



# Energy and Chemical Change

## What You'll Learn

- ▶ You will measure and calculate the energy involved in chemical changes.
- ▶ You will write thermochemical equations and use them to calculate changes in enthalpy.
- ▶ You will explain how changes in enthalpy, entropy, and free energy affect the spontaneity of chemical reactions and other processes.

## Why It's Important

Energy enables you to live, move from place to place, and stay comfortably warm or cool. Almost all of the energy you use comes from chemical reactions, including those that take place in your own body.



Visit the Chemistry Web site at [chemistrymc.com](http://chemistrymc.com) to find links about energy and chemical change.

Each time the roller coaster zooms up and down the track, its energy changes back and forth between kinetic energy of motion and potential energy of position.





## DISCOVERY LAB



### Materials

test tubes (2)  
 thermometer  
 25-mL graduated cylinder  
 test tube rack  
 distilled water  
 5M HCl  
 5M NaOH

### Temperature of a Reaction

**D**oes a temperature change occur when a chemical reaction takes place?

### Safety Precautions



Use care when handling HCl and NaOH solutions.

### Procedure

1. Measure about 5 mL 5M NaOH solution and pour it into a large test tube. Determine the temperature of the solution.
2. Rinse the thermometer and the graduated cylinder with distilled water as directed by your teacher. Repeat step 1 using 5M HCl.
3. Pour the HCl solution into the NaOH solution. Immediately insert the thermometer and record the temperature of the mixture. How does it compare to the temperatures of NaOH and HCl solutions?

### Analysis

What evidence do you have that a chemical reaction has occurred? Write the balanced chemical equation for the reaction between aqueous sodium hydroxide and aqueous hydrochloric acid.

## Section

## 16.1

# Energy

### Objectives

- **Explain** what energy is and distinguish between potential and kinetic energy.
- **Relate** chemical potential energy to the heat lost or gained in chemical reactions.
- **Calculate** the amount of heat absorbed or released by a substance as its temperature changes.

### Vocabulary

energy  
 law of conservation of energy  
 chemical potential energy  
 heat  
 calorie  
 joule  
 specific heat

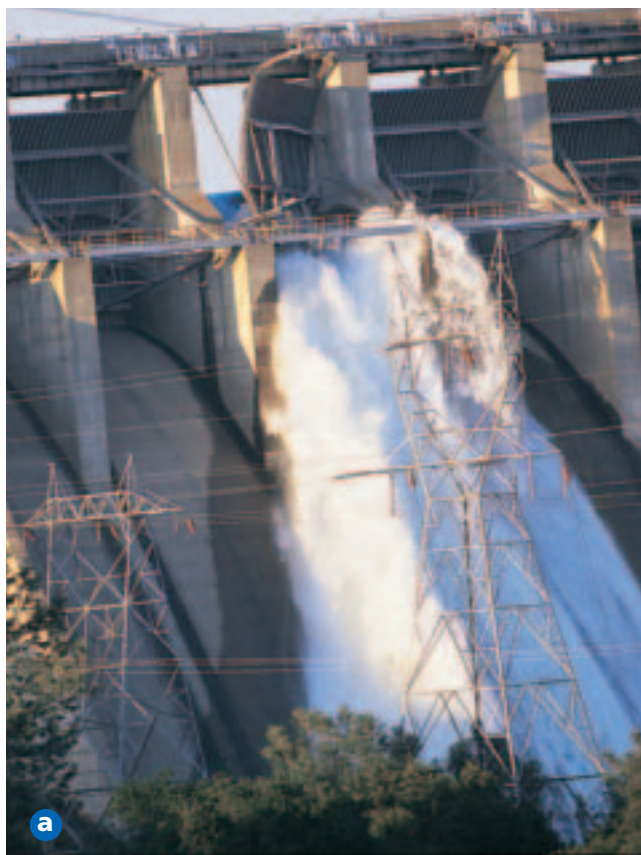
You're familiar with the term *energy*. Perhaps you've heard someone say, "I just ran out of energy," after a strenuous game or a difficult day. Solar energy, nuclear energy, energy-efficient automobiles, and other energy-related topics are often discussed in the media. In the **DISCOVERY LAB**, you observed a temperature change associated with the release of energy during a chemical reaction. But does energy affect your everyday life?

### The Nature of Energy

Energy cooks the food you eat and propels the vehicles that transport you. If the day is especially hot or cold, energy from burning fuels helps keep your home and school comfortable. Electrical energy provides light and operates devices from computers and TV sets to cellular phones, wristwatches, and calculators. Energy helped manufacture and deliver every material and device in your home, including the clothes you wear. Your every movement and thought requires energy. In fact, you can think of each cell in your body as a miniature factory that runs on energy derived from the food you eat. These examples only begin to define the role that energy plays in your life.

What is energy? **Energy** is the ability to do work or produce heat. It exists in two basic forms, potential energy and kinetic energy. Potential energy is energy due to the composition or position of an object. A macroscopic example of potential energy of position is water stored behind a dam above the turbines of a hydroelectric generating plant. When the dam gates are opened,





**Figure 16-1**

Energy is conserved in these energy transformations. In **a**, some of the potential energy of water stored behind Folsom Dam in California is converted to electrical energy. In **b**, the chemical potential energy stored in wood is converted to heat.

the water rushes down and does work by turning the turbines to produce electrical energy.

Kinetic energy is energy of motion. You can observe kinetic energy in the motion around you. The potential energy of the dammed water is converted to kinetic energy as the dam gates are opened and the water flows out.

Chemical systems contain both kinetic energy and potential energy. Recall from Chapter 13 that the kinetic energy of a substance is directly related to the constant random motion of its atoms or molecules and is proportional to temperature. As temperature increases, the motion of submicroscopic particles increases. The potential energy of a substance depends upon its composition: the type of atoms in the substance, the number and type of chemical bonds joining the atoms, and the particular way the atoms are arranged.

**Law of conservation of energy** When water rushes through turbines in the hydroelectric plant in **Figure 16-1a**, some of the water's potential energy is converted to electrical energy. When wood burns in a fireplace, as shown in **Figure 16-1b**, potential energy is liberated as heat. In both of these examples, energy changes from one form to another. But does the amount of energy change? No. As energy changes from one form to another, the total amount of energy remains constant. Energy is conserved. To better understand the conservation of energy, suppose you have money in two accounts at a bank and you transfer funds from one account to the other. Although the amount of money in each account has changed, the total amount of your money in the bank remains the same. When applied to energy, this analogy embodies the law of conservation of energy. The **law of conservation of energy** states that in any chemical reaction or physical process, energy can be converted from one form to another, but it is neither created nor destroyed. This also is known as the first law of thermodynamics.

**Chemical potential energy** The energy stored in a substance because of its composition is called **chemical potential energy**. Chemical potential energy plays an important role in chemical reactions. For example, consider octane ( $C_8H_{18}$ ), one of the principal components of gasoline. The chemical potential energy of octane results from the arrangement of the carbon and



hydrogen atoms and the strength of the bonds that join them. When gasoline burns in an automobile's engine, some of octane's stored energy is converted to work in moving the pistons, which ultimately move the wheels and propel the automobile and its occupants from place to place. However, much of the potential energy of octane is released as heat. **Heat**, which is represented by the symbol  $q$ , is energy that is in the process of flowing from a warmer object to a cooler object. When the warmer object loses heat, its temperature decreases. When the cooler object absorbs heat, its temperature rises.

**Measuring heat** The flow of energy and the resulting change in temperature are clues to how heat is measured. In the metric system of units, the amount of heat required to raise the temperature of one gram of pure water by one degree Celsius ( $1^{\circ}\text{C}$ ) is defined as a **calorie** (cal). You've heard much about the caloric content of various foods. When your body breaks down sugars and fats to form carbon dioxide and water, these exothermic reactions generate heat that can be measured in Calories. Note that the nutritional Calorie is capitalized. That's because one nutritional Calorie, also known as one kilocalorie (kcal), equals 1000 calories. Suppose you eat a tablespoon of butter. One tablespoon of butter "has" 100 Calories. That means that if the butter was burned completely to produce carbon dioxide and water, 100 kcal (100 000 cal) of heat would be released.

The SI unit of heat and energy is the **joule** (J). One joule is the equivalent of 0.2390 calories, or one calorie equals 4.184 joules. **Table 16-1** shows the relationships among calories, nutritional Calories, joules, and kilojoules (kJ) and the conversion factors you can use to convert from one unit to another.

**Table 16-1**

Relationships Among Energy Units	
Relationship	Conversion factors
$1 \text{ J} = 0.2390 \text{ cal}$	$\frac{1 \text{ J}}{0.2390 \text{ cal}}$ $\frac{0.2390 \text{ cal}}{1 \text{ J}}$
$1 \text{ cal} = 4.184 \text{ J}$	$\frac{1 \text{ cal}}{4.184 \text{ J}}$ $\frac{4.184 \text{ J}}{1 \text{ cal}}$
$1 \text{ kJ} = 1000 \text{ J}$	$\frac{1 \text{ kJ}}{1000 \text{ J}}$ $\frac{1000 \text{ J}}{1 \text{ kJ}}$
$1 \text{ Calorie} = 1 \text{ kcal}$	$\frac{1 \text{ Calorie}}{1000 \text{ cal}}$
$1 \text{ kcal} = 1000 \text{ cal}$	$\frac{1000 \text{ cal}}{1 \text{ kcal}}$

## EXAMPLE PROBLEM 16-1

### Converting Energy Units

The breakfast shown in the photograph contains 230 nutritional Calories. How much energy in joules will this healthy breakfast supply?

#### 1. Analyze the Problem

You are given an amount of energy in nutritional Calories. You must convert nutritional Calories to calories and then calories to joules.

**Known**

amount of energy = 230 Calories

**Unknown**

amount of energy = ? J

#### 2. Solve for the Unknown

Use a conversion factor from **Table 16-1** to convert nutritional Calories to calories.

$$230 \text{ Calories} \times \frac{1000 \text{ cal}}{1 \text{ Calorie}} = 2.3 \times 10^5 \text{ cal}$$

Use a conversion factor to convert calories to joules.

$$2.3 \times 10^5 \text{ cal} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 9.6 \times 10^5 \text{ J}$$

#### 3. Evaluate the Answer

The minimum number of significant figures used in the conversion is two, so the answer correctly has two digits. A value of the order of  $10^5$  or  $10^6$  is expected because the given number of kilocalories is of the order of  $10^2$  and it must be multiplied by  $10^3$  to convert it to calories. Then, the calories must be multiplied by a factor of approximately 4. Therefore, the answer is reasonable.



It's important to eat the appropriate number of Calories. It's also important that the foods you select provide the nutrients your body needs.







For more practice converting from one energy unit to another, go to **Supplemental Practice Problems** in Appendix A.

## PRACTICE PROBLEMS

1. A fruit and oatmeal bar contains 142 nutritional Calories. Convert this energy to calories.
2. An exothermic reaction releases 86.5 kJ. How many kilocalories of energy are released?
3. If an endothermic process absorbs 256 J, how many kilocalories are absorbed?

**Table 16-2**

Specific Heats of Common Substances at 298 K (25°C)	
Substance	Specific heat J/(g·°C)
Water(l) (liquid)	4.184
Water(s) (ice)	2.03
Water(g) (steam)	2.01
Ethanol(l) (grain alcohol)	2.44
Aluminum(s)	0.897
Granite(s)	0.803
Iron(s)	0.449
Lead(s)	0.129
Silver(s)	0.235
Gold(s)	0.129

## Specific Heat

You've learned that one calorie, or 4.184 J, is required to raise the temperature of one gram of pure water by one degree Celsius (1°C). That quantity, 4.184 J/(g·°C), is defined as the specific heat ( $c$ ) of water. The **specific heat** of any substance is the amount of heat required to raise the temperature of one gram of that substance by one degree Celsius. Because different substances have different compositions, each substance has its own specific heat. The specific heats of several common substances are listed in **Table 16-2**.

Note how different the specific heats of the various substances are. If the temperature of water is to rise by one degree, 4.184 joules must be absorbed by each gram of water. But only 0.129 joule is required to raise the temperature of an equal mass of gold by one degree. Because of its high specific heat, water can absorb and release large quantities of heat. Have you ever noticed that vineyards and orchards are often planted near large bodies of water, as shown in **Figure 16-2**? During hot weather, the water in the lake or ocean absorbs heat from the air and thereby cools the surrounding area. During a cold snap, the water releases heat, warming the air in the surrounding area so that fruit trees and fruit are less susceptible to frost damage.

The high specific heat of water is also the basis for the use of water-filled plastic enclosures by gardeners in northern climates. Usually the planting of tender seedlings must wait until all danger of frost is past. However, the growing season can be extended into early spring if each plant is surrounded by a clear plastic enclosure filled with water. The water absorbs the heat of the Sun during the day. As the temperature drops at night, the water releases the absorbed

**Figure 16-2**

Ocean and lake fronts are preferred places for growing fruit because the water absorbs heat during sunny days and releases heat when the air cools, thus moderating temperatures.





heat. The plant is kept warm even when the temperature of the air drops to 0°C.

### Calculating heat evolved and absorbed

If you've taken an early morning dive into a swimming pool similar to the one in **Figure 16-3**, you know that the water might be cold at that time of the day. Later in the day, especially if the Sun shines, the temperature of the water will be warmer. How much



warmer depends upon the specific heat of water, but other factors also are important. For example, suppose an architect designs a house that is to be partially heated by solar energy. Heat from the Sun will be stored in a solar pond similar to the swimming pool. The pond is to be made of 14 500 kg of granite rock and contain 22 500 kg of water. Both the granite and the water will absorb energy from the Sun during daylight hours. At night, the energy will not be released to the air, as happens with the swimming pool, but harnessed for use in the home. After conducting several experiments, the architect finds that the temperature of the water and granite increases an average of 22°C during the daylight hours and decreases the same amount during the night. Given these data, how much heat will the pond absorb and release during an average 24-hour period?

The specific heats of water and granite indicate how much heat one gram of each substance absorbs or releases when its temperature changes by 1°C. However, the pond contains much more than one gram of water and one gram of granite. And the temperatures of the two substances will increase and decrease an average of 22°C each day. How do mass and change in temperature affect the architect's calculations?

For the same change in temperature, 100 grams of water or granite absorb or release 100 times as much heat as one gram. Also, for the same 100 grams, increasing the temperature by 20 degrees Celsius requires 20 times as much heat as increasing the temperature by one degree Celsius. Therefore, the heat absorbed or released by a substance during a change in temperature depends not only upon the specific heat of the substance, but also upon the mass of the substance and the amount by which the temperature changes. You can express these relationships in an equation.

$$q = c \times m \times \Delta T$$

In the equation,  $q$  = the heat absorbed or released,  $c$  = the specific heat of the substance,  $m$  = the mass of the sample in grams, and  $\Delta T$  is the change in temperature in °C.  $\Delta T$  is the difference between the final temperature and the initial temperature or,  $T_{\text{final}} - T_{\text{initial}}$ .

You can use this equation to calculate the total amount of heat the solar pond will absorb and release on a typical day. A mass of 22 500 kg of water equals  $2.25 \times 10^7$  g and 14 500 kg of granite equals  $1.45 \times 10^7$  g. The change in temperature for both the water and the granite is 22°C. The specific heat of water is 4.184 J/(g·°C) and the specific heat of granite is 0.803 J/(g·°C). Because each substance has its own specific heat, the amount of heat absorbed or released by water and granite must be calculated separately.

**Figure 16-3**

The cold water of a swimming pool in the morning demonstrates that heat is lost by the water during the night.

**Chemistry**online

**Topic: Solar Heating**

To learn more about solar heating, visit the Chemistry Web site at [chemistrymc.com](http://chemistrymc.com)

**Activity:** Research different ways that people capture solar energy, and what they use it for. Design a solar oven or other solar heat device. Explain how the energy is transferred from the sun through the device.





$$q = c \times m \times \Delta T$$

$$q_{\text{water}} = 4.184 \text{ J/(g}\cdot\text{°C)} \times (2.25 \times 10^7 \text{ g}) \times 22\text{°C} = 2.1 \times 10^9 \text{ J}$$

$$q_{\text{granite}} = 0.803 \text{ J/(g}\cdot\text{°C)} \times (1.45 \times 10^7 \text{ g}) \times 22\text{°C} = 2.6 \times 10^8 \text{ J}$$

The total amount of heat absorbed or released by the pond is the sum of the two quantities.

$$q_{\text{total}} = q_{\text{water}} + q_{\text{granite}}$$

$$q_{\text{total}} = (2.1 \times 10^9 \text{ J}) + (2.6 \times 10^8 \text{ J}) = 2.4 \times 10^9 \text{ J or } 2.4 \times 10^6 \text{ kJ}$$

The solar pond will absorb 2.4 million kJ of heat during a sunny day and release 2.4 million kJ during the night.

## EXAMPLE PROBLEM 16-2

### Calculating Specific Heat

In the construction of bridges and skyscrapers, gaps must be left between adjoining steel beams to allow for the expansion and contraction of the metal due to heating and cooling. The temperature of a sample of iron with a mass of 10.0 g changed from 50.4°C to 25.0°C with the release of 114 J heat. What is the specific heat of iron?



Architects must make provision for the expansion and contraction of the steel frameworks of buildings because metals expand as they absorb heat and contract as they release heat.

#### 1. Analyze the Problem

You are given the mass of the sample, the initial and final temperatures, and the quantity of heat released. The specific heat of iron is to be calculated. The equation that relates these variables can be rearranged to solve for  $c$ .

##### Known

joules of energy released = 114 J

$\Delta T = 50.4\text{°C} - 25.0\text{°C} = 25.4\text{°C}$

mass of iron = 10.0 g Fe

##### Unknown

specific heat of iron,  $c = ? \text{ J/(g}\cdot\text{°C)}$

#### 2. Solve for the Unknown

Rearrange the equation  $q = c \times m \times \Delta T$  to isolate  $c$  by dividing each side of the equation by  $m$  and  $\Delta T$ .

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

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

Solve the equation using the known values.

$$c = \frac{114 \text{ J}}{(10.0 \text{ g})(25.4\text{°C})} = 0.449 \text{ J/(g}\cdot\text{°C)}$$

#### 3. Evaluate the Answer

The values used in the calculation have three significant figures. Therefore, the answer is correctly stated with three digits. The value of the denominator of the equation is approximately two times the value of the numerator, so the final result (0.449), which is approximately 0.5, is reasonable. The calculated value is the same as that recorded for iron in **Table 16-2**.



## PRACTICE PROBLEMS

- If the temperature of 34.4 g of ethanol increases from 25.0°C to 78.8°C, how much heat has been absorbed by the ethanol?
- A 4.50-g nugget of pure gold absorbed 276 J of heat. What was the final temperature of the gold if the initial temperature was 25.0°C? The specific heat of gold is 0.129 J/(g·°C).
- A 155-g sample of an unknown substance was heated from 25.0°C to 40.0°C. In the process, the substance absorbed 5696 J of energy. What is the specific heat of the substance? Identify the substance among those listed in **Table 16-2**.



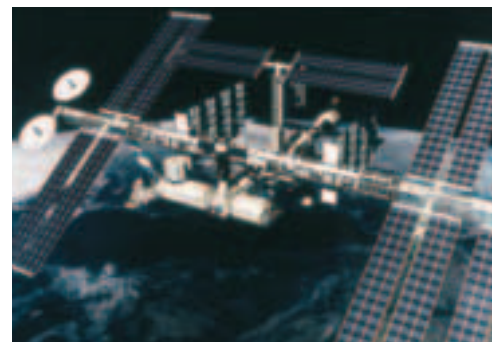
For more practice calculating and using specific heat, go to **Supplemental Practice Problems** in Appendix A.

**Using the Sun's energy** The Sun is a virtually inexhaustible source of energy. Radiation from the Sun could supply all the energy needs of the world and reduce or eliminate the use of carbon dioxide-producing fuels, but practical problems have delayed the development of solar energy. The Sun shines for only a fraction of the day. Clouds often reduce the amount of available radiation. Because of this variability, effective storage of energy is critical. Solar ponds, such as the one you have been reading about, take up large land areas and can lose heat to the atmosphere.

Another method for storage involves the use of hydrates such as sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), which you learned about in Chapter 11. When heated by the Sun, the hydrate undergoes an endothermic process in which the sodium sulfate dissolves in the water of hydration. When the temperature drops at night, the hydrate re-crystallizes with the release of the absorbed solar energy.

A more promising approach to the harnessing of solar energy is the development of photovoltaic cells. These electronic devices convert solar radiation directly to electricity. Photovoltaic cells are now being used to provide the energy needs of space vehicles, as shown in **Figure 16-4**. At present, the cost of supplying electricity by means of photovoltaic cells is high compared to the cost of burning coal and oil. Therefore, although photovoltaic cells are clean and efficient, they remain a choice for the future.

The specific heat of a substance is a measure of how efficiently that substance absorbs heat. Water is particularly efficient and, for this reason, plays an important role in calorimetry, an experimental procedure you will learn about in Section 16.2.



**Figure 16-4**

Photovoltaic cells, positioned to absorb energy from the Sun, are the source of energy for the operation of this artist's conception of a space station.

## Section 16.1 Assessment

- Explain what is meant by energy and list two units in which energy is measured.
- Distinguish between kinetic and potential energy in the following examples: two separated magnets; an avalanche of snow; books on library shelves; a mountain stream; a stock car race; separation of charge in a battery.
- What is the relationship between a calorie and a joule?
- Thinking Critically** One lawn chair is made of aluminum and another is made of iron. Both chairs are painted the same color. On a sunny day, which chair will be hottest to sit in? Explain why.
- Using Numbers** What is the specific heat of an unknown substance if a 2.50-g sample releases 12.0 cal as its temperature changes from 25.0°C to 20.0°C?







## Objectives

- **Describe** how a calorimeter is used to measure energy absorbed or released.
- **Explain** the meaning of enthalpy and enthalpy change in chemical reactions and processes.

## Vocabulary

calorimeter  
thermochemistry  
system  
surroundings  
universe  
enthalpy  
enthalpy (heat) of reaction

You have learned that some chemical reactions and processes must absorb energy in order to occur. These are called endothermic reactions. Others release energy and are called exothermic reactions. Whenever you cook food using methane or propane gas in your kitchen range, you utilize the heat released in the combustion of these fuels. But how do you measure the amount of heat released or absorbed when chemical reactions such as these occur?

## Measuring Heat

Heat changes that occur during chemical and physical processes can be measured accurately and precisely using a calorimeter. A **calorimeter** is an insulated device used for measuring the amount of heat absorbed or released during a chemical or physical process. A known mass of water is placed in an insulated chamber in the calorimeter to absorb the energy released from the reacting system or to provide the energy absorbed by the system. The data to be collected is the change in temperature of this mass of water. Good results can be obtained in your calorimetry experiments by using a calorimeter made from nested plastic foam cups similar to the one shown in **Figure 16-5**. Because the foam cup is not tightly sealed, it is, in effect, open to the atmosphere. Reactions carried out in this type of calorimeter, therefore, occur at constant pressure.

**Determining specific heat** You can use a calorimeter to determine the specific heat of an unknown metal. Suppose you put 125 g of water into a foam-cup calorimeter and find that its initial temperature is 25.6°C, as shown in **Figure 16-5a**. Then, you heat a 50.0-g sample of the unknown metal to a temperature of 115.0°C and put the metal sample into the water. Heat flows from the hot metal to the cooler water and the temperature of the water rises. The flow of heat stops only when the temperature of the metal and the water are equal. In **Figure 16-5b**, the temperature of the water is constant. Both water and metal have attained a final temperature of 29.3°C. Assuming no heat is lost to the surroundings, the heat gained by the water is equal to the heat lost by the metal. This quantity of heat can be calculated using the equation you learned in Section 16.1.

$$q = c \times m \times \Delta T$$

First, calculate the heat gained by the water. For this you need the specific heat of water, 4.184 J/(g·°C).

$$q_{\text{water}} = 4.184 \text{ J/(g}\cdot\text{°C)} \times 125 \text{ g} \times (29.3\text{°C} - 25.6\text{°C})$$

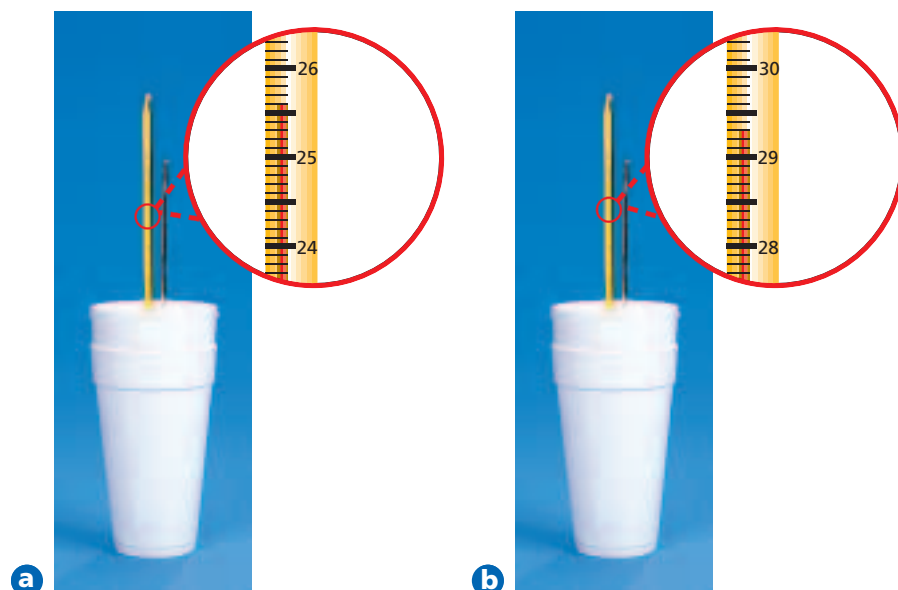
$$q_{\text{water}} = 4.184 \text{ J/(g}\cdot\text{°C)} \times 125 \text{ g} \times 3.7\text{°C}$$

$$q_{\text{water}} = 1900 \text{ J}$$

The heat gained by the water, 1900 J, equals the heat lost by the metal,  $q_{\text{metal}}$ , so you can write this equation.

$$q_{\text{metal}} = 1900 \text{ J} = c_{\text{metal}} \times m \times \Delta T$$

$$1900 \text{ J} = c_{\text{metal}} \times m \times \Delta T$$

**Figure 16-5**

In **(a)**, the measured mass of water has an initial temperature of 25.6°C. A piece of hot metal is added. The metal transfers heat to the water until metal and water attain the same temperature. That final temperature is shown in **(b)** as 29.3°C.

Now, solve the equation for the specific heat of the metal,  $c_{\text{metal}}$ , by dividing both sides of the equation by  $m \times \Delta T$ .

$$c_{\text{(metal)}} = \frac{1900 \text{ J}}{m \times \Delta T}$$

The change in temperature for the metal,  $\Delta T$ , is the difference between the final temperature of the water and the initial temperature of the metal ( $115.0^\circ\text{C} - 29.3^\circ\text{C} = 85.7^\circ\text{C}$ ). Substitute the known values of  $m$  and  $\Delta T$  (50.0 g and  $85.7^\circ\text{C}$ ) into the equation and solve.

$$c_{\text{metal}} = \frac{1900 \text{ J}}{(50.0 \text{ g})(85.7^\circ\text{C})} = 0.44 \text{ J}/(\text{g}\cdot^\circ\text{C})$$

The unknown metal has a specific heat of  $0.44 \text{ J}/(\text{g}\cdot^\circ\text{C})$ . From **Table 16-2** on page 492, you can infer that the metal could be iron. The **CHEMLAB** at the end of this chapter will give you practice in calorimetry.

### EXAMPLE PROBLEM 16-3

#### Using Data from Calorimetry

A piece of metal with a mass of 4.68 g absorbs 256 J of heat when its temperature increases by  $182^\circ\text{C}$ . What is the specific heat of the metal? Could the metal be one of the alkaline earth metals listed in **Table 16-3**?

#### 1. Analyze the Problem

You are given the mass of the metal, the amount of heat it absorbs, and the temperature change. You must calculate the specific heat. The equation for  $q$ , the quantity of heat, should be used, but it must be solved for specific heat,  $c$ .

#### Known

mass of metal = 4.68 g metal  
 quantity of heat absorbed,  $q = 256 \text{ J}$   
 $\Delta T = 182^\circ\text{C}$

#### Unknown

specific heat,  $c = ? \text{ J}/(\text{g}\cdot^\circ\text{C})$

*Continued on next page*

**Table 16-3**

Periodic Trend in Specific Heats	
Alkaline earth elements	Specific heat ( $\text{J}/\text{g}\cdot^\circ\text{C}$ )
Beryllium	1.825
Magnesium	1.023
Calcium	0.647
Strontium	0.301
Barium	0.204







## 2. Solve for the Unknown

Solve for  $c$  by dividing both sides of the equation by  $m \times \Delta T$ .

$$q = c \times m \times \Delta T$$

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

Substitute the known values into the equation.

$$c = \frac{256 \text{ J}}{(4.68 \text{ g})(182^\circ\text{C})} = 0.301 \text{ J}/(\text{g}\cdot^\circ\text{C})$$

Table 16-3 indicates that the metal could be strontium.

## 3. Evaluate the Answer

The three quantities used in the calculation have three significant figures, so the answer is correctly stated with three digits. The calculations are correct and yield the expected unit. The calculated specific heat is the same as that of strontium.

Practice!

For more practice using calorimetry data, go to **Supplemental Practice Problems** in Appendix A.

## PRACTICE PROBLEMS

- If 335 g water at  $65.5^\circ\text{C}$  loses 9750 J of heat, what is the final temperature of the water?
- The temperature of a sample of water increases from  $20.0^\circ\text{C}$  to  $46.6^\circ\text{C}$  as it absorbs 5650 J of heat. What is the mass of the sample?

Figure 16-6

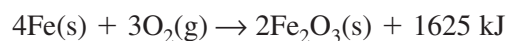
The energy released in the reaction of iron with oxygen provides comforting warmth for cold hands.



## Chemical Energy and the Universe

Virtually every chemical reaction and change of physical state either releases or absorbs heat. Recall that an exothermic reaction is one in which energy is released and an endothermic reaction is one in which energy is absorbed. What happens to the heat released by an exothermic chemical reaction? What is the source of the heat absorbed by an endothermic reaction? Thermochemistry provides answers to these questions. **Thermochemistry** is the study of heat changes that accompany chemical reactions and phase changes.

Think about what happens when you warm your hands on a cold day by using a heat pack similar to the one shown in **Figure 16-6**. When you remove the plastic wrap, oxygen from the air enters the pack. The oxygen reacts with iron in the pack in an exothermic reaction described by the following equation. Note that energy is shown as a product of the reaction, which means that heat is released.

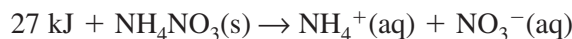


Because you are interested in the heat evolved by the chemical reaction going on inside the pack, it's convenient to think of the pack and its contents as the system. In thermochemistry, the **system** is the specific part of the universe that contains the reaction or process you wish to study. Everything in the universe other than the system is considered the **surroundings**. Therefore, the **universe** is defined as the system plus the surroundings.

$$\text{universe} = \text{system} + \text{surroundings}$$

What kind of energy transfer occurs during the exothermic heat-pack reaction? Heat produced by the reaction flows from the heat pack (the system) to your cold hands (part of the surroundings).

What happens in an endothermic reaction or process? The flow of heat is reversed. Heat flows from the surroundings to the system. For example, if you dissolve ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) in water, the temperature of the water decreases. This is the equation for that process. Note that energy is on the reactant side of the equation, which means energy is absorbed.



The athletic trainer in **Figure 16-7** can cause this reaction to occur in a cold pack by breaking a membrane in the pack and allowing ammonium nitrate to mix with water. When the cold pack is placed on an injured knee, heat flows from the knee (part of the surroundings) into the cold pack (the system).

**Enthalpy and enthalpy changes** The total amount of energy a substance contains depends upon many factors, some of which are not totally understood today. Therefore, it's impossible to know the total heat content of a substance. Fortunately, chemists are usually more interested in changes in energy during reactions than in the absolute amounts of energy contained in the reactants and products.

For many reactions, the amount of energy lost or gained can be measured conveniently in a calorimeter at constant pressure, as in the experiment illustrated in **Figure 16-5** on page 497. The foam cup is not sealed, so the pressure is constant. Many reactions of interest take place at constant atmospheric pressure; for example, those that occur in living organisms on Earth's surface, in lakes and oceans, and in open beakers and flasks in the laboratory. To more easily measure and study the energy changes that accompany such reactions, chemists have defined a property called enthalpy. **Enthalpy** ( $H$ ) is the heat content of a system at constant pressure.

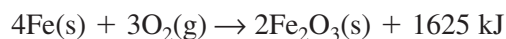
But why define a property if you can't know its absolute value? Although you can't measure the actual energy or enthalpy of a substance, you can measure the change in enthalpy, which is the heat absorbed or released in a chemical reaction. The change in enthalpy for a reaction is called the **enthalpy (heat) of reaction** ( $\Delta H_{\text{rxn}}$ ). You have already learned that a symbol preceded by the Greek letter  $\Delta$  means a change in the property. Thus,  $\Delta H_{\text{rxn}}$  is the difference between the enthalpy of the substances that exist at the end of the reaction and the enthalpy of the substances present at the start.

$$\Delta H_{\text{rxn}} = H_{\text{final}} - H_{\text{initial}}$$

Because the reactants are present at the beginning of the reaction and the products are present at the end,  $\Delta H_{\text{rxn}}$  is defined by this equation.

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

**The sign of the enthalpy of reaction** Recall the heat-pack reaction of iron with oxygen.



According to the equation, the reactants in this exothermic reaction lose heat. Therefore,  $H_{\text{products}} < H_{\text{reactants}}$ . When  $H_{\text{reactants}}$  is subtracted from the smaller  $H_{\text{products}}$ , a negative value for  $\Delta H_{\text{rxn}}$  is obtained. Enthalpy changes for exothermic reactions are always negative. The equation for the heat-pack reaction and its enthalpy change are usually written like this.



**Figure 16-7**

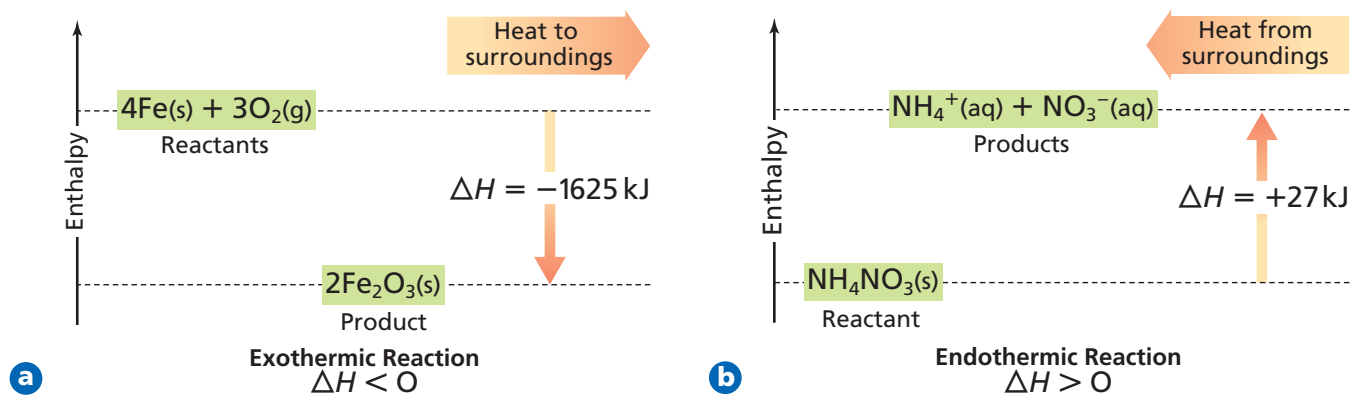
Heat is absorbed when ammonium nitrate dissolves in water in a cold pack. In this photograph, heat is transferred from the injured knee to the chemical process.

## Careers Using Chemistry

### Heating and Cooling Specialist

*Are you fascinated by complex mechanical systems? Can you quickly figure out how they work? Then consider a career as a heating and cooling specialist.*

Heating and cooling system mechanics install, maintain, and repair refrigeration and heating equipment. They must know how to make the equipment work as efficiently as possible. They must be able to read blueprints and use a wide range of tools, from pipe cutters to computerized diagnostic devices. Mechanics might specialize in one aspect of this field—or do it all.

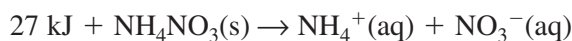


**Figure 16-8**

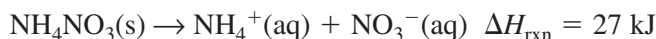
The downward arrow in **a** shows that 1625 kJ of heat is released to the surroundings in the reaction between Fe and O<sub>2</sub> to form Fe<sub>2</sub>O<sub>3</sub>. In contrast, the upward arrow in **b** indicates that 27 kJ of heat is absorbed from the surroundings in the process of dissolving NH<sub>4</sub>NO<sub>3</sub>.

**Figure 16-8a** is a diagram of the energy change for the exothermic reaction between iron and oxygen. You can see that the enthalpy of the product, Fe<sub>2</sub>O<sub>3</sub>, is 1625 kJ less than the enthalpy of the reactants Fe and O<sub>2</sub> because energy is released.

Similarly, recall the cold-pack reaction.



For this endothermic reaction,  $\Delta H_{\text{products}} > \Delta H_{\text{reactants}}$ . Therefore, when  $\Delta H_{\text{reactants}}$  is subtracted from the larger  $\Delta H_{\text{products}}$ , a positive value for  $\Delta H_{\text{rxn}}$  is obtained. Enthalpy changes for endothermic reactions are always positive. Chemists write the equation for the cold-pack reaction and its enthalpy change in this way.



**Figure 16-8b** shows the energy change for the cold-pack reaction. In this endothermic reaction, the enthalpy of the products, aqueous NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions, is 27 kJ greater than the enthalpy of the reactant, NH<sub>4</sub>NO<sub>3</sub> because energy is absorbed in the reaction. Compare **Figure 16-8a** and **Figure 16-8b** and then study **Table 16-4**, which shows the sign of  $\Delta H_{\text{rxn}}$  for exothermic and endothermic reactions.

Recall that  $q$  was defined as the heat gained or lost in a chemical reaction or process. When the reaction takes place at constant pressure, the subscript p is sometimes added to the symbol  $q$ . The enthalpy change,  $\Delta H$ , is equal to  $q_p$ , the heat gained or lost in a reaction or process carried out at constant pressure. Because all reactions presented in this textbook occur at constant pressure, you may assume that  $q = \Delta H_{\text{rxn}}$ .

**Table 16-4**

Enthalpy Changes for Exothermic and Endothermic Reactions	
Type of reaction	Sign of $\Delta H_{\text{rxn}}$
Exothermic	Negative
Endothermic	Positive

## Section 16.2 Assessment

- Describe how you would calculate the amount of heat absorbed or released by a substance when its temperature changes.
- Why does  $\Delta H$  for an exothermic reaction have a negative value?
- Why is a measured volume of water an essential part of a calorimeter?
- Explain the meaning of  $\Delta H_{\text{rxn}}$ . Why is  $\Delta H_{\text{rxn}}$  sometimes positive and sometimes negative?
- Thinking Critically** Could another liquid be used just as effectively as water in a calorimeter? Why or why not?
- Designing an Experiment** Explain how you would design an experiment to determine the specific heat of a 45-g piece of metal.

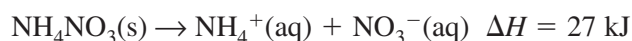




Chemical reactions either release energy (exothermic reactions) or absorb energy (endothermic reactions). The change in energy is an important part of chemical reactions so chemists include  $\Delta H$  as part of the chemical equation.

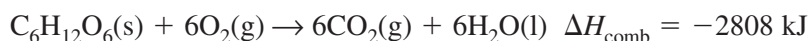
## Writing Thermochemical Equations

The equations for the heat-pack and cold-pack reactions that you learned about in Section 16.2 are called thermochemical equations when they are written like this.



A **thermochemical equation** is a balanced chemical equation that includes the physical states of all reactants and products and the energy change, usually expressed as the change in enthalpy,  $\Delta H$ .

The nature of the reaction or process described by a thermochemical equation is often written as a subscript of  $\Delta H$ . For example, the highly exothermic combustion (comb) of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) occurs in the body as food is metabolized to produce energy for activities such as the one shown in **Figure 16-9**. The thermochemical equation for the combustion of glucose is



The energy released ( $-2808 \text{ kJ}$ ) is the enthalpy of combustion. The **enthalpy (heat) of combustion** ( $\Delta H_{\text{comb}}$ ) of a substance is the enthalpy change for the complete burning of one mole of the substance. Standard enthalpies of combustion for several common substances are given in **Table 16-5**. Standard enthalpy changes have the symbol  $\Delta H^\circ$ . The zero superscript tells you that the reactions were carried out under standard conditions. Standard conditions are one atmosphere pressure and 298 K ( $25^\circ\text{C}$ ) and should not be confused with standard temperature and pressure (STP).

**Table 16-5**

Standard Enthalpies of Combustion		
Substance	Formula	$\Delta H^\circ_{\text{comb}}$ (kJ/mol)
Sucrose (table sugar)	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)$	-5644
Octane (a component of gasoline)	$\text{C}_8\text{H}_{18}(l)$	-5471
Glucose (a simple sugar found in fruit)	$\text{C}_6\text{H}_{12}\text{O}_6(s)$	-2808
Propane	$\text{C}_3\text{H}_8(g)$	-2219
Ethanol	$\text{C}_2\text{H}_5\text{OH}(l)$	-1367
Methane (the major component of natural gas)	$\text{CH}_4(g)$	-891
Methanol (wood alcohol)	$\text{CH}_3\text{OH}(l)$	-726
Carbon (graphite)	$\text{C}(s)$	-394
Hydrogen	$\text{H}_2(g)$	-286

## Objectives

- **Write** thermochemical equations for chemical reactions and other processes.
- **Describe** how energy is lost or gained during changes of state.
- **Calculate** the heat absorbed or released in a chemical reaction.

## Vocabulary

thermochemical equation  
enthalpy (heat) of combustion  
molar enthalpy (heat) of vaporization  
molar enthalpy (heat) of fusion

**Figure 16-9**

The energy expended by both horse and rider is obtained through the exothermic combustion of glucose in cells.





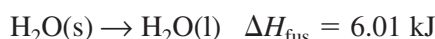
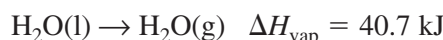
## Changes of State

Many processes other than chemical reactions absorb or release heat. For example, think about what happens when you step out of a hot shower. You shiver as water evaporates from your skin. That's because your skin provides the heat needed to vaporize the water. As heat is taken from your skin to vaporize the water, you cool down. The heat required to vaporize one mole of a liquid is called its **molar enthalpy (heat) of vaporization** ( $\Delta H_{\text{vap}}$ ). Similarly, if you want a glass of cold water, you might drop an ice cube into it. The water cools as it provides the heat to melt the ice. The heat required to melt one mole of a solid substance is called its **molar enthalpy (heat) of fusion** ( $\Delta H_{\text{fus}}$ ). Because vaporizing a liquid and melting a solid are endothermic processes, their  $\Delta H$  values are positive. Standard molar enthalpies of vaporization and fusion for four common compounds are shown in **Table 16-6**.

**Table 16-6**

Standard Enthalpies of Vaporization and Fusion			
Substance	Formula	$\Delta H_{\text{vap}}^{\circ}$ (kJ/mol)	$\Delta H_{\text{fus}}^{\circ}$ (kJ/mol)
Water	H <sub>2</sub> O	40.7	6.01
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	38.6	4.94
Methanol	CH <sub>3</sub> OH	35.2	3.22
Ammonia	NH <sub>3</sub>	23.3	5.66

**Thermochemical equations for changes of state** The vaporization of water and the melting of ice can be described by the following equations.



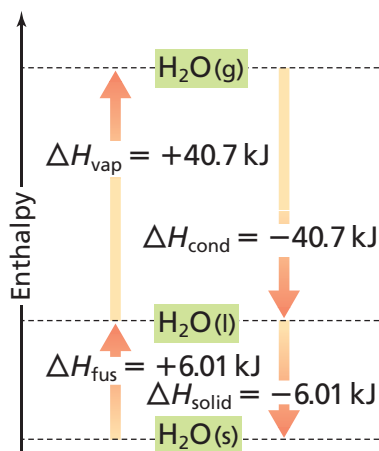
The first equation indicates that 40.7 kJ of energy is absorbed when one mole of water is converted to one mole of water vapor. The second equation shows that when one mole of ice melts to form one mole of liquid water, 6.01 kJ of energy is absorbed.

What happens in the reverse processes, when water vapor condenses to liquid water or liquid water freezes to ice? The same amounts of energy are released in these exothermic processes as are absorbed in the endothermic processes of vaporization and melting. Thus, the molar enthalpy (heat) of condensation ( $\Delta H_{\text{cond}}$ ) and the molar enthalpy of vaporization have the same numerical value but opposite signs. Similarly, the molar enthalpy (heat) of solidification ( $\Delta H_{\text{solid}}$ ) and the molar enthalpy of fusion have the same numerical value but differ in sign.

$$\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$$

$$\Delta H_{\text{fus}} = -\Delta H_{\text{solid}}$$

Compare the following equations for the condensation and freezing of water with the equations above for the vaporization and melting of water. How would you summarize your observations? The relationships are illustrated in **Figure 16-10**.



**Figure 16-10**

The left arrows show that the energy of the system increases as water melts and then vaporizes. The right arrows show that the energy of the system decreases as gaseous water condenses and then solidifies. What would be the energy of the process called sublimation in which ice is converted directly to water vapor?





Some farmers make use of the heat of fusion of water to protect fruit from freezing. They flood their orchards or fields with water, as shown in **Figure 16-11**. The energy released as the water freezes ( $\Delta H_{\text{fus}}$ ) often increases the temperature of the air enough to prevent frost damage to the fruit.



**Figure 16-11**

If the temperature should drop to freezing, the water that floods this field will release heat ( $\Delta H_{\text{fus}}$ ) as it freezes and warm the surrounding air.

In the **problem-solving LAB**, you will interpret the heating curve of water using the heats of fusion and vaporization. The **How It Works** feature, at the end of the chapter, describes a practical application of the vaporization of a liquid.

## problem-solving LAB

### How much energy is needed to heat water from a solid to a vapor?

**Making and Using Heating Curves** Water molecules have a strong attraction for one another because they are polar. The polarity of water accounts for its high specific heat and relatively high enthalpies of fusion and vaporization. Water's high specific heat and the presence of an enormous amount of water on Earth's surface have a large influence on the weather.

#### Analysis

Use the data in the table to plot a heating curve of temperature versus time for a 180-g sample of water as it is heated at a constant rate from  $-20^{\circ}\text{C}$  to  $120^{\circ}\text{C}$ . Draw a best-fit line through the points. Note the time required for water to pass through each segment of the graph.

#### Thinking Critically

- For each of the five regions of the graph, indicate how the absorption of heat changes the energy (kinetic or potential) of the water molecules.
- Calculate the amount of heat required to pass through each region of the graph (180 g  $\text{H}_2\text{O}$  = 10 mol  $\text{H}_2\text{O}$ ,  $\Delta H_{\text{fus}} = 6.01$  kJ/mol,  $\Delta H_{\text{vap}} = 40.7$  kJ/mol,  $c = 4.184$  J/g $\cdot^{\circ}\text{C}$ ). How does the length of time needed to pass through each region relate to the amount of heat absorbed?
- What would the heating curve of ethanol look like? Make a rough sketch of ethanol's curve from  $-120^{\circ}\text{C}$  to  $90^{\circ}\text{C}$ . Ethanol melts at  $-114^{\circ}\text{C}$  and boils at  $78^{\circ}\text{C}$ . What factors determine the

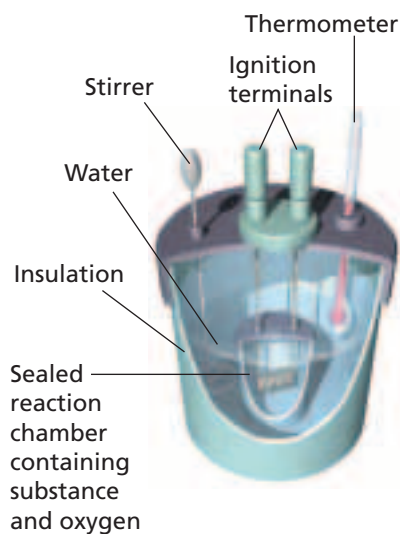
**Time and Temperature Data for Water**

Time (min)	Temperature $^{\circ}\text{C}$	Time (min)	Temperature $^{\circ}\text{C}$
0.0	-20	13.0	100
0.5	-11	13.5	100
1.0	0	14.0	100
1.5	0	14.5	100
2.0	0	15.0	100
2.5	0	15.5	100
3.0	9	16.0	100
3.5	18	16.5	100
4.0	26	17.0	100
4.5	34	17.5	100
5.0	42	18.0	100
5.5	51	18.5	100
6.0	58	19.0	100
6.5	65	19.5	100
7.0	71	20.0	100
7.5	77	20.5	100
8.0	83	21.0	100
8.5	88	21.5	100
9.0	92	22.0	100
9.5	95	22.5	100
10.0	98	23.0	100
10.5	100	23.5	100
11.0	100	24.0	100
11.5	100	24.5	108
12.0	100	25.0	120
12.5	100		

lengths of the flat regions of the graph and the slope of the curve between the flat regions?





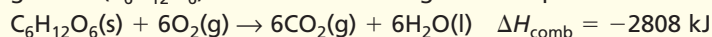


Inside the central chamber or bomb of a bomb calorimeter, reactions are carried out at constant volume. A sample of known mass is ignited by an electric spark and burned in an excess of oxygen. The heat released is transferred to a known mass of water in the well insulated outer chamber.

## EXAMPLE PROBLEM 16-4

### Calculating Energy Released in a Reaction

A bomb calorimeter is useful for measuring the energy released in combustion reactions. The reaction is carried out in a constant volume bomb with a high pressure of oxygen. How much heat is evolved when 54.0 g glucose ( $C_6H_{12}O_6$ ) is burned according to this equation?



#### 1. Analyze the Problem

You are given a mass of glucose, the equation for the combustion of glucose, and  $\Delta H_{\text{comb}}$ . Grams of glucose must be converted to moles of glucose. Because the molar mass of glucose is more than three times the given mass of glucose, you can predict that the energy evolved will be less than one-third  $\Delta H_{\text{comb}}$ .

**Known**

mass of glucose = 54.0 g  $C_6H_{12}O_6$

$\Delta H_{\text{comb}} = -2808 \text{ kJ}$

**Unknown**

$q = ? \text{ kJ}$

#### 2. Solve for the Unknown

Convert grams of  $C_6H_{12}O_6$  to moles of  $C_6H_{12}O_6$  by multiplying by the conversion factor that relates moles and mass, the inverse of molar mass.

$$54.0 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.18 \text{ g } C_6H_{12}O_6} = 0.300 \text{ mol } C_6H_{12}O_6$$

Multiply moles of  $C_6H_{12}O_6$  by the conversion factor that relates kJ and moles, the enthalpy of combustion,  $\Delta H_{\text{comb}}$ .

$$\frac{\text{kJ released}}{1 \text{ mole substance burned}} \\ 0.300 \text{ mol } C_6H_{12}O_6 \times \frac{2808 \text{ kJ}}{1 \text{ mol } C_6H_{12}O_6} = 842 \text{ kJ}$$

#### 3. Evaluate the Answer

All values in the calculation have at least three significant figures, so the answer is correctly stated with three digits. As predicted, the released energy is less than one-third  $\Delta H_{\text{comb}}$ .

## PRACTICE PROBLEMS

20. Calculate the heat required to melt 25.7 g of solid methanol at its melting point.
21. How much heat is evolved when 275 g of ammonia gas condenses to a liquid at its boiling point?
22. What mass of methane must be burned in order to liberate 12 880 kJ of heat?

Example Problem 16-4 shows that when glucose is burned in a bomb calorimeter, a significant amount of energy is released. The same amount of energy is produced in your body when an equal mass of glucose is metabolized (converted to carbon dioxide and water). The reaction, which occurs in every cell of your body, may not occur in the same way as the combustion in Example Problem 16-4, but the overall result is the same. The metabolism of glucose and other sugars provides the energy you need to breathe, move, think, and grow.

Practice!

For more practice calculating the energy released in a reaction, go to **Supplemental Practice Problems** in Appendix A.

## miniLAB

### Enthalpy of Fusion for Ice

**Applying Concepts** When ice is added to water at room temperature, the water provides the energy for two processes. The first process is the melting of the ice. The energy required to melt ice is the enthalpy of fusion ( $\Delta H_{\text{fus}}$ ). The second process is raising the temperature of the melted ice from its initial temperature of  $0.0^{\circ}\text{C}$  to the final temperature of the liquid water. In this experiment, you will collect data to calculate the enthalpy of fusion for ice.

**Materials** foam cup, thermometer, stirring rod, ice, water, balance

#### Procedure

1. Measure the mass of an empty foam cup and record it in your data table.
2. Fill the foam cup about one-third full of water. Measure and record the mass.
3. Place the thermometer in the cup. Read and record the initial temperature of the water.
4. Quickly place a small quantity of ice in the plastic cup. Gently stir the water with a stirring rod until the ice melts. Record the lowest temperature reached as the final temperature.
5. Measure the mass of the cup and water.

#### Analysis

1. The heat lost by the liquid water equals the heat needed to melt the ice plus the heat needed to increase the temperature of the melted ice from  $0.0^{\circ}\text{C}$  to the final temperature. Calculate the heat lost by the water.
2. Calculate the heat gained by the melted ice as its temperature rose from  $0.0^{\circ}\text{C}$  to the final temperature.
3. The difference between the heat lost by the water and the heat gained by the melted ice equals the heat of fusion. Calculate the heat of fusion in joules per gram of ice.
4. Calculate  $\Delta H_{\text{fus}}$  in kJ/mol.
5. Calculate the percent error of your experimental  $\Delta H_{\text{fus}}$ . Compare your value to the actual value  $6.01 \text{ kJ/mol}$ .

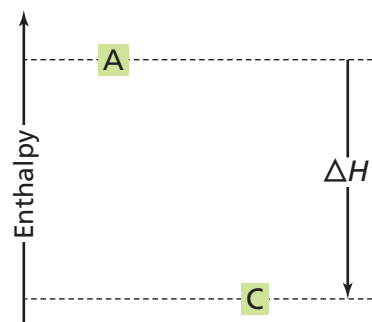
As in the **miniLAB** above, you can use calorimetry to measure the energy released or absorbed in a chemical reaction or change of state. However, sometimes carrying out an experiment is difficult or even impossible. In the next section, you'll see that there are ways to calculate energy changes.

## Section 16.3 Assessment

23. List the information contained in a thermochemical equation.
24. Which of the following processes are exothermic? Endothermic?
  - a.  $\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$
  - b.  $\text{NH}_3(\text{g}) \rightarrow \text{NH}_3(\text{l})$
  - c.  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{s})$
  - d.  $\text{NaCl}(\text{s}) \rightarrow \text{NaCl}(\text{l})$
  - e.  $\text{C}_5\text{H}_{12}(\text{g}) + 8\text{O}_2(\text{g}) \rightarrow 5\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
25. Explain how you could calculate the heat released in freezing  $0.250 \text{ mol}$  water.
26. **Thinking Critically** The freezing of water at  $0.0^{\circ}\text{C}$  is an exothermic process. Explain how the positions and thus, the chemical potential energy of the water molecules change as water goes from

a liquid to a solid. Does the kinetic energy of the water molecules change?

27. **Interpreting Scientific Illustrations** The reaction  $\text{A} \rightarrow \text{C}$  is shown in the enthalpy diagram. Is the reaction exothermic or endothermic? Explain your answer.



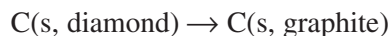
## Objectives

- **Use** Hess's law of summation of enthalpies of reaction to calculate the enthalpy change for a reaction.
- **Explain** the basis for the table of standard enthalpies of formation.
- **Calculate**  $\Delta H_{\text{rxn}}$  using thermochemical equations.
- **Determine** the enthalpy change for a reaction using standard enthalpies of formation data.

## Vocabulary

Hess's law  
standard enthalpy (heat) of formation

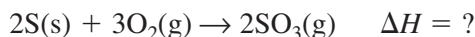
In principle, you can determine  $\Delta H$  for any chemical reaction by using a calorimeter to measure the heat evolved or absorbed during the reaction. However, consider the reaction involving the conversion of carbon in its allotropic form diamond to carbon in its allotropic form graphite.



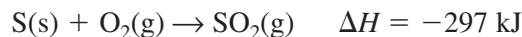
This reaction occurs over millions of years—so slowly that measuring the enthalpy change is virtually impossible. Other reactions occur under conditions difficult to duplicate in a laboratory. Still others don't occur cleanly; that is, products other than the desired ones may be formed. For reactions such as these, chemists use a theoretical way to determine  $\Delta H$ .

## Hess's Law

Suppose you are studying the formation of acid rain that results from the reaction of water in the atmosphere with sulfur trioxide expelled during a volcanic eruption such as the one shown in **Figure 16-12**. You would need to determine  $\Delta H$  for this reaction.

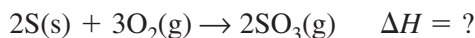


Unfortunately, when you try to duplicate the reaction in the laboratory by burning sulfur in air, only small quantities of sulfur trioxide are formed. What results is a mixture containing mostly sulfur dioxide produced according to this equation.



In situations such as this, you can calculate  $\Delta H$  for the formation of sulfur trioxide using Hess's law of heat summation. **Hess's law** states that if you can add two or more thermochemical equations to produce a final equation for a reaction, then the sum of the enthalpy changes for the individual reactions is the enthalpy change for the final reaction. Hess's law enables you to calculate enthalpy changes for an enormous number of chemical reactions by imagining that each reaction occurs through a series of steps for which the enthalpy changes are known.

**Applying Hess's law** How can Hess's law be used to calculate the energy change for the reaction that produces  $\text{SO}_3$ ?



First, chemical equations are needed that contain the substances found in the desired equation and have known enthalpy changes. The following equations contain S,  $\text{O}_2$ , and  $\text{SO}_3$ .

- $\text{S(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \quad \Delta H = -297 \text{ kJ}$
- $2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = 198 \text{ kJ}$

The desired equation shows two moles of sulfur reacting, so Equation **a** must be rewritten for two moles of sulfur by multiplying the coefficients by 2. The enthalpy change,  $\Delta H$ , must also be doubled because twice the energy will be

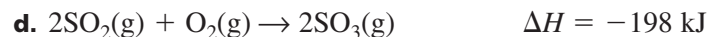




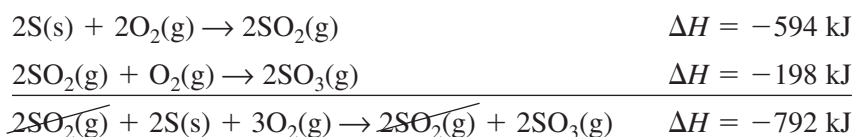
released if two moles of sulfur react. When these changes are made, Equation **a** becomes the following (Equation **c**).



Because you want to determine  $\Delta H$  for a reaction in which  $\text{SO}_3$  is a product rather than a reactant, Equation **b** must be reversed. Recall that when you reverse an equation, the sign of  $\Delta H$  changes. The reverse of Equation **b** is Equation **d**.



Now, add Equations **c** and **d** to obtain the equation for the desired reaction. Add the  $\Delta H$  values for the two equations to determine  $\Delta H$  for the desired reaction. Any terms that are common to both sides of the combined equation should be canceled.



The sum of the two equations is the equation for the burning of sulfur to form  $\text{SO}_3$ , and the sum of the  $\Delta H$  values is the enthalpy change for the reaction.

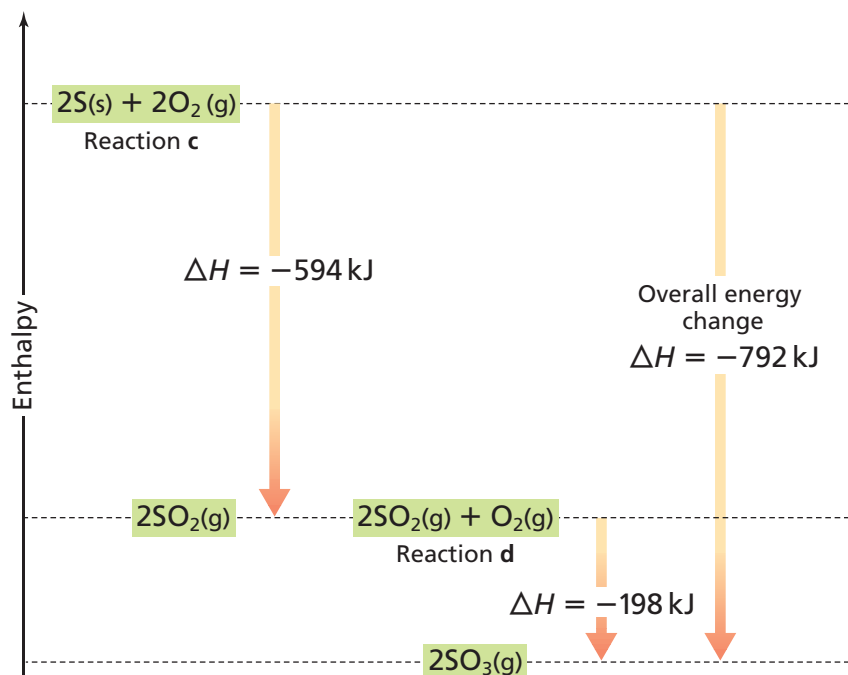


The diagram in **Figure 16-13** will help you visualize the calculation.

Sometimes thermochemical equations are written with fractional coefficients because they are balanced for one mole of product. For example, the thermochemical equation for the reaction between sulfur and oxygen to form one mole of sulfur trioxide is the following.



What factor would you need to multiply this equation and its enthalpy change by to obtain the equation you worked with above?



**Figure 16-12**

A volcanic eruption releases solid materials, gases, and heat into the atmosphere. Carbon dioxide and water account for more than 90% of the gases emitted. An eruption can send as much as 20 million tons of sulfur dioxide and sulfur trioxide into the stratosphere.

**Figure 16-13**

The arrow on the left indicates the release of 594 kJ as S and  $\text{O}_2$  react to form  $\text{SO}_2$  (Reaction **c**). Then,  $\text{SO}_2$  and  $\text{O}_2$  react to form  $\text{SO}_3$  (Reaction **d**) with the release of 198 kJ (middle arrow). The overall energy change (the sum of the two processes) is shown by the arrow on the right. What is the enthalpy change for the conversion of S and  $\text{O}_2$  to  $\text{SO}_3$ ?

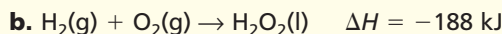
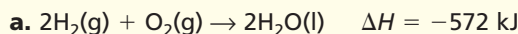
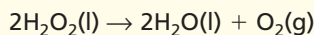
## EXAMPLE PROBLEM 16-5



The photo shows an X-15 rocket-powered aircraft used to test the effects of high-speed, high-altitude flight on humans and materials. The rocket engines, mounted under the wing of a B52 bomber, are powered by the reaction of  $\text{H}_2$  and  $\text{O}_2$ . Data from 199 runs made by such aircraft were used in the development of the space shuttle.

### Applying Hess's Law

Use thermochemical Equations **a** and **b** to determine  $\Delta H$  for the decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), a compound that has uses ranging from bleaching hair to energizing rocket engines.



### 1. Analyze the Problem

You have been given two chemical equations and their enthalpy changes. These two equations contain all the substances found in the desired equation.

#### Known

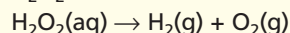
Equations **a** and **b** and their enthalpy changes

#### Unknown

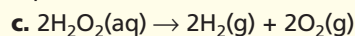
$$\Delta H = ? \text{ kJ}$$

### 2. Solve for the Unknown

$\text{H}_2\text{O}_2$  is a reactant, so reverse Equation **b**.



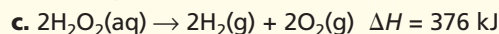
Two moles of  $\text{H}_2\text{O}_2$  are needed. Multiply the equation by 2 to obtain Equation **c**.



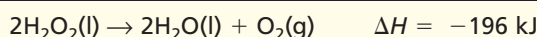
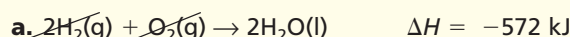
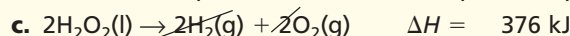
When you reverse an equation, you must change the sign of  $\Delta H$ . When you double an equation, you must double  $\Delta H$ .

$$\Delta H \text{ for Equation c} = -(\Delta H_{\text{Equation b}})(2)$$

$$\Delta H \text{ for Equation c} = -(-188 \text{ kJ})(2) = 376 \text{ kJ}$$



Add Equations **a** and **c** canceling any terms common to both sides of the combined equation. Add the enthalpies of Equations **a** and **c**.

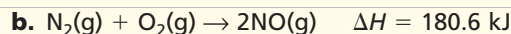
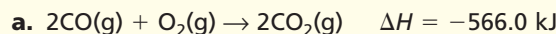


### 3. Evaluate the Answer

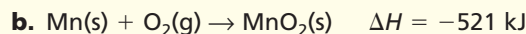
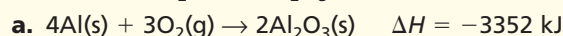
All values are accurate to the units place, so  $\Delta H$  is correctly stated. The two equations produce the desired equation.

## PRACTICE PROBLEMS

**28.** Use reactions **a** and **b** to determine  $\Delta H$  for the following reaction.



**29.** Use reactions **a** and **b** to determine  $\Delta H$  for the following reaction.



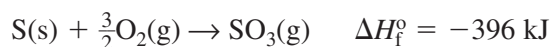
Practice!

For more practice using Hess's law, go to **Supplemental Practice Problems** in Appendix A.

## Standard Enthalpy (Heat) of Formation

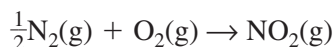
You have seen the usefulness of Hess's law in allowing you to calculate unknown  $\Delta H$  values using known reactions and their experimentally determined  $\Delta H$  values. However, recording and storing  $\Delta H$  values for all known chemical reactions would be a huge and constantly evolving task. To avoid this problem, scientists have chosen to record and use enthalpy changes for one type of reaction—a reaction in which a compound is formed from its constituent elements in their standard states. The standard state of a substance means the normal physical state of the substance at one atmosphere pressure and 298 K (25°C). For example, in its standard state, iron is a solid, mercury is a liquid, and oxygen is a diatomic gas.

The  $\Delta H$  value for such reactions is called the standard enthalpy (heat) of formation of the compound. The **standard enthalpy (heat) of formation** ( $\Delta H_f^\circ$ ) is defined as the change in enthalpy that accompanies the formation of one mole of the compound in its standard state from its constituent elements in their standard states. A typical standard heat of formation reaction is the formation of one mole of  $\text{SO}_3$  from its elements.



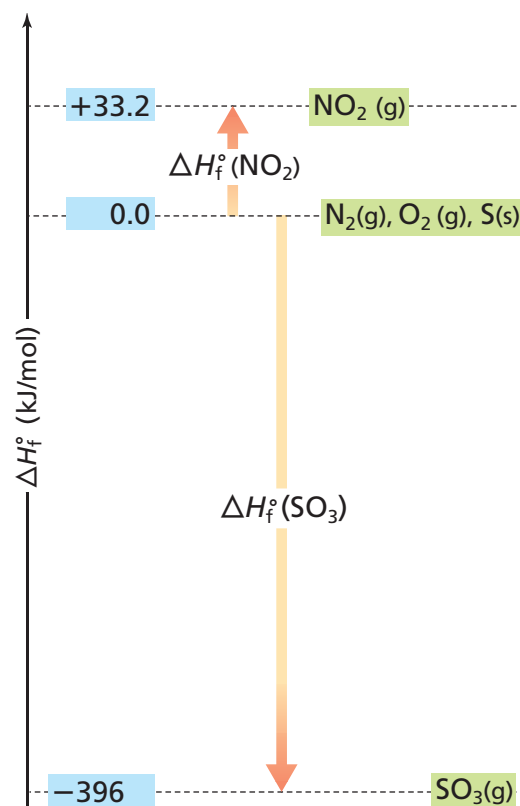
**Where do standard heats of formation come from?** When you state the height of a mountain, you do so relative to some point of reference—usually sea level. In a similar way, standard enthalpies of formation are stated based on the following arbitrary standard: Every free element in its standard state is assigned a  $\Delta H_f^\circ$  of exactly 0.0 kJ. With zero as the starting point, the experimentally determined enthalpies of formation of compounds can be placed on a scale above and below the elements in their standard states. Think of the zero of the enthalpy scale as being similar to the arbitrary assignment of 0.0°C to the freezing point of water. All substances warmer than freezing water have a temperature above zero. All substances colder than freezing water have a temperature below zero.

Standard enthalpies of formation of many compounds have been measured experimentally. For example, consider the equation for the formation of nitrogen dioxide.



The elements nitrogen and oxygen are diatomic gases in their standard states, so their standard enthalpies of formation are zero. When nitrogen and oxygen gases react to form one mole of nitrogen dioxide, the experimentally determined  $\Delta H$  for the reaction is 33.2 kJ. That means that 33.2 kJ of energy is absorbed in this endothermic reaction. Thus, the energy content of the product,  $\text{NO}_2$ , is 33.2 kJ greater than the energy content of the reactants. On a scale on which the  $\Delta H_f^\circ$  of reactants is defined as zero,  $\Delta H_f^\circ$  of  $\text{NO}_2(\text{g})$  is +33.2 kJ. **Figure 16-14** shows that on the scale of standard enthalpies of formation,  $\text{NO}_2$  is placed 33.2 kJ above the elements from which it was formed. Sulfur trioxide ( $\text{SO}_3$ ) is placed 396 kJ below zero on the scale because the formation of  $\text{SO}_3(\text{g})$  is an exothermic reaction. The energy content of the product  $\text{SO}_3(\text{g})$  is 396 kJ less than the energy content of the elements from which it was formed.

**Table 16-7** on the next page lists standard enthalpies of formation for some common compounds. A more complete list is in Appendix C, **Table C-13**.



**Figure 16-14**

Note  $\Delta H_f^\circ$  for the elements  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{S}$  is 0.0 kJ. When  $\text{N}_2$  and  $\text{O}_2$  react to form 1 mole of  $\text{NO}_2$ , 33.2 kJ is absorbed. One mole of  $\text{NO}_2$  has 33.2 kJ/mol more energy than the elements from which it is formed. Thus,  $\Delta H_f^\circ$  for  $\text{NO}_2$  is +33.2 kJ/mol. When  $\text{S}$  and  $\text{O}_2$  react to form one mole of  $\text{SO}_3$ , 396 kJ is released. Thus,  $\Delta H_f^\circ$  for  $\text{SO}_3$  is -396 kJ/mol.





Table 16-7

Standard Enthalpies of Formation for Selected Compounds		
Compound	Formation equation	$\Delta H_f^\circ$ (kJ/mol)
NO <sub>2</sub> (g)	$\frac{1}{2}\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g})$	33
H <sub>2</sub> S(g)	$\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightarrow \text{H}_2\text{S}(\text{g})$	-21
NH <sub>3</sub> (g)	$\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$	-46
CH <sub>4</sub> (g)	$\text{C}(\text{s, graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$	-75
HF(g)	$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{HF}(\text{g})$	-273
CCl <sub>4</sub> (l)	$\text{C}(\text{s, graphite}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{l})$	-128
H <sub>2</sub> O(l)	$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-286
SO <sub>2</sub> (g)	$\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$	-297
CO <sub>2</sub> (g)	$\text{C}(\text{s, graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-394
Fe <sub>2</sub> O <sub>3</sub> (s)	$2\text{Fe}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s})$	-824
SF <sub>6</sub> (g)	$\text{S}(\text{s}) + 3\text{F}_2(\text{g}) \rightarrow \text{SF}_6(\text{g})$	-1220
Al <sub>2</sub> O <sub>3</sub> (s)	$2\text{Al}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{s})$	-1680



Figure 16-15

Sulfur hexafluoride, one of the heaviest known gases, is used in this electrical substation to insulate circuit breakers, transformers, and other electrical equipment including high voltage transmission lines.

**Using standard enthalpies of formation** What is the significance of standard enthalpies of formation? How are they used? Standard enthalpies of formation provide useful data for calculating the enthalpies of reactions under standard conditions ( $\Delta H_{\text{rxn}}^\circ$ ) using Hess's law. Suppose you want to calculate  $\Delta H_{\text{rxn}}^\circ$  for this reaction, in which sulfur hexafluoride is produced. Sulfur hexafluoride is a stable, unreactive gas with some interesting applications, one of which is shown in **Figure 16-15**.



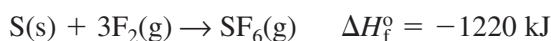
Recall that Hess's law allows you to combine equations and their  $\Delta H$  values to produce the desired equation and its  $\Delta H$  value. To apply Hess's law using standard enthalpies of formation data, you must have one equation for the formation of each compound in the desired equation. You can find these in **Table 16-7**. Three compounds are in the equation, HF, SF<sub>6</sub>, and H<sub>2</sub>S, so the three equations are these.

- $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{HF}(\text{g}) \quad \Delta H_f^\circ = -273 \text{ kJ}$
- $\text{S}(\text{s}) + 3\text{F}_2(\text{g}) \rightarrow \text{SF}_6(\text{g}) \quad \Delta H_f^\circ = -1220 \text{ kJ}$
- $\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightarrow \text{H}_2\text{S}(\text{g}) \quad \Delta H_f^\circ = -21 \text{ kJ}$

Equations **a** and **b** are for the formation of the products HF and SF<sub>6</sub>. Therefore, they can be used in the direction in which they are written. But because two moles of HF are required, Equation **a** and its enthalpy change must be multiplied by 2.

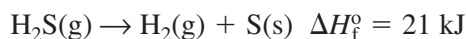


Equation **b** can be used as it is.

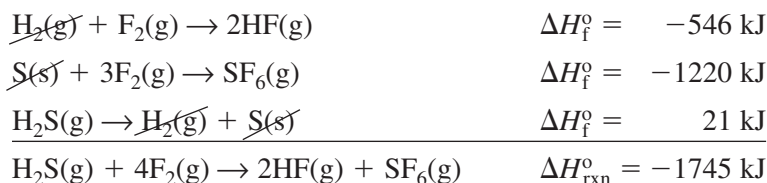


In the desired equation, H<sub>2</sub>S is a reactant rather than a product. Therefore, Equation **c** must be reversed. Recall that reversing a reaction changes the sign of  $\Delta H$ , so the sign of  $\Delta H$  for Equation **c** becomes positive.





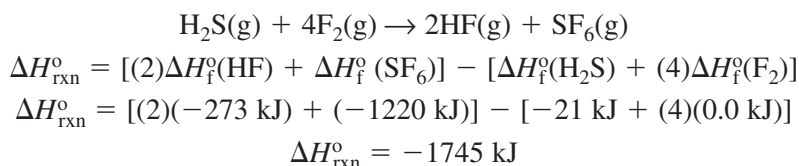
The three equations and their enthalpy changes can now be added. The elements  $\text{H}_2$  and  $\text{S}$  cancel.



This example shows how standard heats of formation equations combine to produce the desired equation and its  $\Delta H_{\text{rxn}}^\circ$ . The entire procedure is summed up in the following formula.

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

The symbol  $\Sigma$  means “to take the sum of the terms.” The formula says to subtract the sum of heats of formation of the reactants from the sum of the heats of formation of the products. You can see how this formula applies to the reaction between hydrogen sulfide and fluorine.



Note that the heat of formation of  $\text{HF}$  is multiplied by 2 because two moles of  $\text{HF}$  are formed. Also note that it is not necessary to change the sign of  $\Delta H_f^\circ(\text{H}_2\text{S})$  and that  $\Delta H_f^\circ(\text{F}_2)$  is 0.0 kJ because the standard heat of formation of an element in its standard state is zero.

## EXAMPLE PROBLEM 16-6

### Enthalpy Change from Standard Enthalpies of Formation

Use standard enthalpies of formation to calculate  $\Delta H_{\text{rxn}}^\circ$  for the combustion of methane. Methane is found in the atmosphere of the planet Pluto.  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

#### 1. Analyze the Problem

You are given an equation and asked to calculate the change in enthalpy. The formula  $\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$  can be used with data from Table 16-7.

##### Known

$$\begin{aligned} \Delta H_f^\circ(\text{CO}_2) &= -394 \text{ kJ} \\ \Delta H_f^\circ(\text{H}_2\text{O}) &= -286 \text{ kJ} \\ \Delta H_f^\circ(\text{CH}_4) &= -75 \text{ kJ} \\ \Delta H_f^\circ(\text{O}_2) &= 0.0 \text{ kJ} \end{aligned}$$

##### Unknown

$$\Delta H_{\text{rxn}}^\circ = ? \text{ kJ}$$

#### 2. Solve for the Unknown

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

Expand the formula to include a term for each reactant and product. Multiply each term by the coefficient of the substance in the balanced chemical equation.

*Continued on next page*



Pluto, the smallest of the Sun's planets and the farthest, on average, from the Sun, is shown with its moon Charon. Methane has been found in the thin atmosphere of Pluto.



$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_f^{\circ}(\text{CO}_2) + (2)\Delta H_f^{\circ}(\text{H}_2\text{O})] - [\Delta H_f^{\circ}(\text{CH}_4) + (2)\Delta H_f^{\circ}(\text{O}_2)]$$

Substitute the  $\Delta H_f^{\circ}$  values into the formula.

$$\Delta H_{\text{rxn}}^{\circ} = [(-394 \text{ kJ}) + (2)(-286 \text{ kJ})] - [(-75 \text{ kJ}) + (2)(0.0 \text{ kJ})]$$

$$\Delta H_{\text{rxn}}^{\circ} = [-966 \text{ kJ}] - [-75 \text{ kJ}] = -966 \text{ kJ} + 75 \text{ kJ} = -891 \text{ kJ}$$

The combustion of 1 mol  $\text{CH}_4$  releases 891 kJ.

### 3. Evaluate the Answer

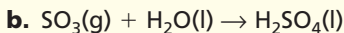
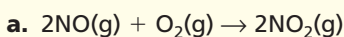
All values are accurate to the units place. Therefore, the answer is correct as stated. The calculated value is the same as that given in **Table 16-5** on page 501.



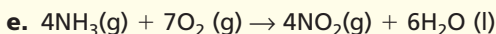
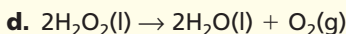
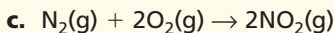
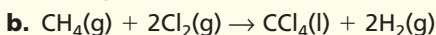
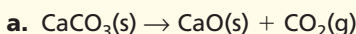
For more practice using standard enthalpies of formation, go to **Supplemental Practice Problems** in Appendix A.

## PRACTICE PROBLEMS

**30.** Show how the sum of enthalpy of formation equations produces each of the following reactions. You need not look up and include  $\Delta H$  values.



**31.** Use standard enthalpies of formation from Appendix C, **Table C-13** to calculate  $\Delta H_{\text{rxn}}^{\circ}$  for each of the following reactions.



You can see how valuable enthalpy of formation data are to a chemist. The  $\Delta H_{\text{rxn}}^{\circ}$  for any reaction can be calculated if  $\Delta H_f^{\circ}$  is known for all of the compounds among the reactants and products.

## Section 16.4 Assessment

- 32.** Explain what is meant by Hess's law and how it is used.
- 33.** What formula can be applied to determining  $\Delta H_{\text{rxn}}^{\circ}$  when using Hess's law? Explain the formula in words.
- 34.** On the scale of standard enthalpies of formations, how are the elements in their standard states defined?
- 35.** Low energy is associated with stability. Examine the data in **Table 16-7**. What conclusion can you draw about the stabilities of the compounds listed relative to the elements in their standard states?
- 36. Thinking Critically** Could the absolute enthalpy or heat content of the elements at  $298^{\circ}\text{C}$  and one atmosphere pressure actually be 0.0 kJ? Explain why or why not.
- 37. Interpreting Scientific Illustrations** Using the data below, draw a diagram similar to **Figure 16-14** and use the diagram to determine the heat of vaporization of water at 298 K.
- Liquid water:  $\Delta H_f^{\circ} = -285.8 \text{ kJ/mol}$   
Gaseous water:  $\Delta H_f^{\circ} = -241.8 \text{ kJ/mol}$



In **Figure 16-16**, you can see a familiar picture of what happens to an iron object when it's left outdoors in moist air. Iron rusts slowly according to the following equation. It's the same chemical reaction that occurs in the heat pack you learned about earlier in the chapter.

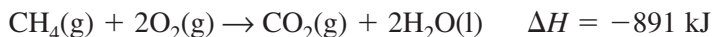


The heat pack goes into action the moment you activate it by ripping off the plastic covering. Similarly, unprotected iron objects rust whether you want them to or not.

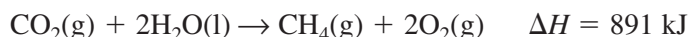
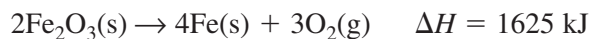
## Spontaneous Processes

Rusting, like many other processes, is spontaneous. A **spontaneous process** is a physical or chemical change that occurs with no outside intervention. However, for many spontaneous processes, some energy must be supplied to get the process started. For example, you may have used a sparker or a match to light a Bunsen burner in your school lab. Or perhaps you are familiar with the continuously burning pilot lights that are used in gas stoves and furnaces to start these appliances immediately. Once the gas has been ignited, the combustion process can proceed spontaneously.

You saw in an earlier problem that the thermochemical equation for the combustion of methane, the major component of natural gas, is this

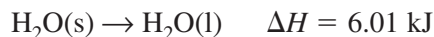


Suppose you reverse the direction of this equation and the equation for the rusting of iron. Recall that when you change the direction of a reaction, the sign of  $\Delta H$  changes. Both reactions become endothermic.



Reversing the equation will not make rust decompose spontaneously into iron and oxygen under ordinary conditions. And carbon dioxide will not react with water to form methane and oxygen. These two equations represent reactions that are not spontaneous.

Do you notice a correlation? Iron rusting and methane burning are exothermic and spontaneous. The reverse reactions are endothermic and nonspontaneous. Based upon reactions such as these, some nineteenth-century scientists concluded that all exothermic processes are spontaneous and all endothermic processes are nonspontaneous. However, you need not look far for evidence that this conclusion is incorrect. For example, you know that ice melts at room temperature. That's a spontaneous, endothermic process.



It's evident that something other than  $\Delta H$  plays a role in determining whether a chemical process occurs spontaneously under a given set of conditions. That something is called entropy.

## Objectives

- **Differentiate** between spontaneous and nonspontaneous processes.
- **Explain** how changes in entropy and free energy determine the spontaneity of chemical reactions and other processes.

## Vocabulary

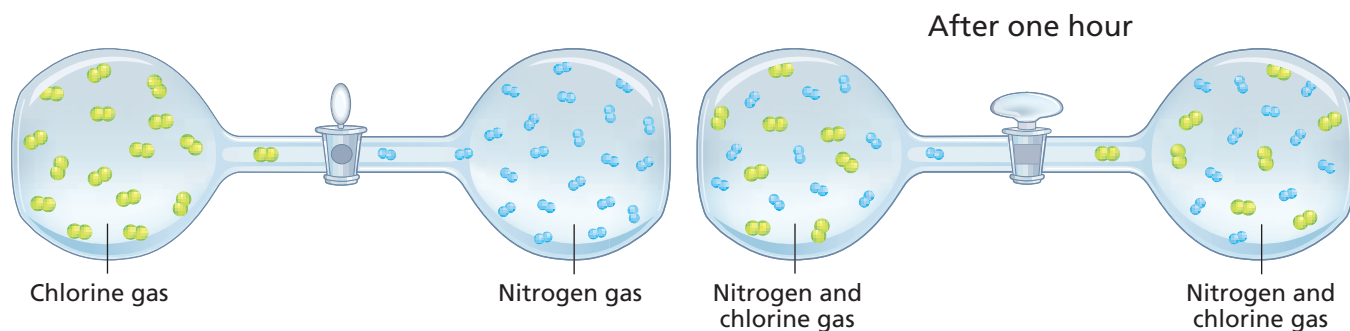
spontaneous process  
entropy  
law of disorder  
free energy

**Figure 16-16**

Year by year, the iron in this abandoned railroad equipment in the Alaskan tundra combines with oxygen to form rust,  $\text{Fe}_2\text{O}_3$ .







**Figure 16-17**

At the beginning of the experiment, chlorine and nitrogen molecules occupy separate bulbs. But when the stopcock is opened, the gas molecules move back and forth between the two bulbs and become thoroughly mixed. Refer to **Table C-1** in Appendix C for a key to atom color conventions.

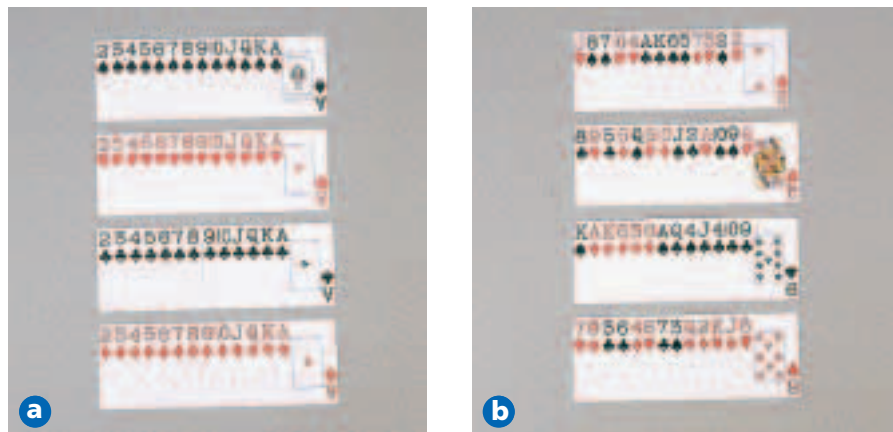
**What is entropy?** Think about what might happen when a glass bulb containing chlorine gas is connected to a similar glass bulb containing nitrogen gas, as shown in **Figure 16-17**. When the stopcock in the tube connecting the two bulbs is opened, the gases can pass freely from one bulb to the other. After an hour, you can see that the chlorine and nitrogen molecules are distributed uniformly between the two bulbs. You're probably not surprised at that result. After all, the delicious smell of brownies baking in the kitchen doesn't stay in the kitchen. It wafts to wherever you are. So, whether it's the aroma of brownies or the chlorine and nitrogen in the experiment, gases tend to mix. Why? The answer is that molecules are more likely to exist in a high state of disorder (mixed) than in a low state of disorder (unmixed). In thermodynamics, the term for disorder is *entropy*. **Entropy** ( $S$ ) is a measure of the disorder or randomness of the particles that make up a system.

The tendency toward disorder or randomness is summarized in the **law of disorder**, which states that spontaneous processes always proceed in such a way that the entropy of the universe increases. This law also is called the second law of thermodynamics. You can observe the law of disorder in many everyday situations. For example, suppose you shuffle a deck of 52 playing cards thoroughly and lay them down one after another to form four rows of 13 cards each. The cards might form the highly ordered arrangement shown in **Figure 16-18a**. However, the probability that you will lay down this exact, low-entropy sequence is one chance in  $8.07 \times 10^{67}$ . In other words, it's nearly impossible. Because there are so many possible highly disordered arrangements, it's almost infinitely more likely that you'll produce a high-entropy sequence such as the one shown in **Figure 16-18b**.

**Predicting changes in entropy** Recall that the change in enthalpy for a reaction is equal to the enthalpy of the products minus the enthalpy of the reactants. The change in entropy ( $\Delta S$ ) during a reaction or process is similar.

**Figure 16-18**

What are the chances that a shuffled deck of cards will lay out into four perfectly ordered rows as shown in **a**? Experience tells you that the chances for an orderly arrangement are almost negligible, and that a random arrangement like the one in **b** is far more likely.



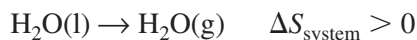


$$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$$

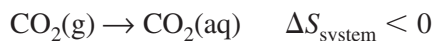
Therefore, if the entropy of a system increases during a reaction or process,  $S_{\text{products}} > S_{\text{reactants}}$  and  $\Delta S_{\text{system}}$  is positive. Conversely, if the entropy of a system decreases during a reaction or process,  $S_{\text{products}} < S_{\text{reactants}}$  and  $\Delta S_{\text{system}}$  is negative.

Can you predict if  $\Delta S_{\text{system}}$  is positive or negative by examining the equation for a reaction or process? In some cases you can.

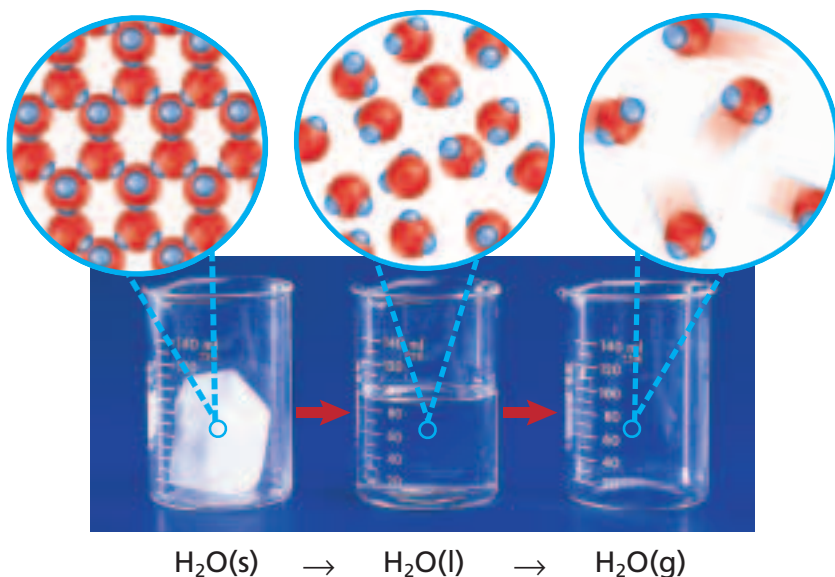
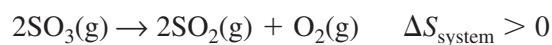
1. *Entropy changes associated with changes in state, such as those shown for water in **Figure 16-19**, can be predicted.* In solids, molecules are tightly packed and have limited movement, but they have some freedom to move in liquids. In gases, molecules are unrestricted in their movements except by the container in which they are held. Therefore, entropy increases as a substance changes from a solid to a liquid and from a liquid to a gas. For example, the entropy of the system increases ( $\Delta S_{\text{system}}$  is positive) as water vaporizes and as methanol melts.



2. *The dissolving of a gas in a solvent always results in a decrease in entropy.* Gas particles have more entropy when they can move freely in the gaseous state than when they are dissolved in a liquid or solid that limits their movements and randomness. For example,  $\Delta S_{\text{system}}$  is negative for the dissolving of carbon dioxide in water.



3. *Assuming no change in physical state, the entropy of a system usually increases when the number of gaseous product particles is greater than the number of gaseous reactant particles.* That's because the larger the number of gaseous particles, the more random arrangements are available. For the following reaction,  $\Delta S_{\text{system}}$  is positive because two gaseous molecules react and three gaseous molecules are produced.

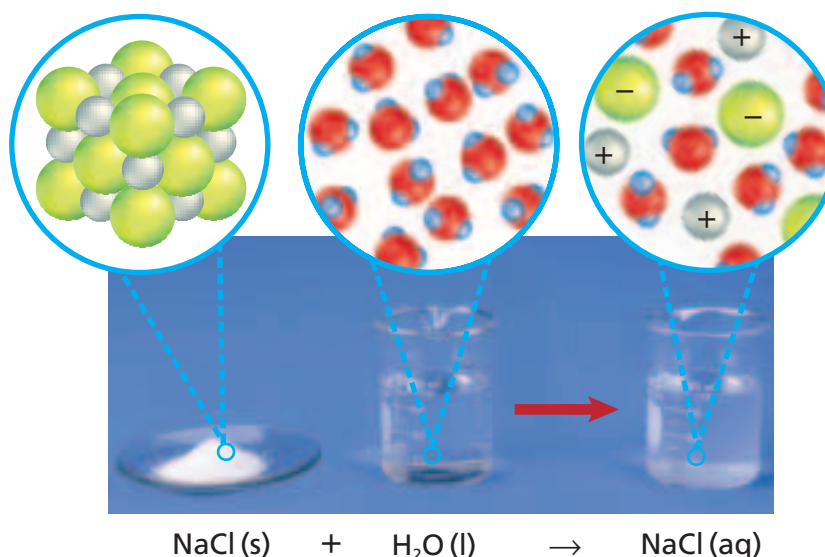


**Figure 16-19**

The molecules in an ice cube are in a rigid, orderly arrangement. The molecules in liquid water have some freedom to move and create different arrangements. Water molecules in the gas phase are completely separated and can create an almost infinite number of arrangements.

**Figure 16-20**

Sodium chloride and liquid water are pure substances each with a degree of orderliness. When sodium chloride dissolves in water, the entropy of the system increases because  $\text{Na}^+$  and  $\text{Cl}^-$  ions and water molecules mix together to create a large number of random arrangements.



4. With some exceptions, you can predict the change in entropy when a solid or a liquid dissolves to form a solution. The solute particles, which are separate and pure before dissolving, become dispersed throughout the solvent. Therefore, dissolution usually increases the randomness and disorder of the particles, as shown in **Figure 16-20**, and the entropy of the system increases. For the dissolving of sodium chloride in water,  $\Delta S_{\text{system}}$  is positive.



5. An increase in the temperature of a substance is always accompanied by an increase in the random motion of its particles. Recall that the kinetic energy of molecules increases with temperature. Increased kinetic energy means faster movement, more possible arrangements, and increased disorder. Therefore, the entropy of any substance increases as its temperature increases, and  $\Delta S_{\text{system}} > 0$ .

Practice!

For more practice predicting the sign of  $\Delta S$ , go to **Supplemental Practice Problems** in Appendix A.

## PRACTICE PROBLEMS

38. Predict the sign of  $\Delta S_{\text{system}}$  for each of the following changes.
- |  |  |
|--|--|
| <p>a. <math>\text{ClF(g)} + \text{F}_2(\text{g}) \rightarrow \text{ClF}_3(\text{g})</math></p> <p>b. <math>\text{NH}_3(\text{g}) \rightarrow \text{NH}_3(\text{aq})</math></p> | <p>c. <math>\text{CH}_3\text{OH(l)} \rightarrow \text{CH}_3\text{OH(aq)}</math></p> <p>d. <math>\text{C}_{10}\text{H}_8(\text{l}) \rightarrow \text{C}_{10}\text{H}_8(\text{s})</math></p> |
|--|--|

## Entropy, the Universe, and Free Energy

You may be wondering whether entropy has an effect on reaction spontaneity. Recall that the law of disorder states that the entropy of the universe must increase as a result of a spontaneous reaction or process. Therefore, the following is true for any spontaneous process.

$$\Delta S_{\text{universe}} > 0$$

Because the universe equals the system plus the surroundings, any change in the entropy of the universe is the sum of changes occurring in the system and surroundings.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$



LAB

See page 959 in Appendix E for **Observing Entropy**



How do changes in a system's enthalpy and entropy affect  $\Delta S_{\text{universe}}$ ? In nature,  $\Delta S_{\text{universe}}$  tends to be positive for reactions and processes under the following conditions.

1. The reaction or process is exothermic, which means  $\Delta H_{\text{system}}$  is negative. The heat released by an exothermic reaction raises the temperature of the surroundings and thereby increases the entropy of the surroundings.  $\Delta S_{\text{surroundings}}$  is positive.
2. The entropy of the system increases, so  $\Delta S_{\text{system}}$  is positive.

Thus, exothermic chemical reactions accompanied by an increase in entropy are all spontaneous.

**Free energy** Can you definitely determine if a reaction is spontaneous? In 1878, J. Willard Gibbs, a physicist at Yale University, defined a combined enthalpy-entropy function called Gibbs free energy that answers that question. For reactions or processes that take place at constant pressure and temperature, Gibbs free energy ( $G_{\text{system}}$ ), commonly called **free energy**, is energy that is available to do work. Thus, free energy is useful energy. In contrast, some entropy is associated with energy that is spread out into the surroundings as, for example, random molecular motion and cannot be recovered to do useful work. The free energy change ( $\Delta G_{\text{system}}$ ) is the difference between the system's change in enthalpy ( $\Delta H_{\text{system}}$ ) and the product of the Kelvin temperature and the change in entropy ( $T\Delta S_{\text{system}}$ ).

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

When a reaction or process occurs under standard conditions (298 K and one atmosphere pressure) the standard free energy change can be expressed by this equation.

$$\Delta G_{\text{system}}^{\circ} = \Delta H_{\text{system}}^{\circ} - T\Delta S_{\text{system}}^{\circ}$$

The sign of the free energy change of the system,  $\Delta G_{\text{system}}$ , tells you whether or not a reaction or process is spontaneous at a constant specified temperature and pressure. If the sign of the free energy change of the system is negative, the reaction is spontaneous. If the sign of the free energy change is positive, the reaction is nonspontaneous. The relationship between  $\Delta G_{\text{system}}$ ,  $\Delta S_{\text{universe}}$ , and reaction spontaneity is summarized in **Table 16-8**.

**Calculating free energy change** How do changes in enthalpy and entropy affect free energy change and spontaneity for the reaction between nitrogen and hydrogen to form ammonia?

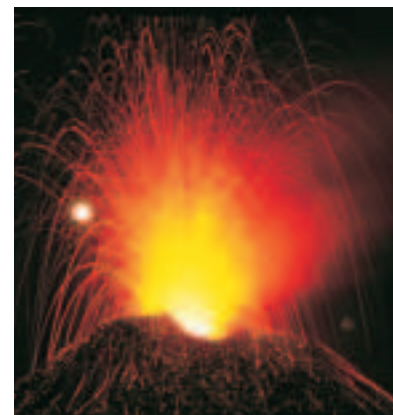


Note that the entropy of the system decreases because four moles of gaseous molecules react and only two moles of gaseous molecules are produced. Therefore,  $\Delta S_{\text{system}}^{\circ}$  is negative. A decrease in the entropy of the system tends

## CONNECTION

**V**olcanoes, fumaroles, hot springs, geysers, and boiling mud pools are manifestations of the great amount of geothermal energy in Earth's interior. Volcanoes are vents in Earth's crust from which flow molten rock (magma), steam, and other materials. When surface water moves downward through Earth's crust, it can interact with magma and/or hot rocks. Water that comes back to the surface in hot springs is heated to temperatures much higher than the surrounding air temperatures. Geysers are actually hot springs that spout hot water and steam into the air. Fumaroles emit steam and other gases such as hydrogen sulfide.

Geothermal energy provides an inexhaustible supply of energy that has been harnessed for a variety of applications. Buildings, homes, and greenhouses are warmed with energy from these sources. Geothermal energy also is used to warm soil to increase crop production in cooler climates. In several countries, electricity is generated by steam from geysers.



**Table 16-8**

$\Delta G_{\text{system}}$ and Reaction Spontaneity		
Type of reaction or process	$\Delta G_{\text{system}}$	$\Delta S_{\text{universe}}$
Spontaneous	negative	positive
Nonspontaneous	positive	negative







to make the reaction nonspontaneous. But the reaction is exothermic ( $\Delta H_{\text{system}}^{\circ}$  is negative), which tends to make the reaction spontaneous. To determine which of the two conflicting tendencies predominates, you must calculate  $\Delta G_{\text{system}}^{\circ}$  for the reaction. First, convert  $\Delta H_{\text{system}}^{\circ}$  to joules.

$$\Delta H_{\text{system}}^{\circ} = -91.8 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = -91\,800 \text{ J}$$

Now, substitute  $\Delta H_{\text{system}}^{\circ}$ ,  $T$ , and  $\Delta S_{\text{system}}^{\circ}$  into the defining equation for  $\Delta G_{\text{system}}^{\circ}$ .

$$\begin{aligned}\Delta G_{\text{system}}^{\circ} &= \Delta H_{\text{system}}^{\circ} - T\Delta S_{\text{system}}^{\circ} \\ \Delta G_{\text{system}}^{\circ} &= -91\,800 \text{ J} - (298 \text{ K})(-197 \text{ J/K}) \\ \Delta G_{\text{system}}^{\circ} &= -91\,800 \text{ J} + 58\,700 \text{ J} = -33\,100 \text{ J}\end{aligned}$$

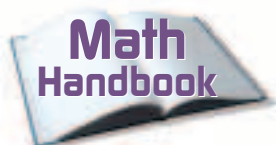
Because  $\Delta G_{\text{system}}^{\circ}$  for this reaction is negative, the reaction is spontaneous under standard conditions.

The reaction between nitrogen and hydrogen demonstrates that the entropy of a system may actually decrease during a spontaneous process. However, it can do so only if the entropy of the surroundings increases more than the entropy of the system decreases. The situation is analogous to that of a company that manufactures two products, A and B. The company can operate profitably if it loses money on product A, but only if it earns more money on product B than it loses on product A. **Table 16-9** shows how reaction spontaneity depends on the signs of  $\Delta H_{\text{system}}$  and  $\Delta S_{\text{system}}$ .

If  $\Delta G_{\text{system}}^{\circ} = 0$ , both reactants and products are present in a state known as chemical equilibrium. Chemical equilibrium describes a state in which the rate of the forward reaction equals the rate of the reverse reaction. You will learn more about chemical equilibrium in Chapter 18.

**Table 16-9**

How $\Delta H_{\text{system}}$ and $\Delta S_{\text{system}}$ Affect Reaction Spontaneity		
	$-\Delta H_{\text{system}}$	$+\Delta H_{\text{system}}$
$+\Delta S_{\text{system}}$	Always spontaneous	Spontaneity depends upon temperature
$-\Delta S_{\text{system}}$	Spontaneity depends upon temperature	Never spontaneous



Review solving algebraic equations in the **Math Handbook** on page 897 of this text.

### EXAMPLE PROBLEM 16-7

#### Determining Reaction Spontaneity

For a process,  $\Delta H_{\text{system}} = 145 \text{ kJ}$  and  $\Delta S_{\text{system}} = 322 \text{ J/K}$ . Is the process spontaneous at 382 K?

#### 1. Analyze the Problem

You are given  $\Delta H_{\text{system}}$  and  $\Delta S_{\text{system}}$  for a process and must calculate  $\Delta G_{\text{system}}$  to determine its sign.

#### Known

$$T = 382 \text{ K}$$

$$\Delta H_{\text{system}} = 145 \text{ kJ}$$

$$\Delta S_{\text{system}} = 322 \text{ J/K}$$

#### Unknown

$$\text{sign of } \Delta G_{\text{system}} = ?$$



## 2. Solve for the Unknown

Convert  $\Delta H_{\text{system}}$ , given in kJ, to joules.

$$145 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 145\,000 \text{ J}$$

Solve the free energy equation using the known values.

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

$$\Delta G_{\text{system}} = 145\,000 \text{ J} - (382 \text{ K})(322 \text{ J/K})$$

$$\Delta G_{\text{system}} = 145\,000 \text{ J} - 123\,000 \text{ J} = 22\,000 \text{ J}$$

Because  $\Delta G_{\text{system}}$  is positive, the reaction is nonspontaneous.

## 3. Evaluate the Answer

The given data have three significant figures. When  $\Delta H_{\text{system}}$  and  $\Delta S_{\text{system}}$  are expressed in joules, they are accurate to the nearest 1000. Therefore,  $\Delta G_{\text{system}}$  is also accurate to the nearest 1000, so the answer is correctly stated. When both  $\Delta H_{\text{system}}$  and  $\Delta S_{\text{system}}$  are positive,  $\Delta G_{\text{system}}$  is positive only if the temperature is low enough. The temperature ( $109^\circ\text{C}$ ) is not high enough to make the second term of the equation greater than the first and so  $\Delta G_{\text{system}}$  is positive.

## PRACTICE PROBLEMS

**39.** Given  $\Delta H_{\text{system}}$ ,  $T$ , and  $\Delta S_{\text{system}}$ , determine if each of the following processes or reactions is spontaneous or nonspontaneous.

- $\Delta H_{\text{system}} = -75.9 \text{ kJ}$ ,  $T = 273 \text{ K}$ ,  $\Delta S_{\text{system}} = 138 \text{ J/K}$
- $\Delta H_{\text{system}} = -27.6 \text{ kJ}$ ,  $T = 535 \text{ K}$ ,  $\Delta S_{\text{system}} = -55.2 \text{ J/K}$
- $\Delta H_{\text{system}} = 365 \text{ kJ}$ ,  $T = 388 \text{ K}$ ,  $\Delta S_{\text{system}} = -55.2 \text{ J/K}$



For more practice predicting the spontaneity of a reaction, go to **Supplemental Practice Problems** in Appendix A.

**Coupled reactions** Many of the chemical reactions that enable plants and animals to live and grow are nonspontaneous, that is,  $\Delta G_{\text{system}}$  is positive. Based on that information, you might ask why these nonspontaneous reactions occur so readily in nature. In living systems, nonspontaneous reactions often occur in conjunction with other reactions that are spontaneous (reactions for which  $\Delta G_{\text{system}}$  is negative). Reactions of this type that occur together are called coupled reactions. In coupled reactions, free energy released by one or more spontaneous reactions is used to drive a nonspontaneous reaction.

## Section 16.5 Assessment

- In terms of energy, explain the difference between a spontaneous and a nonspontaneous reaction.
- If a system becomes more disordered during a process, how does the system's entropy change?
- When you dissolve a teaspoonful of sugar in a cup of tea, does the entropy of the system increase or decrease? Define the system and explain your answer.
- Thinking Critically** Evaluate the following statement and explain why it is true or false: The law of disorder means that the entropy of a system can never decrease during a spontaneous reaction or process.
- Predicting** Predict the sign of  $\Delta S_{\text{system}}$  for the following reaction. Explain the basis for your prediction.  
$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$$



## Calorimetry

In this laboratory investigation, you will use the methods of calorimetry to approximate the amount of energy contained in a potato chip. The burning of a potato chip releases heat stored in the substances contained in the chip. The heat will be absorbed by a mass of water.

### Problem

How many Calories of energy does the potato chip contain? How can the experiment be improved to provide a more accurate answer?

### Objectives

- **Identify** the reactants and products in the reaction.
- **Measure** mass and temperature in order to calculate the amount of heat released in the reaction.
- **Propose** changes in the procedure and design of the equipment to decrease the percent error.

### Materials

large potato chip  
250-mL beaker  
100-mL graduated cylinder  
evaporating dish  
thermometer  
ring stand with ring  
wire gauze  
matches  
stirring rod  
balance

### Safety Precautions



- Always wear safety goggles and a lab apron.
- Tie back long hair.
- Hot objects may not appear to be hot.
- Do not heat broken, chipped, or cracked glassware.
- Do not eat any items used in the lab.

### Pre-Lab

1. Read the entire CHEMLAB.
2. Prepare all written materials that you will take into the laboratory. Be sure to include safety precautions, procedure notes, and a data table.
3. Form a hypothesis about how the quantity of heat produced by the combustion reaction will compare with the quantity of heat absorbed by the water.
4. What formula will you use to calculate the quantity of heat absorbed by the water?
5. Assuming that the potato chip contains compounds made up of carbon and hydrogen, what gases will be produced in the combustion reaction?

#### Observations of the Burning of a Potato Chip

Mass of beaker and 50 mL of water	
Mass of empty beaker	
Mass of water in beaker	
Mass of potato chip	
Highest temperature of water	
Initial temperature of water	
Change in temperature	

## Procedure

1. Measure the mass of a potato chip and record it in the data table.
2. Place the potato chip in an evaporating dish on the metal base of the ring stand. Position the ring and wire gauze so that they will be 10 cm above the top of the potato chip.
3. Measure the mass of an empty 250-mL beaker and record it in the data table.
4. Using the graduated cylinder, measure 50 mL of water and pour it into the beaker. Measure the mass of the beaker and water and record it in the data table.
5. Place the beaker on the wire gauze on the ring stand.
6. Measure and record the initial temperature of the water.
7. Use a match to ignite the bottom of the potato chip.
8. With a stirring rod, stir the water in the beaker while the chip burns. Measure the highest temperature of the water and record it in the data table.

## Cleanup and Disposal

1. Clean all lab equipment and return it to its proper place.
2. Wash your hands thoroughly after all lab work and cleanup is complete.

## Analyze and Conclude

1. **Classifying** Is the reaction exothermic or endothermic? Explain how you know.
2. **Observing and Inferring** Describe the reactant and products of the chemical reaction. Was the reactant (potato chip) completely consumed? What evidence supports your answer?
3. **Using Numbers** Calculate the mass of water in the beaker and the temperature change of the water. Use  $q = c \times m \times \Delta T$  to calculate how much heat in joules was transferred to the water in the beaker by the burning of one chip.
4. **Using Numbers** Convert the quantity of heat in joules/chip to Calories/chip.



5. **Using Numbers** From the information on the chip's container, determine the mass in grams of one serving. Using your data, calculate the number of Calories that would be released by the combustion of one serving of chips.
6. **Error Analysis** Use the chip's container to determine how many Calories are contained in one serving. Compare your calculated Calories per serving with the value on the chip's container. Calculate the percent error.
7. **Observing and Inferring** Was all of the heat that was released collected by the water in the beaker? How can the experimental equipment be improved to decrease the percent error?

## Real-World Chemistry

1. From the ingredients identified on the potato chip container, list the actual substances that burned to produce energy. Are there any ingredients that did not produce energy? Explain.
2. You have discovered that potato chips provide a significant number of Calories per serving. Would it be advisable to make potato chips a substantial part of your diet? Explain.



# How It Works

## Refrigerator

When you put soft drinks into a cooler containing ice, heat is absorbed from the soft drinks to melt the ice. The energy involved in the phase change from solid water to liquid water is responsible for cooling the soft drinks.

A refrigerator also uses the phase changes (evaporation and condensation) of a substance to move heat from the inside of the refrigerator to

the outside. A liquid called a refrigerant circulates through coils within the refrigerator and absorbs heat from the interior. The absorbed heat changes the refrigerant from a liquid to a gas. The gas is then compressed and circulated in condenser coils outside the refrigerator where it releases heat to the environment and is converted to a liquid.

**1** Liquid refrigerant enters the cooling coils inside the refrigerator at a temperature lower than the temperature of the air in the refrigerator.

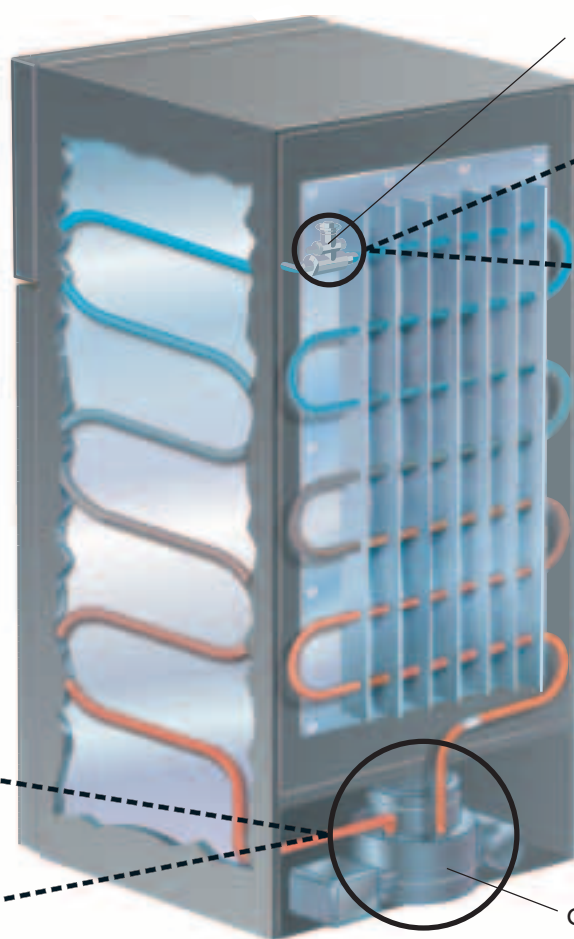
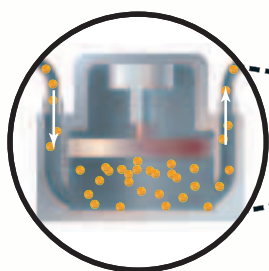
**2** The refrigerant absorbs heat from the air in the refrigerator and is converted from a liquid to a gas.

**3** The gaseous refrigerant leaves the refrigerator and enters a compressor, which squeezes the gas molecules together increasing their temperature and pressure.

Expansion valve

**5** The liquid refrigerant passes through an expansion valve which lowers its pressure and increases its volume. The refrigerant is now ready to re-enter the refrigerator.

**4** The hot, dense gas enters the condenser coils outside the refrigerator. Heat is released to the environment and the refrigerant condenses to a liquid.



Compressor

### Thinking Critically

**1. Predicting** What would happen if too much refrigerant was present in the system? Too little? Use phase changes to explain your predictions.

**2. Hypothesizing** A heat pump is a device that can either heat or cool a house. It is constructed in a fashion similar to a refrigerator. Explain how you think a heat pump works.

## Summary

### 16.1 Energy

- Energy is the capacity to do work or to produce heat. Energy may change from one form to another, but the amount of energy does not change.
- Chemical potential energy is energy stored in chemical bonds of a substance by virtue of the arrangement of the atoms and molecules.
- Chemical potential energy is released or absorbed as heat during chemical processes or reactions.

### 16.2 Heat in Chemical Reactions and Processes

- In thermochemistry, the universe is defined as the system plus the surroundings. The system is the reaction or process that is being studied, and the surroundings include everything in the universe except the system.
- The heat lost or gained by a system during a reaction or process carried out at constant pressure is called the change in enthalpy ( $\Delta H$ ).
- When  $\Delta H$  is positive, the reaction is endothermic. When  $\Delta H$  is negative, the reaction is exothermic.

### 16.3 Thermochemical Equations

- A thermochemical equation includes the physical states of the reactants and products and specifies the change in enthalpy.

- The molar enthalpy (heat) of vaporization,  $\Delta H_{\text{vap}}$ , is the amount of energy required to evaporate one mole of a liquid.
- The molar enthalpy (heat) of fusion,  $\Delta H_{\text{fus}}$ , is the amount of energy needed to melt one mole of a solid.

### 16.4 Calculating Enthalpy Change

- Using Hess's law, the enthalpy change for a reaction can be calculated by adding two or more thermochemical equations and their enthalpy changes.
- Standard enthalpies of formation are based upon assigning a standard enthalpy of 0.0 kJ to all elements in their standard states.

### 16.5 Reaction Spontaneity

- Exothermic reactions tend to be spontaneous because they increase the entropy of the surroundings.
- Entropy is a measure of the disorder or randomness of the particles of a system. Spontaneous processes always result in an increase in the entropy of the universe.
- Free energy is the energy available to do work.
- If the change in a system's free energy is negative, the reaction is spontaneous. If the change in free energy is positive, the reaction is nonspontaneous.

## Key Equations and Relationships

- $q = c \times m \times \Delta T$   
(p. 493)
- $\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum \Delta H_{\text{f}}^{\circ}(\text{reactants})$   
(p. 511)
- $\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$   
(p. 517)

## Vocabulary

- calorie (p. 491)
- calorimeter (p. 496)
- chemical potential energy (p. 490)
- energy (p. 489)
- enthalpy (p. 499)
- enthalpy (heat) of combustion (p. 501)
- enthalpy (heat) of reaction (p. 499)
- entropy (p. 514)
- free energy (p. 517)
- heat (p. 491)
- Hess's law (p. 506)
- joule (p. 491)
- law of conservation of energy (p. 490)
- law of disorder (p. 514)
- molar enthalpy (heat) of fusion (p. 502)
- molar enthalpy (heat) of vaporization (p. 502)
- specific heat (p. 492)
- spontaneous process (p. 513)
- standard enthalpy (heat) of formation (p. 509)
- surroundings (p. 498)
- system (p. 498)
- thermochemical equation (p. 501)
- thermochemistry (p. 498)
- universe (p. 498)

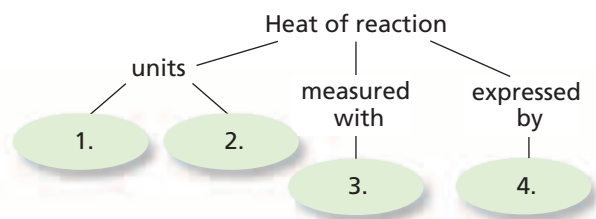




Go to the Chemistry Web site at [chemistrymc.com](http://chemistrymc.com) for additional Chapter 16 Assessment.

## Concept Mapping

45. Fill in the boxes with the following terms: calorimeter, calorie, thermochemical equation, joule.



## Mastering Concepts

46. Compare and contrast temperature and heat. (16.1)
47. How does the chemical potential energy of a system change during an endothermic reaction? (16.1)
48. How does the nutritional Calorie compare with the calorie? (16.1)
49. What quantity has the units  $J/(g \cdot ^\circ C)$ ? (16.1)
50. Describe a situation that illustrates potential energy changing to kinetic energy. (16.1)
51. In describing a chemical reaction, what is meant by the system? The surroundings? (16.2)
52. Under what condition is the heat ( $q$ ) evolved or absorbed in a chemical reaction equal to a change in enthalpy ( $\Delta H$ )? (16.2)
53. The enthalpy change for a reaction,  $\Delta H$ , is negative. What does this indicate about the chemical potential energy of the system before and after the reaction? (16.2)
54. How does the enthalpy of the products compare with the enthalpy of the reactants in an exothermic reaction? An endothermic reaction? (16.2)
55. What is the sign of  $\Delta H$  for an exothermic reaction? An endothermic reaction? (16.2)
56. Explain why you need to know the specific heat of a substance in order to calculate how much heat is gained or lost by the substance as a result of a temperature change. (16.2)
57. How is the quantity of heat lost by the system related to the quantity of heat gained by the surroundings during an exothermic process? (16.2)
58. How is a thermochemical equation different from a balanced chemical equation? (16.3)
59. Which has the higher heat content, a mole of liquid water or a mole of ice? (16.3)
60. Write the correct sign of  $\Delta H_{\text{system}}$  for each of the following changes in physical state. (16.3)
- $C_2H_5OH(s) \rightarrow C_2H_5OH(l)$
  - $H_2O(g) \rightarrow H_2O(l)$
  - $CH_3OH(l) \rightarrow CH_3OH(g)$
  - $NH_3(l) \rightarrow NH_3(s)$
61. How are the chemical elements in their standard states used as references for standard enthalpies of formation? (16.4)
62. Write the formula that can be used to calculate the enthalpy of a reaction from the enthalpies of formation of the reactants and products. (16.4)
63. Compare and contrast enthalpy and entropy. (16.5)
64. What does the entropy of a substance measure? (16.5)
65. What must happen to the entropy of the universe during a spontaneous reaction or process? (16.5)
66. From each pair, pick the one with the greater entropy. (16.5)
- $NH_3(g)$  and  $NH_3(l)$
  - $NH_3(g)$  and  $NH_3(aq)$
  - $CO_2(s)$  and  $CO_2(g)$
  - $KBr(s)$  and  $KBr(l)$
67. What is meant by the free energy of a system? (16.5)
68. What is the equation that defines free energy? (16.5)
69. How is the free energy change for a reaction related to its spontaneity? (16.5)
70. Explain how an exothermic reaction changes the entropy of the surroundings. Does the enthalpy change for such a reaction increase or decrease  $\Delta G_{\text{system}}$ ? Explain your answer. (16.5)
71. Explain how an endothermic reaction changes the entropy of the surroundings. How does the enthalpy change for such a reaction affect  $\Delta G_{\text{system}}$ ? (16.5)
72. Under what circumstance might a nonspontaneous reaction become spontaneous when the temperature increases? Decreases? (16.5)

- 73.** Explain why the gaseous state of a substance has a greater entropy than the liquid state of the same substance. (16.5)
- 74.** Predict the sign of  $\Delta S_{\text{system}}$  for each of these chemical reactions. Explain your predictions. (16.5)
- $2\text{SO}_3(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{CS}_2(\text{g}) + 4\text{O}_2(\text{g})$
  - $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
  - $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
  - $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{CO}_2(\text{g})$
  - $\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{SO}_3(\text{g})$

## Mastering Problems

### Energy (16.1)

- 75.** A fast-food item contains 544 nutritional Calories. Convert this energy to calories and to joules.
- 76.** An endothermic process absorbs 138 kJ. How many calories of heat are absorbed?
- 77.** An exothermic reaction releases 325 000 calories. Convert this energy to kJ.

### Measuring Heat (16.2)

- 78.** How many joules of heat are lost by 3580 kg granite as it cools from  $41.2^\circ\text{C}$  to  $-12.9^\circ\text{C}$ ?
- 79.** How much heat is absorbed by a 2000 kg granite boulder as energy from the sun causes its temperature to change from  $10^\circ\text{C}$  to  $29^\circ\text{C}$ ?
- 80.** A sample of silver with a mass of 63.3 g is heated to a temperature of 384.4 K and placed in a container of water at 290.0 K. The final temperature of the silver and water is 292.4 K. Assuming no heat loss, what mass of water was in the container? The specific heat of water is  $4.184 \text{ J}/(\text{g}\cdot^\circ\text{C})$  and of silver,  $0.24 \text{ J}/(\text{g}\cdot^\circ\text{C})$ .
- 81.** A swimming pool,  $20.0 \text{ m} \times 12.5 \text{ m}$ , is filled with water to a depth of 3.75 m. If the initial temperature of the water is  $18.4^\circ\text{C}$ , how much heat must be added to the water to raise its temperature to  $29.0^\circ\text{C}$ ? Assume that the density of water is  $1.000 \text{ g/mL}$ .

### Calculating Energy Change (16.3)

- 82.** How much heat is required to vaporize 343 g of liquid ethanol at its boiling point?  $\Delta H_{\text{vap}} = 38.6 \text{ kJ/mol}$
- 83.** How much heat is evolved when 1255 g of water condenses to a liquid at  $100^\circ\text{C}$ ?  $\Delta H_{\text{cond}} = -40.7 \text{ kJ/mol}$
- 84.** How much heat is liberated by the combustion of 206 g of hydrogen?  $\Delta H_{\text{comb}} = -286 \text{ kJ/mol}$
- 85.** A sample of ammonia liberates 5.66 kJ of heat as it solidifies at its melting point. What is the mass of the sample?  $\Delta H_{\text{solid}} = -5.66 \text{ kJ/mol}$ .

- 86.** How much heat is required to warm 225 g of ice from  $-46.8^\circ\text{C}$  to  $0.0^\circ\text{C}$ , melt the ice, warm the water from  $0.0^\circ\text{C}$  to  $100.0^\circ\text{C}$ , boil the water, and heat the steam to  $173.0^\circ\text{C}$ ?
- 87.** How much energy is involved in the dissolving of sodium hydroxide in water? The table shows data from an experiment in which a measured amount of NaOH is dissolved in water in a foam cup calorimeter. Calculate  $\Delta H$  for the process in kJ/mol. If the enthalpy change for the solution of NaOH is  $-44.51 \text{ kJ/mol}$ , what is the percent error of the experiment?

Table 16-10

Data for the Dissolving of NaOH	
Mass of NaOH + weighing paper	4.71 g
Mass of weighing paper	0.70 g
Mass of NaOH	
Mass of foam cup + water	109.85 g
Mass of foam cup	10.25 g
Mass of water	
Final temperature of water	$35.9^\circ\text{C}$
Initial temperature of water	$25.5^\circ\text{C}$
Change in temperature, $\Delta T$	

### Using Hess's Law (16.4)

- 88.** You are given these two equations.
- $$\text{Sn}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{SnCl}_2(\text{s}) \quad \Delta H = -325 \text{ kJ}$$
- $$\text{SnCl}_2(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{SnCl}_4(\text{l}) \quad \Delta H = -186 \text{ kJ}$$
- Calculate  $\Delta H$  for this reaction.
- $$\text{Sn}(\text{s}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{SnCl}_4(\text{l})$$
- 89.** Use standard enthalpies of formation from Table C-13 in Appendix C to calculate  $\Delta H_{\text{rxn}}^\circ$  for each of these reactions.
- $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
  - $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l})$
  - $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
  - $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + 2\text{SO}_2(\text{g})$
  - $4\text{FeS}(\text{s}) + 7\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s}) + 4\text{SO}_2(\text{g})$



**Reaction Spontaneity (16.5)**

- 90.** Calculate  $\Delta G_{\text{system}}$  for each process and state if the process is spontaneous or nonspontaneous.
- $\Delta H_{\text{system}} = 145 \text{ kJ}$ ,  $T = 293 \text{ K}$ ,  
 $\Delta S_{\text{system}} = 195 \text{ J/K}$
  - $\Delta H_{\text{system}} = -232 \text{ kJ}$ ,  $T = 273 \text{ K}$ ,  
 $\Delta S_{\text{system}} = 138 \text{ J/K}$
  - $\Delta H_{\text{system}} = -15.9 \text{ kJ}$ ,  $T = 373 \text{ K}$ ,  
 $\Delta S_{\text{system}} = -268 \text{ J/K}$
- 91.** Calculate the temperature at which  $\Delta G_{\text{system}} = -34.7 \text{ kJ}$  if  $\Delta H_{\text{system}} = -28.8 \text{ kJ}$  and  $\Delta S_{\text{system}} = 22.2 \text{ J/K}$ ?
- 92.** Under certain conditions, iron ore ( $\text{Fe}_3\text{O}_4$ ) can be converted to iron by the following reaction.
- $$\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g})$$
- $$\Delta H_{\text{system}} = 149.8 \text{ kJ}$$
- $$\Delta S_{\text{system}} = 610.0 \text{ J/K}$$
- Is the reaction spontaneous at 298 K? Explain why or why not based upon how the entropy of the system, surroundings, and universe change as a result of the reaction.

**Mixed Review**

Sharpen your problem-solving skills by answering the following.

- 93.** What mass of octane must be burned in order to liberate 5340 kJ of heat?  $\Delta H_{\text{comb}} = -5471 \text{ kJ/mol}$ .
- 94.** How much heat is released to the surroundings when 200 g of water at 96.0°C cools to 25.0°C? The specific heat of water is 4.184 J/(g·°C).
- 95.** What is the final temperature of 1280 g of water, originally at 20.0°C, if it absorbs 47.6 kJ of heat?
- 96.** Is the following reaction spontaneous at 456 K? If not, is it spontaneous at some other temperature? Explain your answer.
- $$\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$$
- $$\Delta H_{\text{system}} = 68 \text{ kJ}$$
- $$\Delta S_{\text{system}} = -122 \text{ J/K}$$
- 97.** Use Hess's law to determine  $\Delta H$  for the reaction  $\text{NO}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{NO}_2(\text{g})$   $\Delta H = ?$  given the following reactions. Show your work.
- $$\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g}) \quad \Delta H = +495 \text{ kJ}$$
- $$2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g}) \quad \Delta H = -427 \text{ kJ}$$
- $$\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = -199 \text{ kJ}$$

**Thinking Critically**

- 98. Using Numbers** A 133-g piece of granite rock is heated to 65.0°C, then placed in 643 g ethanol at 12.7°C. Assuming no heat loss, what is the final temperature of the granite and ethanol? See **Table 16-2**.
- 99. Applying Concepts** Write the thermochemical equation for the decomposition of liquid hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to water vapor and oxygen gas. Calculate  $\Delta H_{\text{system}}$  for the reaction using standard enthalpies of formation. Analyze the reaction and explain why NASA found this reaction suitable for providing thrust in the control jets of some space vehicles.
- 100. Recognizing Cause and Effect** Explain why the equation  $\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$  is especially valuable in recognizing how reactions and processes affect the entropy of the universe.

**Writing in Chemistry**

- 101.** Research and explain how hydrogen might be produced, transported, and used as a fuel for automobiles. Summarize the benefits and drawbacks of using hydrogen as an alternative fuel for internal combustion engines.
- 102.** Research the use of wind as a source of electrical power. Explain the possible benefits, disadvantages, and limitations of its use.

**Cumulative Review**

Refresh your understanding of previous chapters by answering the following.

- 103.** Why is it necessary to perform repeated experiments in order to support a hypothesis? (Chapter 1)
- 104.** Phosphorus has the atomic number 15 and an atomic mass of 31 amu. How many protons, neutrons, and electrons are in a neutral phosphorus atom? (Chapter 4)
- 105.** What element has the electron configuration  $[\text{Ar}]4s^13d^5$ ? (Chapter 5)
- 106.** Name the following molecular compounds. (Chapter 8)
- $\text{S}_2\text{Cl}_2$
  - $\text{CS}_2$
  - $\text{SO}_3$
  - $\text{P}_4\text{O}_{10}$
- 107.** Determine the molar mass for the following compounds. (Chapter 11)
- $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
  - $\text{Fe}(\text{OH})_3$

# STANDARDIZED TEST PRACTICE

## CHAPTER 16

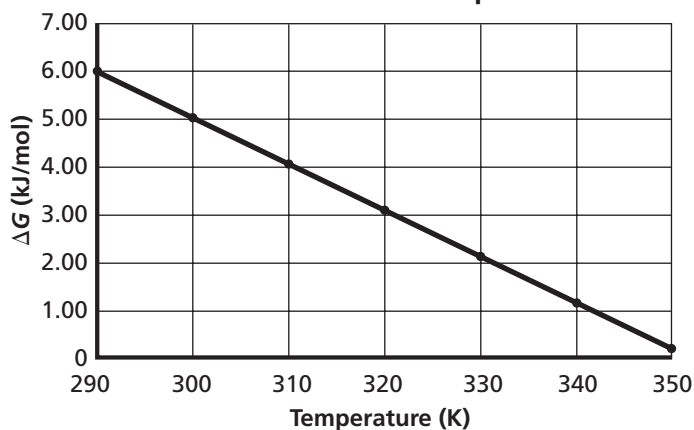
Use these questions and the test-taking tip to prepare for your standardized test.

- The specific heat of ethanol is 2.44 J/g·°C. How many kilojoules of energy are required to heat 50.0 g of ethanol from -20.0°C to 68.0°C?
  - 10.7 kJ
  - 8.30 kJ
  - 2.44 kJ
  - 1.22 kJ
- When a reaction takes place at constant pressure, what is  $q$  for the reaction?
  - $\Delta S_{\text{rxn}}$
  - $\Delta H_{\text{rxn}}$
  - $\Delta G_{\text{rxn}}$
  - $c_{\text{rxn}}$
- Determine  $\Delta H$  for the reaction of aluminum and sulfur dioxide.
 
$$4\text{Al(s)} + 3\text{SO}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)} + 3\text{S(s)}$$
 Use the following equations:
 
$$4\text{Al(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)} \quad \Delta H = -3352 \text{ kJ/mol}$$

$$\text{S(s)} + \text{O}_2\text{(g)} \rightarrow \text{SO}_2\text{(g)} \quad \Delta H = -297 \text{ kJ/mol}$$
  - 4243 kJ
  - 3649 kJ
  - 3055 kJ
  - 2461 kJ

**Interpreting Graphs** Use the graph to answer questions 4–6.

**$\Delta G$  for the Vaporization of Cyclohexane as a Function of Temperature**



- In the range of temperatures shown, the vaporization of cyclohexane
  - does not occur at all.
  - will occur spontaneously.
  - is not spontaneous.
  - occurs only at high temperatures.

- The standard free energy, enthalpy, and entropy of vaporization are often written with the subscript *vap* to indicate that they are associated with a vaporization reaction. What is the  $\Delta G_{\text{vap}}^{\circ}$  of cyclohexane at 300 K?
  - 5.00 kJ/mol
  - 4.00 kJ/mol
  - 3.00 kJ/mol
  - 2.00 kJ/mol
- When  $\Delta G_{\text{vap}}^{\circ}$  is plotted as a function of temperature, the slope of the line equals  $\Delta S_{\text{vap}}^{\circ}$  and the y-intercept of the line equals  $\Delta H_{\text{vap}}^{\circ}$ . What is the approximate standard entropy of vaporization of cyclohexane.
  - 50.0 J/mol·K
  - 10.0 J/mol·K
  - 5.0 J/mol·K
  - 100 J/mol·K
- 3.00 g of aluminum foil is placed in an oven and heated from 20.0°C to 662.0°C. If it absorbs 1728 J of heat, what is the specific heat of aluminum?
  - 0.131 J/g·°C
  - 0.870 J/g·°C
  - 0.897 J/g·°C
  - 2.61 J/g·°C
- $\text{AB(s)} + \text{C}_2\text{(l)} \rightarrow \text{AC(g)} + \text{BC(g)}$   
Which cannot be predicted about this reaction?
  - the entropy of the system decreases
  - the entropy of the products is higher than that of the reactants
  - the change in entropy for this reaction,  $\Delta S_{\text{rxn}}$ , is positive
  - the disorder of the system increases
- $\text{Co(s)} + \text{S(s)} + 2\text{O}_2\text{(g)} \rightarrow \text{CoSO}_4\text{(s)}$   
 $\Delta H_f^{\circ} = -888.3 \text{ kJ/mol}$ ,  $\Delta S_f^{\circ} = 118.0 \text{ J/mol}\cdot\text{K}$   
 Given the above thermochemical data for the formation of cobalt(II) sulfate from its elements, what is  $\Delta G_f^{\circ}$  for  $\text{CoSO}_4$  at 25°C?
  - 853.1 kJ/mol
  - 885.4 kJ/mol
  - 891.3 kJ/mol
  - 923.5 kJ/mol

### TEST-TAKING TIP

**Stock Up On Supplies** Bring all your test-taking tools: number two pencils, black and blue pens, erasers, correction fluid, a sharpener, a ruler, a calculator, and a protractor. Bring munchies, too. You might not be able to eat them in the testing room, but they come in handy for the break, if you're allowed to go outside.

