaction.

 $\Delta H = ?$ 

$$C(s, graphite) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

Although it is easy to write the equation, carrying out the reaction in the laboratory as written is virtually impossible. Carbon dioxide is produced along with carbon monoxide. Therefore, any measured heat of reaction is related to the formation of both  $\mathrm{CO}(g)$  and  $\mathrm{CO}_2(g)$ , and not  $\mathrm{CO}(g)$  alone. However, you can calculate the desired enthalpy change by using Hess's law and the following two reactions that can be carried out in the laboratory:

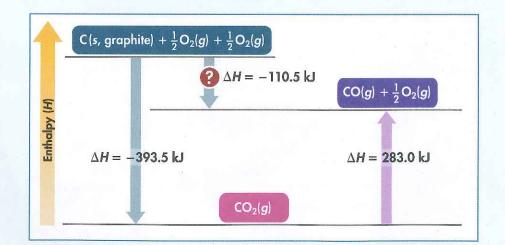
**a.** C(s, graphite) + O<sub>2</sub>(g) 
$$\longrightarrow$$
 CO<sub>2</sub>(g)  $\Delta H = -393.5 \text{ kJ}$   
**b.** CO(g) +  $\frac{1}{2}$ O<sub>2</sub>(g)  $\longrightarrow$  CO<sub>2</sub>(g)  $\Delta H = -283.0 \text{ kJ}$ 

Writing the reverse of equation  $\mathbf{b}$  yields equation  $\mathbf{c}$ .

c. 
$$CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g)$$
  $\Delta H = 283.0 \text{ kJ}$ 

Adding equations **a** and **c** gives the expression for the formation of CO(g) from its elements. The enthalpy diagram for this heat summation is shown in Figure 17.15. Notice that only  $\frac{1}{2}O_2(g)$  cancels from each equation.

C(s, graphite) + O<sub>2</sub>(g) 
$$\longrightarrow$$
 CO<sub>2</sub>(g)  $\Delta H = -393.5 \text{ kJ}$   
CO<sub>2</sub>(g)  $\longrightarrow$  CO(g) +  $\frac{1}{2}$ O<sub>2</sub>(g)  $\Delta H = 283.0 \text{ kJ}$   
C(s, graphite) +  $\frac{1}{2}$ O<sub>2</sub>(g)  $\longrightarrow$  CO(g)  $\Delta H = -110.5 \text{ kJ}$ 



#### CHEMISTRY YOU

**Q:** How can you determine ΔH for the conversion of diamond to graphite without performing the reaction?

# Figure 17.15 Formation of CO(g) From Its Elements

Hess's law is used to determine the enthalpy change for the formation of CO(g) from its elements.

Interpret Diagrams How does the diagram represent endothermic and exothermic reactions differently?

Table 17.4	State of the state				The second second					
Standard Heats of Formation (△H <sub>f</sub> °) at 25°C and 101.3 kPa										
Substance	∆H <sub>f</sub> ° (kJ/mol)	Substance	∆H <sub>f</sub> ° (kJ/mol)	Substance	∆H <sub>f</sub> ° (kJ/mol)					
Al <sub>2</sub> O <sub>3</sub> (s)	-1676.0	F <sub>2</sub> (g)	0.0	NO(g)	90.37					
Br <sub>2</sub> (g)	30.91	Fe(s)	0.0	NO <sub>2</sub> (g)	33.85					
Br <sub>2</sub> (/)	0.0	Fe <sub>2</sub> O <sub>3</sub> (s)	-822.1	NaCl(s)	-411.2					
C(s, diamond)	1.9	H <sub>2</sub> (g)	0.0	O <sub>2</sub> (g)	0.0					
C(s, graphite)	0.0	H <sub>2</sub> O(g)	-241.8	O <sub>3</sub> (g)	142.0					
CH <sub>4</sub> (g)	-74.86	H <sub>2</sub> O(I)	-285.8	P(s, white)	0.0					
CO(g)	-110.5	H <sub>2</sub> O <sub>2</sub> (I)	-187.8	P(s, red)	-18.4					
CO <sub>2</sub> (g)	-393.5	l <sub>2</sub> (g)	62.4	S(s, rhombic)	0.0					
CaCO <sub>3</sub> (s)	-1207.0	l <sub>2</sub> (s)	0.0	S(s, monoclinic)	0.30					
CaO(s)	-635.1	N <sub>2</sub> (g)	0.0	SO <sub>2</sub> (g)	-296.8					
Cl <sub>2</sub> (g)	0.0	NH <sub>3</sub> (g)	-46.19	SO <sub>3</sub> (g)	-395.7					

#### **Standard Heats of Formation**

How can you calculate the heat of reaction when it cannot be directly measured?

Enthalpy changes generally depend on conditions of the process. To compare enthalpy changes, scientists specify a common set of conditions. These conditions, called the standard state, refer to the stable form of a substance at 25°C and 101.3 kPa. The **standard heat of formation** ( $\Delta H_{\rm f}^{\rm o}$ ) of a compound is the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states. The  $\Delta H_{\rm f}^{\rm o}$  of a free element in its standard state is arbitrarily set at zero. Thus,  $\Delta H_{\rm f}^{\rm o}=0$  kJ/mol for the diatomic molecules  $H_2(g)$ ,  $N_2(g)$ ,  $O_2(g)$ ,  $F_2(g)$ ,  $Cl_2(g)$ ,  $Pl_2(g)$ , and  $Pl_2(g)$ , and  $Pl_2(g)$ ,  $Pl_2(g)$ ,

Standard heats of formation provide an alternative to Hess's law in determining heats of reaction indirectly. For a reaction that occurs at standard conditions, you can calculate the heat of reaction by using standard heats of formation. Such an enthalpy change is called the standard heat of reaction ( $\Delta H^{\circ}$ ). The standard heat of reaction is the difference between the standard heats of formation of all the reactants and products.

#### $\Delta H^{\circ} = \Delta H_{\scriptscriptstyle m f}^{\circ}$ (products) $-\Delta H_{\scriptscriptstyle m f}^{\circ}$ (reactants)

Figure 17.16 is an enthalpy diagram for the formation of water from its elements at standard conditions. The enthalpy difference between the reactants and products, -285.8 kJ/mol, is the standard heat of formation of liquid water from the gases hydrogen and oxygen. Notice that water has a lower enthalpy than the elements from which it is formed.

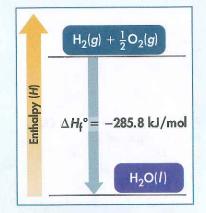


Figure 17.16 Standard Heat of Formation of Water

This enthalpy diagram shows the standard heat of formation of water.

Classify Is the reaction endothermic or exothermic?

#### Calculating the Standard Heat of Reaction

What is the standard heat of reaction ( $\Delta H^{\circ}$ ) for the reaction of CO(g) with O<sub>2</sub>(g) to form CO<sub>2</sub>(g)?

- **1** Analyze List the knowns and the unknown. Balance the equation of the reaction of CO(g) with  $O_2(g)$  to form  $CO_2(g)$ . Then determine  $\Delta H^\circ$  using the standard heats of formation of the reactants and products.
- 2 Calculate Solve for the unknown.

#### KNOWNS

(from Table 17.4)

 $\Delta H_f^{\circ}CO(g) = -110.5 \text{ kJ/mol}$ 

 $\Delta H_f^{\circ}O_2(g) = O \text{ kJ/mol (free element)}$ 

 $\Delta H_f^{\circ}CO_2(g) = -393.5 \text{ kJ/mol}$ 

#### UNKNOWN

 $\Delta H^{\circ} = ? kJ$ 

First, write the balanced equation.

 $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ 

Find and add  $\Delta H_{\rm f}^{\circ}$  of all of the reactants.

 $\Delta H_{\rm f}^{\circ}$  (reactants) = 2 mol  $CO(g) \times \Delta H_{\rm f}^{\circ}CO(g) + 1$  mol  $O_2(g) \times \Delta H_{\rm f}^{\circ}O_2(g)$ 

 $= 2 \operatorname{mol} \frac{60(g)}{1 \cdot \operatorname{mol} \frac{60(g)}{1 \cdot \operatorname{mol} \frac{60(g)}{2}} + 1 \operatorname{mol} \frac{0 \text{ kJ}}{1 \cdot \operatorname{mol} \frac{0}{2}(g)} \times \frac{0 \text{ kJ}}{1 \cdot \operatorname{mol} \frac{0}{2}(g)}$ 

 $= -221.0 \, kJ$ 

Find  $\Delta H_i^{\circ}$  of the product in a similar way.

 $\Delta H_{\rm f}^{\circ}({\rm products}) = 2 \, {\rm mol} \, {\rm CO}_2(g) \times \Delta H_{\rm f}^{\circ} {\rm CO}_2(g)$ 

 $= -787.0 \, \text{kJ}$ 

 $= 2 \operatorname{mol} \frac{60_{2}(g)}{1 \operatorname{mol} \frac{60_{2}(g)}{1}} \times \frac{-393.5 \,\mathrm{kJ}}{1 \operatorname{mol} \frac{60_{2}(g)}{1}}$ 

moles of each reactant and product.

Remember to take into account the number of

Calculate  $\Delta H^{\circ}$  for the reaction.

 $\Delta H^{\circ} = \Delta H_{\rm f}^{\circ} ({\rm products}) - \Delta H_{\rm f}^{\circ} ({\rm reactants})$ 

= (-787.0 kJ) - (-221.0 kJ)

 $= -566.0 \, \text{kJ}$ 

**3** Evaluate Does the result make sense? The  $\Delta H^{\circ}$  is negative, so the reaction is exothermic. This outcome makes sense because combustion reactions always release heat.

**35.** Calculate  $\Delta H^{\circ}$  for the following reaction:

$$Br_2(g) \longrightarrow Br_2(l)$$

Remember,  $Br_2(l)$  is a free element.



**36.** What is the standard heat of reaction  $(\Delta H^\circ)$  for the formation of  $NO_2(g)$  from NO(g) and  $O_2(g)$ ?

To do Problem 36, first write the balanced equation for the reaction. Figure 17.17 Reaction of Carbon Monoxide and Oxygen
Standard heats of formation are used to calculate the enthalpy change for the reaction of carbon monoxide and oxygen.

Explain How does this diagram also demonstrate Hess's law?

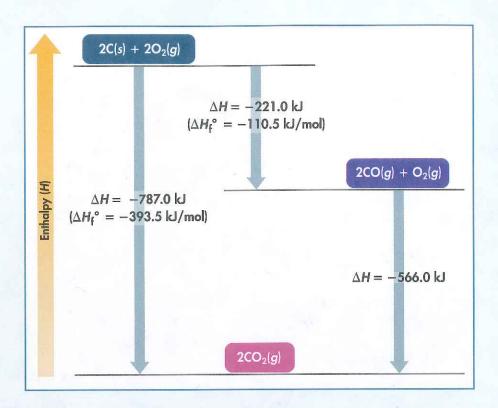


Figure 17.17 is an enthalpy diagram that shows how the standard heat of reaction was calculated in Sample Problem 17.8.

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

The standard heat of formation of the product,  $CO_2(g)$ , is -393.5 kJ/mol. The standard heats of formation of the reactants, CO(g) and  $O_2(g)$ , are -110.5 kJ/mol and 0 kJ/mol, respectively. The diagram shows the difference between  $\Delta H_{\rm f}$ °(product) and  $\Delta H_{\rm f}$ °(reactants) after taking into account the number of moles of each.

# 17.4 LessonCheck

- **37.** Describe What are two ways the heat of reaction can be determined when it cannot be directly measured?
- **38.** Calculate What is the enthalpy change  $(\Delta H)$  in kJ for the following reaction?

$$2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$$

Use the enthalpy changes for the combustion of aluminum and iron:

2Al(s) + 
$$\frac{3}{2}$$
O<sub>2</sub>(g)  $\longrightarrow$  Al<sub>2</sub>O<sub>3</sub>(s)  $\Delta H = -1676.0 \text{ kJ}$   
2Fe(s) +  $\frac{3}{2}$ O<sub>2</sub>(g)  $\longrightarrow$  Fe<sub>2</sub>O<sub>3</sub>(s)  $\Delta H = -822.1 \text{ kJ}$ 

- **39. Explain** How can you calculate the standard heat of reaction?
- **40.** Calculate What is the standard heat of reaction ( $\Delta H^{\circ}$ ) for the decomposition of hydrogen peroxide?

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

#### **BIGIDEA** MATTER AND ENERGY

**41.** Use Hess's law and two thermochemical equations on page R34 to calculate  $\Delta H$  for the following reaction:

$$2H_2O(g) + CH_4(g) \longrightarrow CO_2(g) + 4H_2(g)$$



#### Heat of Combustion of a Candle

Probe or sensor version of this lab is available in the *Probeware Lab Manual*.

#### **Purpose**

To observe a burning candle and calculate the heat associated with the combustion reaction

#### Materials

- ruler candle aluminum foil
- balance safety matches

# Procedure @ P () T

- 1. Measure and record the length of a candle in centimeters.
- **2.** Place the candle on a small piece of aluminum foil and measure the mass of the foil-candle system.
- **3.** Note the time as you light the candle. Let the candle burn for about five minutes. **CAUTION** *Keep clothing away from the flame.* While you wait, begin answering the Analyze and Conclude questions.
- **4.** Extinguish the candle and record the time.
- **5.** Measure the mass of the foil-candle system again. **DO NOT** try to measure the mass while the candle is burning.

#### **Analyze and Conclude**

- **1. Observe** While the candle is burning, draw a picture of what you see.
- **2. Observe** Examine the flame closely. Is it the wax or the wick that burns?
- **3.** Infer If you said the wax, how does the wax burn without touching the flame? If you said the wick, what is the function of the wax?
- **4. Analyze Data** If you could measure the temperature near the flame, you would find that the air is much hotter above the flame than it is beside it. Why?
- **5.** Draw Conclusions How much length and mass did the candle lose? Are these data more consistent with the wax or the wick burning?



- **6. Infer** Keeping in mind that *wick* is also a verb, explain how a candle works.
- **7. Describe** The formula for candle wax can be approximated as  $C_{20}H_{42}$ . Write a balanced equation for the complete combustion of candle wax.
- **8.** Calculate Determine the number of moles of candle wax burned in the experiment.
- **9. Calculate** What is the heat of combustion of candle wax in kJ/mol? The standard heat of formation of candle wax ( $C_{20}H_{42}$ ) is -2230 kJ/mol. The standard heats of formation of carbon dioxide gas and liquid water are -394 kJ/mol and -286 kJ/mol, respectively.
- **10.** Calculate Determine the amount of heat (in kJ) released in your reaction. (*Hint*: Multiply the number of moles of candle wax burned in the experiment by the heat of combustion of candle wax.)

#### You're the Chemist

- **1.** Design an Experiment Design an experiment to show that the candle wax does not burn with complete combustion.
- **2.** Design an Experiment Design an experiment to show that water is a product of the combustion of a candle.

# 17 Study Guide

#### **BIGIDEA** MATTER AND ENERGY

During a chemical or physical process, the energy of the universe is conserved. If energy is absorbed by the system in a chemical or physical process, the same amount of energy is released by the surroundings. Conversely, if energy is released by the system, the same amount of energy is absorbed by the surroundings. The heat of reaction or process can be determined experimentally through calorimetry. The heat of reaction can also be calculated by using the known heats of reaction of two or more thermochemical equations or by using standard heats of formation.

#### 17.1 The Flow of Energy

- Energy changes occur as either heat transfer or work, or a combination of both.
- During any chemical or physical process, the energy of the universe remains unchanged.
- The heat capacity of an object depends on both its mass and its chemical composition.
- thermochemistry (556)
- chemical potential energy (556) heat (556)
- system (557) surroundings (557)
- law of conservation of energy (557)
- endothermic process (557)
- exothermic process (557)
- heat capacity (559) specific heat (559)

$$C = \frac{q}{m \times \Delta T}$$

# **17.2** Measuring and Expressing Enthalpy Changes

- The value of  $\Delta H$  of a reaction can be determined by measuring the heat flow of the reaction at constant pressure.
- In a chemical equation, the enthalpy change for the reaction can be written as either a reactant or a product.

- calorimetry (562)
- calorimeter (562)
- enthalpy (562)
- thermochemical equation (565)
- heat of reaction (565)
- heat of combustion (568)

Key Equation 
$$q_{
m sys} = \Delta H = -q_{
m surr} = -m imes C imes \Delta T$$

#### 17.3 Heat in Changes of State

- The quantity of heat absorbed by a melting solid is exactly the same as the quantity of heat released when the liquid solidifies; that is,  $\Delta H_{\rm fus} = -\Delta H_{\rm solid}$ .
- The quantity of heat absorbed by a vaporizing liquid is exactly the same as the quantity of heat released when the vapor condenses; that is,

$$\Delta H_{\rm vap} = -\Delta H_{\rm cond}$$
.

- During the formation of a solution, heat is either released or absorbed.
- molar heat of fusion (569)
- molar heat of solidification (569)
- molar heat of vaporization (571)
- molar heat of condensation (572)
- molar heat of solution (574)

#### 17.4 Calculating Heats of Reaction

- Hess's law allows you to determine the heat of reaction indirectly by using the known heats of reaction of two or more thermochemical equations.
- For a reaction that occurs at standard conditions, you can calculate the heat of reaction by using standard heats of formation.
- Hess's law of heat summation (578)
- standard heat of formation (580)

 $\Delta H^{\circ} = \Delta H_{\rm f}^{\circ} (\text{products}) - \Delta H_{\rm f}^{\circ} (\text{reactants})$ 



# Math Tune-Up: Calculating Enthalpy Changes

#### Problem

When 75.0 mL of water containing 0.100 mol HCl at 21.0°C is added to 75.0 mL of water containing 0.100 mol NaOH at 21.0°C in a foam cup calorimeter, the temperature of the solution increases to 29.6°C. Calculate the enthalpy change (in kJ) during this reaction.

#### Analyze

#### Knowns:

 $C_{\text{water}} = 4.18 \text{ J/(g} \cdot ^{\circ}\text{C})$  $V_{\rm final} = V_{\rm HCl} + V_{\rm NaOH}$  $= 75.0 \, \text{mL} + 75.0 \, \text{mL}$  $= 150.0 \,\mathrm{mL}$  $\Delta T = T_{\rm f} - T_{\rm i}$ = 29.6°C - 21.0°C  $= 8.6^{\circ}C$  $density_{solution} = 1.00 \text{ g/mL}$ 

#### Unknown:

 $\Delta H = ? kJ$ 

Use 
$$\Delta H = -q_{\text{surr}}$$
  
=  $-m \times C \times \Delta T$ 

#### 2 Calculate

Calculate the mass of water.

$$m_{\text{water}} = 150.0 \text{ m/L} \times \frac{1.00 \text{ g}}{1 \text{ m/L}}$$
  
= 150.0 g

Use the values for  $m_{\text{water}}$ ,  $C_{\text{water}}$ , and  $\Delta T$  to calculate  $\Delta H$ .

$$\Delta H = -(150.0 \text{ g})(4.18 \text{ J/(g·V)})$$
  
× (8.6%)  
= -5400 J

 $\Delta H = -5.4 \text{ kJ}$ 

#### Evaluate

About 4 J of heat raises the temperature of 1 g of water 1°C, so 600 J of heat is required to raise the temperature of 150 g of water 1°C. To heat 150 g of water 9°C requires about 5400 J, or 5.4 kJ.

Note: For reactions in aqueous solutions, you can assume that the densities of the solutions are 1.00 g/mL.

How much heat is absorbed when 54.9 g H<sub>2</sub>O(l) at 100°C and 101.3 kPa is converted to  $H_2O(g)$  at 100°C?

Knowns:

Initial and final conditions are 100°C and 101.3 kPa mass of liquid water converted to steam =

$$\Delta H_{\rm vap} = 40.7~{\rm kJ/mol}$$

Unknown:

$$\Delta H = ? kJ$$

Refer to the thermochemical equation  $H_2O(l) + 40.7 \text{ kJ} \longrightarrow$  $H_2O(g)$  The required conversion factors come from the molar mass of water and  $\Delta H_{\text{van}}$ .

$$\frac{1 \operatorname{mol} H_2O(l)}{18.0 \operatorname{g} H_2O(l)} \operatorname{and} \frac{40.7 \operatorname{kJ}}{1 \operatorname{mol} H_2O(l)}$$

Multiply the mass of water by the conversion factors.

$$\Delta H = 54.9 \text{ g H}_{2}\Theta(l) \times \frac{1 \text{ mol H}_{2}O(l)}{18.0 \text{ g H}_{2}O(l)} \times \frac{40.7 \text{ kJ}}{1 \text{ mol H}_{2}O(l)}$$
$$\Delta H = 124 \text{ kJ}$$

Knowing the molar mass of water is 18.0 g/mol,  $54.9 \text{ g H}_{2}O(l)$  is about 3 mol H<sub>2</sub>O. The calculated enthalpy change should be about  $3 \text{ mol} \times 40 \text{ kJ/mol}$  $= 120 \, \text{kJ}$ , and it is.

What is the standard heat of reaction  $(\Delta H^{\circ})$  for the reaction of SO<sub>2</sub>(g) with  $O_2(g)$  to form  $SO_3(g)$ ?

Knowns:

(from Table 17.4)  $\Delta H_{\rm f}^{\circ} SO_2(g) = -296.8 \,\mathrm{kJ/mol}$  $\Delta H_f^{\circ}O_2(g) = 0 \text{ kJ/mol}$  $\Delta H_f \circ SO_3(g) = -395.7 \text{ kJ/mol}$ 

Unknown:

$$\Delta H^{\circ} = ? kJ$$

Use the standard heats of formation for the reactants and products to calculate

$$\Delta H^{\circ} = \Delta H_{\rm f}^{\circ} (\text{products}) - \Delta H_{\rm f}^{\circ} (\text{reactants})$$

Write the balanced equation.  $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ Find  $\Delta H_{\rm f}^{\circ}$  of the reactants.

$$\Delta H_{\rm f}^{\circ} \text{(reactants)} = 2 \text{ mol } SO_2(g) \times \frac{-296.8 \text{ kJ}}{1 \text{ mol } SO_2(g)} + 0 \text{ kJ} = -593.6 \text{ kJ}$$

Find  $\Delta H_{\rm f}^{\circ}$  of the product.

$$\Delta H_{\rm f}^{\circ}(\text{product}) = 2 \text{ mol } SO_3(g) \times \frac{-395.7 \text{ kJ}}{1 \text{ mol } SO_3(g)} = -791.4 \text{ kJ}$$

Calculate  $\Delta H^{\circ}$  for the reaction.  $\Delta H^{\circ} = (-791.4 \text{ kJ}) - (-593.6 \text{ kJ})$  $\Delta H^{\circ} = -197.8 \text{ kJ}$ 

The  $\Delta H^{\circ}$  is negative, so the reaction is exothermic. This makes sense because combustion reactions always release heat.

Remember: The  $\Delta H_{\rm f}^{\circ}$  of a free element in its standard state



#### Lesson by Lesson

#### 17.1 The Flow of Energy

- 42. Define chemical potential energy.
- **43.** What always happens when two objects of different temperatures come in contact? Give an example from your own experience.
- **44.** Why do you think it is important to define the system and the surroundings?
- **45.** Explain in your own words the law of conservation of energy.
- **46.** How do endothermic processes differ from exothermic processes?
- \*47. Two substances in a glass beaker chemically react, and the beaker becomes too hot to touch.
  - a. Is the reaction endothermic or exothermic?
  - **b.** If the two substances are defined as the system, what constitutes the surroundings?
- **\*48.** Classify these processes as endothermic or exothermic.
  - a. condensing steam
  - **b.** evaporating alcohol
  - c. burning alcohol
  - d. baking a potato
  - **49.** Describe the sign convention that is used when describing heat flow in a system.
- **50.** What is the relationship between a calorie and a Calorie?
- **★51.** Make the following conversions.
  - **a.**  $8.50 \times 10^2$  cal to Calories
  - b. 444 cal to joules
  - c. 1.8 kJ to joules
  - **d.**  $4.5 \times 10^{-1}$  kJ to calories
  - **52.** What factors determine the heat capacity of an object?
- **★53.** How much heat is required to raise the temperature of 400.0 g of silver 45°C?

# 17.2 Measuring and Expressing Enthalpy Changes

- **54.** Calorimetry is based on what basic concepts?
- 55. What is the function of a calorimeter?

- **56.** What is the property that describes heat change at constant pressure?
- **57.** What device would you use to measure the heat released at constant volume?
- **58.** What information is given in a thermochemical equation?
- **★59.** The burning of magnesium is a highly exothermic reaction.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s) + 1204 kJ$$

How many kilojoules of heat are released when 0.75 mol of Mg burn in an excess of O<sub>2</sub>?

**60.** Give the standard conditions for heat of combustion.

#### 17.3 Heat in Changes of State

- **61.** Explain why ice melts at 0°C without an increase of temperature, even though heat flows from the surroundings to the system (the ice).
- **★62.** Calculate the quantity of heat gained or lost in the following changes:
  - a. 3.50 mol of water freezes at 0°C
  - b. 0.44 mol of steam condenses at 100°C
  - c. 1.25 mol NaOH(s) dissolves in water
  - **d.**  $0.15 \text{ mol } C_2H_6O(l) \text{ vaporizes at } 78.3^{\circ}\text{C}$
- **63.** Sodium ethanoate dissolves readily in water according to the following equation:

$$NaC_2H_3O_2(s) \longrightarrow NaC_2H_3O_2(aq)$$
  
 $\Delta H = -17.3 \text{ kJ/mol}$ 

Would this process increase or decrease the temperature of the water?

#### 17.4 Calculating Heats of Reaction

- 64. Explain Hess's law of heat summation.
- **\*65.** A considerable amount of heat is required for the decomposition of aluminum oxide.

$$2\text{Al}_2\text{O}_3(s) \longrightarrow 4\text{Al}(s) + 3\text{O}_2(g)$$
  
 $\Delta H = 3352 \text{ kJ}$ 

- **a.** What is the enthalpy change for the formation of 1 mol of aluminum oxide from its elements?
- **b.** Is the reaction endothermic or exothermic?

**\*66.** Calculate the enthalpy change for the formation of lead(IV) chloride by the reaction of lead(II) chloride with chlorine.

$$PbCl_2(s) + Cl_2(g) \longrightarrow PbCl_4(l)$$
  
 $\Delta H = ?$ 

Use the following thermochemical equations:

$$Pb(s) + 2Cl_{2}(g) \longrightarrow PbCl_{4}(l)$$

$$\Delta H = -329.2 \text{ kJ}$$

$$Pb(s) + Cl_{2}(g) \longrightarrow PbCl_{2}(s)$$

$$\Delta H = -359.4 \text{ kJ}$$

- **67.** What is the standard heat of formation of a compound?
- **68.** What is the standard heat of formation of a free element in its standard state?

#### **Understand Concepts**

- **69.** How many kilojoules of heat are absorbed when 1.00 L of water is heated from 18°C to 85°C?
- \*70. Equal masses of two substances absorb the same amount of heat. The temperature of substance A increases twice as much as the temperature of substance B. Which substance has the higher specific heat? Explain.
  - **71.** Identify each enthalpy change by name and classify each change as endothermic or exothermic.
    - **a.** 1 mol  $C_3H_8(l) \longrightarrow 1$  mol  $C_3H_8(g)$
    - **b.** 1 mol Hg(l)  $\longrightarrow$  1 mol Hg(s)
    - c.  $1 \mod NH_3(g) \longrightarrow 1 \mod NH_3(l)$
    - **d.** 1 mol NaCl(s) +  $3.88 \text{ kJ} \longrightarrow$

1 mol NaCl(aq)

- e. 1 mol NaCl(s)  $\longrightarrow$  1 mol NaCl(l)
- **72.** Name at least three sources of error in experiments that use foam cups as calorimeters.
- **73.** Calculate the enthalpy change in calories when 45.2 g of steam at 100°C condenses to water at the same temperature. What is the enthalpy change in joules?
- \*74. A 1.55-g piece of stainless steel absorbs 141 J of heat when its temperature increases by 178°C. What is the specific heat of the stainless steel?
  - **75.** With one exception, the standard heats of formation of Na(s),  $O_2(g)$ ,  $Br_2(l)$ , CO(g), Fe(s), and He(g) are identical. What is the exception?

**\*76.** Calculate the change in enthalpy (in kJ) for the following reactions using standard heats of formation ( $\Delta H_f^{\circ}$ ):

**a.** 
$$CH_4(g) + \frac{3}{2}O_2(g) \longrightarrow CO(g) + 2H_2O(l)$$
  
**b.**  $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ 

**77.** The amounts of heat required to change different quantities of carbon tetrachloride,  $CCl_4(l)$ , into vapor are given in the table.

Mass of CCl <sub>4</sub>	Heat						
(g)	(J)	(cal)					
2.90	652	156					
7.50	1689	404					
17.0	3825	915					
26.2	5894	1410					
39.8	8945	2140					
51.0	11453	2740					

- **a.** Graph the data, using heat as the dependent variable.
- **b.** What is the slope of the line?
- **c.** The heat of vaporization of  $CCl_4(l)$  is 53.8 cal/g. How does this value compare with the slope of the line?
- **\*78.** Find the enthalpy change for the formation of phosphorus pentachloride from its elements.

$$2P(s) + 5Cl_2(g) \longrightarrow 2PCl_5(s)$$

Use the following thermochemical equations:

$$PCl_5(s) \longrightarrow PCl_3(g) + Cl_2(g)$$
  
 $\Delta H = 156.5 \text{ kJ}$   
 $2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(g)$   
 $\Delta H = -574.0 \text{ kJ}$ 

- **79.** Use standard heats of formation ( $\Delta H_{\rm f}^{\circ}$ ) to calculate the change in enthalpy for these reactions.
  - **a.**  $2C(s, graphite) + O_2(g) \longrightarrow 2CO(g)$
  - **b.**  $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$
  - c.  $4NH_3(g) + 5O_2(g) \longrightarrow$

 $4NO(g) + 6H_2O(g)$ 

- **d.**  $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
- **80.** The molar heat of vaporization of ethanol, C<sub>2</sub>H<sub>6</sub>O(*l*), is 38.6 kJ/mol. Calculate the heat required to vaporize 25.0 g of ethanol at its boiling point.

- **★81.** An orange contains 106 Calories. What mass of water could this same amount of energy raise from 25.0°C to the boiling point?
  - 82. The combustion of ethene (C<sub>2</sub>H<sub>4</sub>) is an exothermic reaction.

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$$
  
 $\Delta H = -1.40 \times 10^3 \text{ kJ}$ 

Calculate the amount of heat liberated when 4.79 g C<sub>2</sub>H<sub>4</sub> reacts with excess oxygen.

**83.** Calculate the enthalpy change  $(\Delta H)$  for the formation of nitrogen monoxide from its elements.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

Use the following thermochemical equations:

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(l)$$
  
 $\Delta H = -1.53 \times 10^3 \text{ kJ}$   
 $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$   
 $\Delta H = -1.17 \times 10^3 \text{ kJ}$ 

- 84. How much heat must be removed from a 45.0-g sample of liquid naphthalene (C<sub>10</sub>H<sub>8</sub>) at its freezing point to bring about solidification? The heat of fusion of naphthalene is 19.1 kJ/mol.
- **★85.** If 3.20 kcal of heat is added to 1.00 kg of ice at 0°C, how much liquid water at 0°C is produced, and how much ice remains?

#### Think Critically

- 86. Relate Cause and Effect Your fingers quickly begin to feel cold when you touch an ice cube. What important thermochemical principle does this change illustrate?
- **87.** Calculate You place a bottle containing 2.0 L of mineral water at 25°C into a refrigerator to cool to 7°C.
  - a. How many kJ of heat are lost by the water?
  - **b.** How many kJ of heat are absorbed by the refrigerator?
  - c. What assumptions did you make in your calculations?
- **88.** Evaluate Consider the statement, "the more negative the value of  $\Delta H_f^{\circ}$ , the more stable the compound." Is this statement true or false? Explain.

**\*89.** Calculate When 1.000 mol of  $N_2(g)$  reacts completely with 3.000 mol of H<sub>2</sub>(g), 2.000 mol of  $NH_3(g)$  and 92.38 kJ of heat are produced.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + 92.38 \text{ kJ}$$

Use this thermochemical equation to calculate  $\Delta H$  for the following reactions:

**a.** 
$$2N_2(g) + 6H_2(g) \longrightarrow 4NH_3(g)$$

**b.** 
$$\frac{3}{2}N_2(g) + \frac{9}{2}H_2(g) \longrightarrow 3NH_3(g)$$
  
**c.**  $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ 

c. 
$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$$

- 90. Explain Why is fusion an endothermic process, but freezing is an exothermic process?
- **★91.** Calculate An ice cube with a mass of 40.0 g melts in water originally at 25.0°C.
  - a. How much heat does the ice cube absorb from the water when it melts? Report your answer in calories, kilocalories, and joules.
  - **b.** Calculate the number of grams of water that can be cooled to 0°C by the melting ice cube.
  - 92. Evaluate and Revise Evaluate this statement: "The energy content of a substance is higher in the liquid phase than in the vapor phase at the same temperature." If the statement is incorrect, restate it so it is correct.
  - 93. Apply Concepts Using the following equations,

$$Ca(s) + 2C(s) \longrightarrow CaC_{2}(s)$$

$$\Delta H = -62.8 \text{ kJ}$$

$$CO_{2}(g) \longrightarrow C(s) + O_{2}(g)$$

$$\Delta H = 393.5 \text{ kJ}$$

$$CaCO_{3}(s) + CO_{2}(g) \longrightarrow CaC_{2}(s) + \frac{5}{2}O_{2}(g)$$

$$\Delta H = 1538 \text{ kJ}$$

determine the heat of reaction (in kJ) for

$$Ca(s) + C(s) + \frac{3}{2}O_2(g) \longrightarrow CaCO_3(s)$$

**\*94.** Calculate The sugar glucose  $(C_6H_{12}O_6)$  is an important nutrient for living organisms to meet their energy needs. The standard heat of formation ( $\Delta H_f^{\circ}$ ) of glucose is -1260 kJ/mol. Calculate how much heat (in kJ/mol) is released at standard conditions if 1 mol of glucose undergoes the following reaction:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

#### **Enrichment**

**95.** Calculate Ethane,  $C_2H_6(g)$ , can be formed by the reaction of ethene,  $C_2H_4(g)$ , with hydrogen gas.

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

Use the heats of combustion for the following reactions to calculate the heat change for the formation of ethane from ethene and hydrogen.

$$2H_{2}(g) + O_{2}(g) \longrightarrow 2H_{2}O(l)$$

$$\Delta H = -5.72 \times 10^{2} \text{ kJ}$$

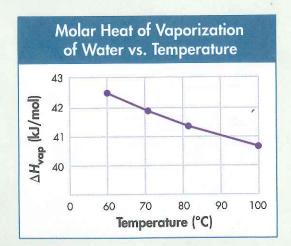
$$C_{2}H_{4}(g) + 3O_{2}(g) \longrightarrow 2CO_{2}(g) + 2H_{2}O(l)$$

$$\Delta H = -1.401 \times 10^{3} \text{ kJ}$$

$$2C_{2}H_{6}(g) + 7O_{2}(g) \longrightarrow 4CO_{2}(g) + 6H_{2}O(l)$$

$$\Delta H = -3.100 \times 10^{3} \text{ kJ}$$

- **96.** Infer An ice cube at 0°C was dropped into 30.0 g of water in a cup at 45.0°C. At the instant that all of the ice was melted, the temperature of the water in the cup was 19.5°C. What was the mass of the ice cube?
- \*97. Calculate A 41.0-g piece of glass at 95°C is placed in 175 g of water at 21°C in an insulated container. They are allowed to come to the same temperature. What is the final temperature of the glass-water mixture? The specific heat of glass is 2.1 cal/(g.°C).
  - **98. Interpret Graphs** The molar heat of vaporization of water at various temperatures is given in the graph. Estimate the amount of heat required to convert 1 L of water to steam on the summit of Mount Everest (8850 m), where the boiling temperature of water is 70°C.



#### Write About Science

- **99. Explain** Use the concept of heat capacity to explain why on a sunny day, the concrete deck around an outdoor swimming pool becomes hot, while the water stays cool.
- **100.** Compare Why is a burn from steam potentially far more serious than a burn from very hot water?

## **CHEM**YSTERY

#### Fighting Frost

If the temperature of the branches, leaves, and fruit of a citrus tree falls below 0°C, severe damage can occur. When ice crystals form in the plant cells, water becomes



unavailable to the plant tissues. This lack of fluids can kill a young tree. The fruit itself can also be damaged by frost. The juice vesicles inside the fruit rupture as ice crystals form within them. These ruptured vesicles cause the fruit to lose water and dry out. Upon an impending frost, if the fruit is not ready for harvest, citrus growers must find a way to protect their precious crops.

Spraying the trees with water throughout the duration of a frost is an effective way to prevent the trees and fruit from freezing. The water freezes directly on the branches, leaves, and fruit. Freezing is an exothermic process. As the water freezes, it releases heat and prevents the plant cells from reaching freezing temperatures.

- **101.** Apply Concepts Identify the system and the surroundings when water freezes on a citrus fruit.
- \*102. Predict Evaporation of the water on a plant surface can occur under dry and windy conditions. How would this affect the citrus tree and fruit?
- 103. Connect to the **BIGIDEA** Explain, in terms of the law of conservation of energy, why the freezing of water on a citrus tree can cause the temperature of the tree to increase.

#### **Cumulative Review**

- **104.** Explain the difference between an independent variable and a dependent variable.
- **105.** Write the correct chemical symbol for each element.
  - a. chromium
  - b. copper
  - c. carbon
  - d. calcium
  - e. cesium
- **★106.** Express the results of the following calculations with the correct number of significant figures.
  - **a.**  $6.723 \text{ m} \times 1.04 \text{ m}$
  - **b.** 8.934 g + 0.2005 g + 1.55 g
  - c.  $864 \text{ m} \div 2.4 \text{ s}$
  - d. 9.258°C 4.82°C
  - **107.** List three kinds of subatomic particles in an atom. Describe each kind in terms of charge, relative mass, and location with respect to the nucleus.
- **\*108.** Calculate the wavelength of a radio wave with a frequency of  $93.1 \times 10^6 \, \text{s}^{-1}$ .
- **109.** List the following atoms in order of increasing atomic radius: phosphorus, germanium, arsenic.
- **110.** How many chloride ions would be required to react with these cations to make an electrically neutral particle?
  - a. strontium cation
  - b. calcium cation
  - c. aluminum cation
  - d. lithium cation
- 111. How does a polar covalent bond differ from a nonpolar covalent bond? Which type of bond is found in molecular oxygen (O<sub>2</sub>)? In carbon monoxide (CO)?
- **★112.** Write formulas for the following compounds:
  - a. potassium nitride
  - **b.** aluminum sulfide
  - c. calcium nitrate
  - d. calcium sulfate

- **\*113.** How many hydrogen molecules are in 44.8 L  $H_2(g)$  at STP?
- **114.** Write the net ionic equation for the reaction of aqueous solutions of sodium chloride and silver acetate.
- \*115. When lightning flashes, nitrogen and oxygen combine to form nitrogen monoxide. The nitrogen monoxide reacts with oxygen to form nitrogen dioxide. Write equations for these two reactions.



**116.** How many grams of oxygen are formed by the decomposition of 25.0 g of hydrogen peroxide?

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

- **117.** What fraction of the average kinetic energy of hydrogen gas at 100 K does hydrogen gas have at 40 K?
- **\*118.** A gas has a volume of 8.57 L at 273 K. What will be the volume at 355 K if its pressure does not change?
- **119.** What property of water makes it impossible to find pure water in nature?
- **120.** Do colloids, suspensions, or solutions contain the smallest particles? Which contain the largest particles?

If You I	Have	Trou	ble V	Vith .													
Question	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
See Chapter	1	2	3	4	5	6	7	8	9	10	11	11	12	13	14	15	15

# Standardized Test Prep

Select the choice that best answers each question or completes each statement.

#### Tips for Success

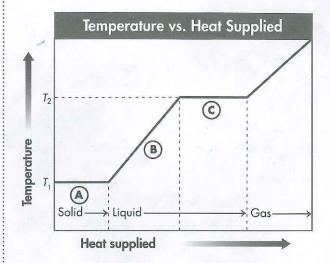
**Eliminate Wrong Answers** If you don't know which response is correct, start by eliminating those you know are wrong. If you can rule out some choices, you'll have fewer left to consider and you'll increase your chances of choosing the correct answer.

- 1. The  $\Delta H_{\text{fus}}$  of ethanol (C<sub>2</sub>H<sub>6</sub>O) is 4.93 kJ/mol. How many kilojoules are required to melt 24.5 g of ethanol at its freezing point?
  - (A) 2.63 kJ
- (C) 9.27 kJ
- (B) 4.97 kJ
- (D) 263 kJ
- **2.** How much heat, in kilojoules, must be added to 178 g of liquid water to increase the temperature of the water by 5.0°C?
  - (A) 890 kJ
- (C) 3.7 kJ
- (B) 36 kJ
- (D) 0.093 kJ
- **3.** The standard heat of formation of a free element in its standard state is always
  - (A) zero.
  - (B) positive.
  - (C) negative.
  - (D) higher for solids than for gases.
- **4.** If  $\Delta H$  for the reaction  $2 \text{HgO}(s) \longrightarrow 2 \text{Hg}(l) + O_2(g)$  is 181.66 kJ, then  $\Delta H$  for the reaction  $\text{Hg}(l) + \frac{1}{2}O_2(g) \longrightarrow \text{HgO}(s)$  is
  - (A) 90.83 kJ.
- (C) -90.83 kJ.
- (B) 181.66 kJ.
- (D) -181.66 kJ.
- 5. The specific heat capacity of ethanol is ten times larger than the specific heat capacity of silver. A hot bar of silver with a mass of 55 g is dropped into an equal mass of cool alcohol. If the temperature of the silver bar drops 45°C, the temperature of the alcohol
  - (A) increases 45°C.
  - (B) decreases 4.5°C.
  - (C) increases 4.5°C.
  - (D) decreases 45°C.

**6.** Hydrogen gas and fluorine gas react to form hydrogen fluoride, HF. Calculate the enthalpy change (in kJ) for the conversion of 15.0 g of  $H_2(g)$  to HF(g) at constant pressure.

$$H_2(g) + F_2(g) \longrightarrow 2HF(g)$$
  
 $\Delta H = -536 \text{ kJ}$ 

Use the graph and table to answer Questions 7–10. Assume 1.00 mol of each substance.



Substance	Freezing point (K)	∆H <sub>fus</sub> (kJ/mol)	Boiling point (K)	$\Delta H_{ m vap} \ ({ m kJ/mol})$
Ammonia	195.3	5.66	239.7	23.3
Benzene	278.7	9.87	353.3	30.8
Methanol	175.5	3.22	337.2	35.2
Neon	24.5	0.33	27.1	1.76

- 7. Calculate heat absorbed in region A for neon.
- 8. Calculate heat absorbed in region C for ammonia.
- **9.** Calculate heat absorbed in regions B and C for methanol. [specific heat = 2.53 J/(g·°C)]
- **10.** Calculate heat absorbed in regions A, B, and C for benzene. [specific heat = 1.74 J/(g·°C)]

If You He	ave Trou	ble Wit	h							
Question	1	2	3	4	5	6	7	8	9	10
See Lesson	1 <i>7</i> .3	17.1	17.4	17.4	17.1	17.2	17.3	17.3	17.3	17.3