

# CAUSES OF CHANGE

**A** chemical reaction can release or absorb energy and can increase or decrease disorder. The forest fire is a chemical reaction in which cellulose and oxygen form carbon dioxide, water, and other chemicals. This reaction also releases energy and increases disorder because the reaction generates energy as heat and breaks down the long molecules found in living trees into smaller and simpler molecules, such as carbon dioxide,  $\text{CO}_2$ , and water,  $\text{H}_2\text{O}$ .

## START-UP ACTIVITY

### SAFETY PRECAUTIONS

#### Heat Exchange

##### PROCEDURE



1. Fill a **film canister** three-fourths full of **hot water**. Insert the **thermometer apparatus** prepared by your teacher in the hot water.
2. Fill a **250 ml beaker** one-third full of **cool water**. Insert another **thermometer apparatus** in the cool water, and record the water's temperature.
3. Record the temperature of the water in the film canister. Place the film canister in the cool water. Record the temperature measured by each thermometer every 30 s.
4. When the two temperatures are nearly the same, stop and graph your data. Plot temperature versus time on the graph. Remember to write "Time" on the  $x$ -axis and "Temperature" on the  $y$ -axis.

##### ANALYSIS

1. How can you tell that energy is transferred? Is energy transferred to or from the hot water?
2. Predict what the final temperatures would become after a long time.

## Pre-Reading Questions

- ① Can a chemical reaction generate energy as heat?
- ② Name two types of energy.
- ③ What is specific heat?
- ④ Does a thermometer measure temperature or heat?

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# Energy Transfer

## KEY TERMS

- heat
- enthalpy
- temperature

### heat

the energy transferred between objects that are at different temperatures

## OBJECTIVES

- 1 Define *enthalpy*.
- 2 Distinguish between heat and temperature.
- 3 Perform calculations using molar heat capacity.

## Energy as Heat

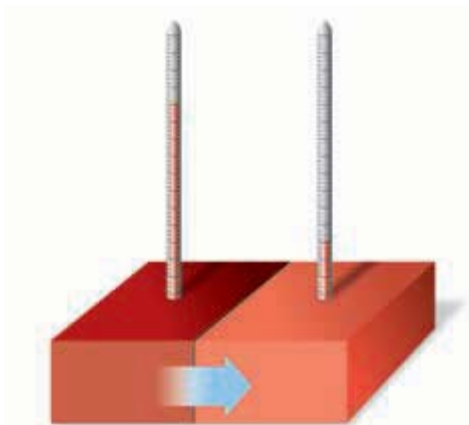
A sample can transfer energy to another sample. Some examples of energy transfer are the electric current in a wire, a beam of light, a moving piston, and a flame used by a welder as shown in **Figure 1**. One of the simplest ways energy is transferred is as **heat**.

Though energy has many different forms, all energy is measured in units called *joules* (J). So, the amount of energy that one sample transfers to another sample as heat is measured in joules. Energy is never created or destroyed. The amount of energy transferred from one sample must be equal to the amount of energy received by a second sample. Therefore, the total energy of the two samples remains exactly the same.

### Figure 1

A welder uses an exothermic combustion reaction to create a high-temperature flame. The iron piece then absorbs energy from the flame.





**Figure 2**

**a** Energy is always transferred from a warmer sample to a cooler sample, as the thermometers show.



**b** Even though both beakers receive the same amount of energy, the beakers do not have the same amount of liquid. So, the beaker on the left has a temperature of 30°C, and the beaker on the right has a temperature of 50°C.

## Temperature

When samples of different temperatures are in contact, energy is transferred from the sample that has the higher **temperature** to the sample that has the lower temperature. **Figure 1** shows a welder at work; he is placing a high-temperature flame very close to a low-temperature piece of metal. The flame transfers energy as heat to the metal. The welder wants to increase the temperature of the metal so that it will begin to melt. Then, he can fuse this piece of metal with another piece of metal.

If no other process occurs, the temperature of a sample increases as the sample absorbs energy, as shown in **Figure 2a**. The temperature of a sample depends on the average kinetic energy of the sample's particles. The higher the temperature of a sample is, the faster the sample's particles move.

The temperature increase of a sample also depends on the mass of the sample. For example, the liquids in both the beakers in **Figure 2b** were initially 10.0°C, and equal quantities of energy were transferred to each beaker. The temperature increase in the beaker on the left is only about one-half of the temperature increase in the beaker on the right, because the beaker on the left has twice as much liquid in it.

## Heat and Temperature are Different

You know that heat and temperature are different because you know that when two samples at different temperatures are in contact, energy can be transferred as heat. Heat and temperature differ in other ways. Temperature is an *intensive property*, which means that the temperature of a sample does not depend on the amount of the sample. However, heat is an *extensive property* which means that the amount of energy transferred as heat by a sample depends on the amount of the sample. So, water in a glass and water in a pitcher can have the same temperature. But the water in the pitcher can transfer more energy as heat to another sample because the water in the pitcher has more particles than the water in the glass.

### temperature

a measure of how hot (or cold) something is; specifically, a measure of the average kinetic energy of the particles in an object

### Topic Link

Refer to the "Matter and Energy" chapter for a discussion of heat, temperature, the Celsius scale, and the Kelvin scale.



**Figure 3**

The boiling in a kettle on a stove shows several physical and chemical processes: a combustion reaction, conduction, and a change of state.

### enthalpy

the sum of the internal energy of a system plus the product of the system's volume multiplied by the pressure that the system exerts on its surroundings

**Figure 3** shows a good example of the relationship between heat and temperature. The controlled combustion in the burner of a gas stove transfers energy as heat to the metal walls of the kettle. The temperature of the kettle walls increases. As a result, the hot walls of the kettle transfer energy to the cool water in the kettle. This energy transferred as heat raises the water's temperature to  $100^{\circ}\text{C}$ . The water boils, and steam exits from the kettle's spout. If the burner on the stove was turned off, the burner would no longer transfer energy to the kettle. Eventually, the kettle and the water would have equal temperatures, and the kettle would not transfer energy as heat to the water.

## A Substance's Energy Can Be Measured by Enthalpy

All matter contains energy. Measuring the total amount of energy present in a sample of matter is impossible, but changes in energy content can be determined. These changes are determined by measuring the energy that enters or leaves the sample of matter. If 73 J of energy enter a piece of silver and no change in pressure occurs, we know that the enthalpy of the silver has increased by 73 J. **Enthalpy**, which is represented by the symbol  $H$ , is the total energy content of a sample. If pressure remains constant, the enthalpy increase of a sample of matter equals the energy as heat that is received. This relationship remains true even when a chemical reaction or a change of state occurs.

## A Sample's Enthalpy Includes the Kinetic Energy of Its Particles

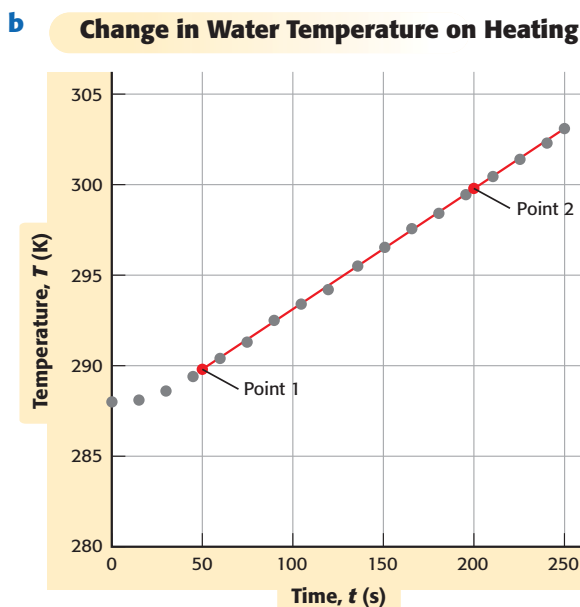
The particles in a sample are in constant motion. In other words, these particles have kinetic energy. You know that the enthalpy of a sample is the energy that a sample has. So, the enthalpy of a sample also includes the total kinetic energy of its particles.

Imagine a gold ring being cooled. As the ring transfers energy as heat to its surroundings, there is a decrease in the motions of the atoms that make up the gold ring. The kinetic energies of the atoms decrease. As the total kinetic energy decreases, the enthalpy of the ring decreases. This decrease in the kinetic energy is observed as a decrease in temperature.

You may think that all the atoms in the ring have the same kinetic energy. However, some of the atoms of the gold ring move faster than other atoms in the ring. Therefore, both the total and average kinetic energies of a substance's particles are important to chemistry, because these quantities account for every particle's kinetic energy.

What happens to the motions of the gold atoms if the ring is cooled to absolute zero ( $T = 0.00\text{ K}$ )? The atoms still move! However, the average and total kinetic energies of the atoms at  $0.00\text{ K}$  are the *minimum* average and total kinetic energies these atoms can have. This idea is true of any substance and its particles. The minimum average and total kinetic energies of particles that make up a substance occur at  $0.00\text{ K}$ .

How can the enthalpy change of a sample be calculated? Enthalpy changes can be calculated by using several different methods. The next section discusses molar heat capacity, which will be used to determine the enthalpy change of a sample.



**Figure 4**  
**a** This figure shows apparatus used for determining the molar heat capacity of water by supplying energy at a known constant rate and recording the temperature rise.  
**b** The graph shows the data points from the experiment. The red points are not data points; they were used in the calculation of the line's slope.

## Molar Heat Capacity

The *molar heat capacity* of a pure substance is the energy as heat needed to increase the temperature of 1 mol of the substance by 1 K. Molar heat capacity has the symbol  $C$  and the unit  $\text{J/K}\cdot\text{mol}$ . Molar heat capacity is accurately measured only if no other process, such as a chemical reaction, occurs.

The following equation shows the relationship between heat and molar heat capacity, where  $q$  is the heat needed to increase the temperature of  $n$  moles of a substance by  $\Delta T$ .

$$q = nC\Delta T$$

heat = (amount in moles)(molar heat capacity)(change in temperature)

Experiments and analyses that are similar to **Figure 4** determine molar heat capacity. **Figure 4a** shows 20.0 mol of water, a thermometer, and a 100 W heater in a beaker. The temperature of the water is recorded every 15 s for 250 s. The data are graphed in **Figure 4b**.

The slope of the straight line that is drawn to closely match the data points can be used to determine water's molar heat capacity. During 150 s, the interval between  $t = 50$  s and  $t = 200$  s, the temperature of the water increased by 9.9 K. The value of the slope is calculated below.

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\Delta T}{\Delta t} = \frac{9.9 \text{ K}}{150 \text{ s}} = 0.066 \text{ K/s}$$

To calculate the molar heat capacity of water, you need to know the heater's power rating multiplied by the amount of time the heater warmed the water. This is because watts are equal to joules per second. So,  $C$  for  $\text{H}_2\text{O}$  can be determined by using the following equation. Also notice that  $\Delta t$  divided by  $\Delta T$  is the inverse of the slope calculated above.

$$C = \frac{q}{n\Delta T} = \frac{1.00 \times 10^2 \text{ J/s}}{n(\text{slope})} = \frac{1.00 \times 10^2 \text{ J/s}}{(20.0 \text{ mol})(0.066 \text{ K/s})} = 76 \text{ J/K}\cdot\text{mol}$$



## SAMPLE PROBLEM A

### Calculating the Molar Heat Capacity of a Sample

Determine the energy as heat needed to increase the temperature of 10.0 mol of mercury by 7.5 K. The value of  $C$  for mercury is  $27.8 \text{ J/K}\cdot\text{mol}$ .

#### PRACTICE HINT

Always convert temperatures to the Kelvin scale before carrying out calculations in this chapter. Notice that in molar heat capacity problems, you will never multiply heat by molar heat capacity. If you did multiply, the joules would not cancel.

#### 1 Gather information.

The amount of mercury is 10.0 mol.  
 $C$  for Hg =  $27.8 \text{ J/K}\cdot\text{mol}$   
 $\Delta T = 7.5 \text{ K}$

#### 2 Plan your work.

Use the values that are given in the problem and the equation  $q = nC\Delta T$  to determine  $q$ .

#### 3 Calculate.

$$q = nC\Delta T$$
$$q = (10.0 \text{ mol})(27.8 \text{ J/K}\cdot\text{mol})(7.5 \text{ K})$$
$$q = 2085 \text{ J}$$

The answer should only have two significant figures, so it is reported as 2100 J or  $2.1 \times 10^3 \text{ J}$ .

#### 4 Verify your results.

The calculation yields an energy as heat with the correct unit, *joules*. This result supports the idea that the answer is the energy as heat needed to raise 10.0 mol Hg 7.5 K.

## PRACTICE



- 1 The molar heat capacity of tungsten is  $24.2 \text{ J/K}\cdot\text{mol}$ . Calculate the energy as heat needed to increase the temperature of 0.40 mol of tungsten by 10.0 K.
- 2 Suppose a sample of NaCl increased in temperature by 2.5 K when the sample absorbed  $1.7 \times 10^2 \text{ J}$  of energy as heat. Calculate the number of moles of NaCl if the molar heat capacity is  $50.5 \text{ J/K}\cdot\text{mol}$ .
- 3 Calculate the energy as heat needed to increase the temperature of 0.80 mol of nitrogen,  $\text{N}_2$ , by 9.5 K. The molar heat capacity of nitrogen is  $29.1 \text{ J/K}\cdot\text{mol}$ .
- 4 A 0.07 mol sample of octane,  $\text{C}_8\text{H}_{18}$ , absorbed  $3.5 \times 10^3 \text{ J}$  of energy. Calculate the temperature increase of octane if the molar heat capacity of octane is  $254.0 \text{ J/K}\cdot\text{mol}$ .

**Table 1 Molar Heat Capacities of Elements and Compounds**

Element	C (J/K•mol)	Compound	C (J/K•mol)
Aluminum, Al(s)	24.2	Aluminum chloride, AlCl <sub>3</sub> (s)	92.0
Argon, Ar(g)	20.8	Barium chloride, BaCl <sub>2</sub> (s)	75.1
Helium, He(g)	20.8	Cesium iodide, CsI(s)	51.8
Iron, Fe(s)	25.1	Octane, C <sub>8</sub> H <sub>18</sub> (l)	254.0
Mercury, Hg(l)	27.8	Sodium chloride, NaCl(s)	50.5
Nitrogen, N <sub>2</sub> (g)	29.1	Water, H <sub>2</sub> O(g)	36.8
Silver, Ag(s)	25.3	Water, H <sub>2</sub> O(l)	75.3
Tungsten W(s)	24.2	Water, H <sub>2</sub> O(s)	37.4

### Molar Heat Capacity Depends on the Number of Atoms

The molar heat capacities of a variety of substances are listed in **Table 1**. One mole of tungsten has a mass of 184 g, while one mole of aluminum has a mass of only about 27 g. So, you might expect that much more heat is needed to change the temperature of 1 mol W than is needed to change the temperature of 1 mol Al. This is not true, however. Notice that the molar heat capacities of all of the metals are nearly the same. The temperature of 1 mol of *any* solid metal is raised 1 K when the metal absorbs about 25 J of heat. The reason the temperature is raised is that the energy is absorbed by increasing the kinetic energy of the atoms in the metal, and every metal has exactly the same number of atoms in one mole.

Notice in **Table 1** that the same “about 25 joule” rule also applies to the molar heat capacities of solid ionic compounds. One mole barium chloride has three times as many ions as atoms in 1 mol of metal. So, you expect the molar heat capacity for BaCl<sub>2</sub> to be  $C = 3 \times 25 \text{ J/K}\cdot\text{mol}$ . The value in **Table 1**, 75.1 J/K•mol, is similar to this prediction.

### Molar Heat Capacity Is Related to Specific Heat

The specific heat of a substance is represented by  $c_p$  and is the energy as heat needed to raise the temperature of one gram of substance by one kelvin. Remember that molar heat capacity of a substance,  $C$ , has a similar definition except that molar heat capacity is related to moles of a substance not to the mass of a substance. Because the molar mass is the mass of 1 mol of a substance, the following equation is true.

$$M \text{ (g/mol)} \times c_p \text{ (J/K}\cdot\text{g)} = C \text{ (J/K}\cdot\text{mol)}$$

(molar mass)(specific heat) = (molar heat capacity)

#### Topic Link

Refer to the “Matter and Energy” chapter for a discussion of specific heat.



## Heat Results in Disorderly Particle Motion

When a substance receives energy in the form of heat, its enthalpy increases and the kinetic energy of the particles that make up the substance increases. The direction in which any particle moves is not related to the direction in which its neighboring particles move. The motions of these particles are *random*.

Suppose the substance was a rubber ball and you kicked the ball across a field. The energy that you gave the ball produces a different result than heat because the energy caused the particles in the ball to move together and in the same direction. The kinetic energy that you gave the particles in the ball is not random but is *concerted*.

Do you notice any relationships between energy and motion? Heat often produces disorderly particle motion. Other types of energy can produce orderly motion or orderly positioning of particles.

# 1

## Section Review

### UNDERSTANDING KEY IDEAS

1. What is heat?
2. What is temperature?
3. How does temperature differ from heat?
4. What is the enthalpy of a substance?
5. Define *molar heat capacity*.
6. How does molar heat capacity differ from specific heat?
7. How is the Kelvin temperature scale different from the Celsius and Fahrenheit scales?

### PRACTICE PROBLEMS

8. Calculate the molar heat capacity of diamond, given that 63 J were needed to heat a 1.2 g of diamond by  $1.0 \times 10^2$  K.
9. Use the molar heat capacity for aluminum from **Table 1** to calculate the amount of energy needed to raise the temperature of 260.5 g of aluminum from  $0^\circ\text{C}$  to  $125^\circ\text{C}$ .
10. Use the molar heat capacity for iron from **Table 1** to calculate the amount of energy needed to raise the temperature of 260.5 g of iron from  $0^\circ\text{C}$  to  $125^\circ\text{C}$ .

11. A sample of aluminum chloride increased in temperature by 3.5 K when the sample absorbed  $1.67 \times 10^2$  J of energy. Calculate the number of moles of aluminum chloride in this sample. Use **Table 1**.
12. Use **Table 1** to determine the final temperature when  $2.5 \times 10^2$  J of energy as heat is transferred to 0.20 mol of helium at 298 K.
13. Predict the final temperature when 1.2 kJ of energy as heat is transferred from  $1.0 \times 10^2$  mL of water at 298 K.
14. Use **Table 1** to determine the specific heat of silver.
15. Use **Table 1** to determine the specific heat of sodium chloride.

### CRITICAL THINKING

16. Why is a temperature difference the same in Celsius and Kelvin?
17. Predict the molar heat capacities of  $\text{PbS}(s)$  and  $\text{Ag}_2\text{S}(s)$ .
18. Use **Table 1** to predict the molar heat capacity of  $\text{FeCl}_3(s)$ .
19. Use your answer from item 18 to predict the specific heat of  $\text{FeCl}_3(s)$ .

# Using Enthalpy

## KEY TERMS

• thermodynamics

## OBJECTIVES

- ① Define *thermodynamics*.
- ② Calculate the enthalpy change for a given amount of substance for a given change in temperature.

## Molar Enthalpy Change

Because enthalpy is the total energy of a system, it is an important quantity. However, the only way to measure energy is through a change. In fact, there's no way to determine the true value of  $H$ . But  $\Delta H$  can be measured as a change occurs. The enthalpy change for one mole of a pure substance is called *molar enthalpy change*. The blacksmith in **Figure 5** is causing a molar enthalpy change by heating the iron horseshoe. Though describing a physical change by a chemical equation is unusual, the blacksmith's work could be described as follows.



This equation indicates that when 1 mol of solid iron is heated from 27°C to 827°C, its molar enthalpy increases by 20 100 joules.



**Figure 5**

The energy as heat supplied to an iron bar increases the enthalpy of the iron, so the iron is easier to reshape.



## Molar Heat Capacity Governs the Changes

The iron that the blacksmith uses does not change state and is not involved in a chemical reaction. So, the change in enthalpy of the iron horseshoe represents only a change in the kinetic energy of the iron atoms. When a pure substance is only heated or cooled, the amount of heat involved is the same as the enthalpy change. In other words,  $\Delta H = q$  for the heating or cooling of substances. So the molar enthalpy change is related to the molar heat capacity by the following equation.

$$\begin{aligned}\text{molar enthalpy change} &= C\Delta T \\ \text{molar enthalpy change} &= (\text{molar heat capacity})(\text{temperature change})\end{aligned}$$

Note that this equation does not apply to chemical reactions or changes of state.

### SAMPLE PROBLEM B

#### Calculating Molar Enthalpy Change for Heating

How much does the molar enthalpy change when ice warms from  $-5.4^\circ\text{C}$  to  $-0.2^\circ\text{C}$ ?

**1 Gather information.**

$T_{\text{initial}} = -5.4^\circ\text{C} = 267.8\text{ K}$  and  $T_{\text{final}} = -0.2^\circ\text{C} = 273.0\text{ K}$   
For  $\text{H}_2\text{O}(s)$ ,  $C = 37.4\text{ J/K}\cdot\text{mol}$ .

**2 Plan your work.**

The change in temperature is  $\Delta T = T_{\text{final}} - T_{\text{initial}} = 5.2\text{ K}$ .  
Because there is no reaction and the ice does not melt, you can use the equation below to determine the molar enthalpy change.

$$\Delta H = C\Delta T$$

**3 Calculate.**

$$\Delta H = C(\Delta T) = \left(37.4 \frac{\text{J}}{\text{K}\cdot\text{mol}}\right)(5.2\text{ K}) = 1.9 \times 10^2 \frac{\text{J}}{\text{mol}}$$

The molar enthalpy change is  $0.19\text{ kJ/mol}$ .

**4 Verify your results.**

The  $C$  of ice is about  $40\text{ J/K}\cdot\text{mol}$  and its temperature change is about  $5\text{ K}$ , so you should expect a molar enthalpy increase of about  $200\text{ J/mol}$ , which is close to the calculated answer.

#### PRACTICE HINT

Remember that molar enthalpy change has units of  $\text{kJ/mol}$ .

#### PRACTICE

- 1 Calculate the molar enthalpy change of  $\text{H}_2\text{O}(l)$  when liquid water is heated from  $41.7^\circ\text{C}$  to  $76.2^\circ\text{C}$ .
- 2 Calculate the  $\Delta H$  of  $\text{NaCl}$  when it is heated from  $0.0^\circ\text{C}$  to  $100.0^\circ\text{C}$ .
- 3 Calculate the molar enthalpy change when tungsten is heated by  $15\text{ K}$ .



## SAMPLE PROBLEM C

### Calculating the Molar Enthalpy Change for Cooling

Calculate the molar enthalpy change when an aluminum can that has a temperature of 19.2°C is cooled to a temperature of 4.00°C.

#### 1 Gather information.

For Al,  $C = 24.2 \text{ J/K}\cdot\text{mol}$ .

$$T_{\text{initial}} = 19.2^\circ\text{C} = 292 \text{ K}$$

$$T_{\text{final}} = 4.00^\circ\text{C} = 277 \text{ K}$$

#### 2 Plan your work.

The change in temperature is calculated by using the following equation.

$$\begin{aligned}\Delta T &= T_{\text{final}} - T_{\text{initial}} = \\ 277 \text{ K} - 292 \text{ K} &= -15 \text{ K}\end{aligned}$$

To determine the molar enthalpy change, use the equation  $\Delta H = C\Delta T$ .

#### 3 Calculate.

$$\begin{aligned}\Delta H &= C\Delta T \\ \Delta H &= (24.2 \text{ J/K}\cdot\text{mol})(-15 \text{ K}) = -360 \text{ J/mol}\end{aligned}$$

#### 4 Verify your results.

The calculation shows the molar enthalpy change has units of joules per mole. The enthalpy value is negative, which indicates a cooling process.

### PRACTICE HINT

Remember that the  $\Delta$  notation always represents initial value subtracted from the final value, even if the initial value is larger than the final value.

### PRACTICE

- 1 The molar heat capacity of Al(s) is 24.2 J/K•mol. Calculate the molar enthalpy change when Al(s) is cooled from 128.5°C to 22.6°C.
- 2 Lead has a molar heat capacity of 26.4 J/K•mol. What molar enthalpy change occurs when lead is cooled from 302°C to 275°C?
- 3 Calculate the molar enthalpy change when mercury is cooled 10 K. The molar heat capacity of mercury is 27.8 J/K•mol.

**PROBLEM SOLVING SKILL**

### Enthalpy Changes of Endothermic or Exothermic Processes

Notice the molar enthalpy change for **Sample Problem B**. This enthalpy change is positive, which means that the heating of a sample requires energy. So, the heating of a sample is an endothermic process. In contrast, the cooling of a sample releases energy or has a negative enthalpy change and is an exothermic process, such as the process in **Sample Problem C**. In fact, you can use enthalpy changes to determine if a process is endothermic or exothermic. Processes that have positive enthalpy changes are endothermic and processes that have negative enthalpy changes are exothermic.

## Enthalpy of a System of Several Substances

You have read about how a substance's enthalpy changes when the substance receives energy as heat. Enthalpy changes can be found for a system of substances, such as the reaction shown in **Figure 6**. In this figure, hydrogen gas reacts with bromine liquid to form the gas hydrogen bromide, HBr, and to generate energy as heat. Energy transfers out of this system in the form of heat because the enthalpy of the product 2HBr is less than the enthalpy of the reactants H<sub>2</sub> and Br<sub>2</sub>. Or, the enthalpy of 2HBr is less than the enthalpy of H<sub>2</sub> and Br<sub>2</sub>, so the enthalpy change is negative for this reaction. This negative enthalpy change reveals that the reaction is exothermic.

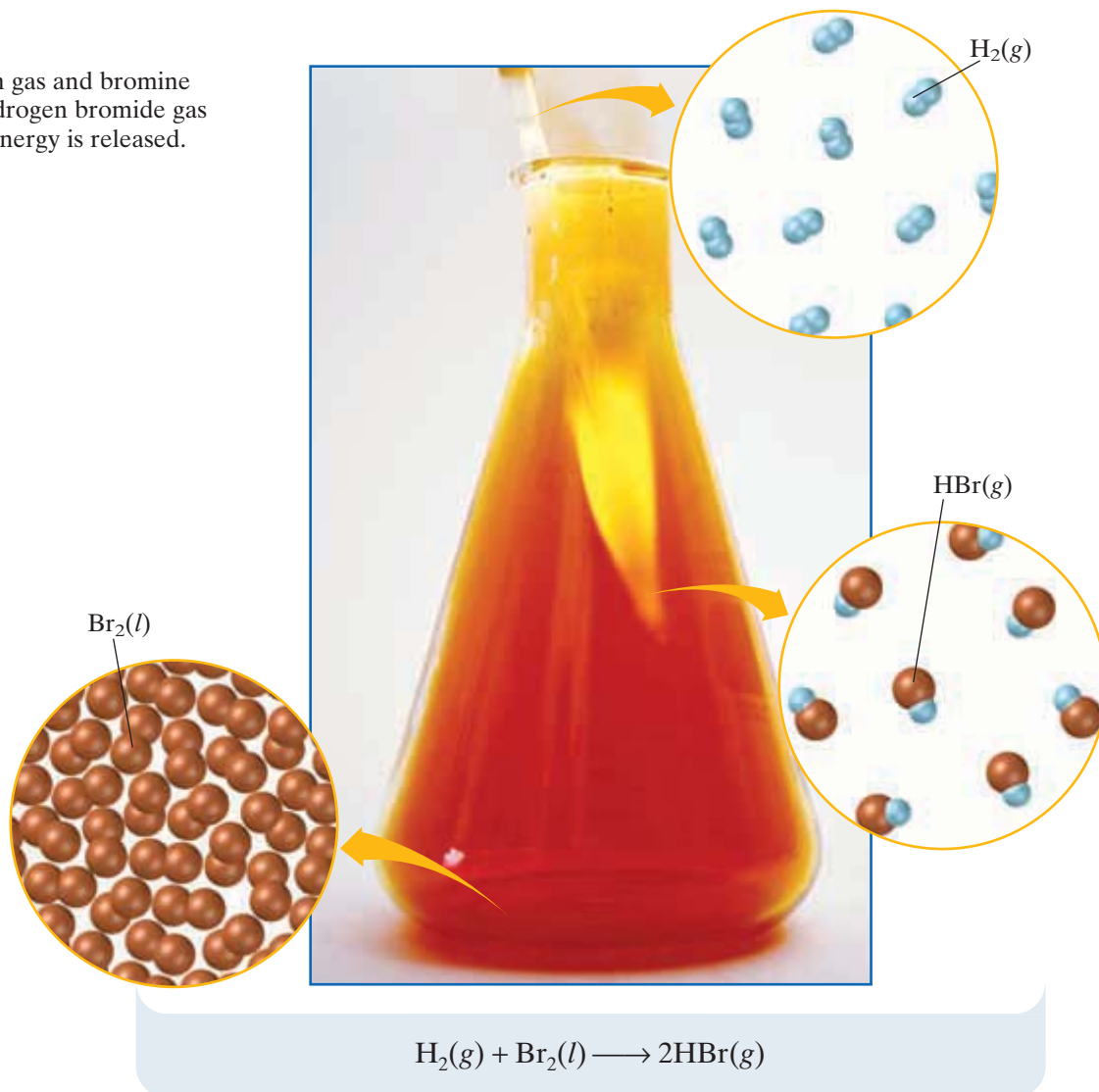
Enthalpy is the first of three thermodynamic properties that you will encounter in this chapter. **Thermodynamics** is a science that examines various processes and the energy changes that accompany the processes. By studying and measuring thermodynamic properties, chemists have learned to predict whether a chemical reaction can occur and what kind of energy change it will have.

### thermodynamics

the branch of science concerned with the energy changes that accompany chemical and physical changes

### Figure 6

When hydrogen gas and bromine liquid react, hydrogen bromide gas is formed and energy is released.

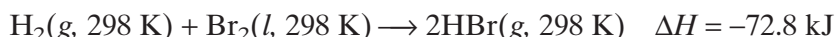


## Writing Equations for Enthalpy Changes

Do you remember the equation that represents the molar enthalpy change when the iron horseshoe is heated?



Just as an equation can be written for the enthalpy change in the blacksmith's iron, an equation can be written for the enthalpy change that occurs during a change of state or a chemical reaction. The thermodynamics of changes of state are discussed in the chapter entitled "States and Intermolecular Forces." An example of an equation for a chemical reaction is the following equation for the hydrogen and bromine reaction.



Notice that the enthalpy change for this reaction and other chemical reactions are written using the symbol  $\Delta H$ . Also, notice that the negative enthalpy change indicates the reaction is exothermic. Enthalpy changes that are involved in chemical reactions are the subject of section three of this chapter.

## 2

## Section Review

### UNDERSTANDING KEY IDEAS

1. Name and define the quantity represented by  $H$ .
2. During a heating or cooling process, how are changes in enthalpy and temperature related?
3. What is thermodynamics?

### PRACTICE PROBLEMS

4. A block of ice is cooled from  $-0.5^\circ\text{C}$  to  $-10.1^\circ\text{C}$ . Calculate the temperature change,  $\Delta T$ , in degrees Celsius and in kelvins.
5. Calculate the molar enthalpy change when a block of ice is heated from  $-8.4^\circ\text{C}$  to  $-5.2^\circ\text{C}$ .
6. Calculate the molar enthalpy change when  $\text{H}_2\text{O}(l)$  is cooled from  $48.3^\circ\text{C}$  to  $25.2^\circ\text{C}$ .

7. The molar heat capacity of benzene,  $\text{C}_6\text{H}_6(l)$ , is  $136 \text{ J/K}\cdot\text{mol}$ . Calculate the molar enthalpy change when the temperature of  $\text{C}_6\text{H}_6(l)$  changes from  $19.7^\circ\text{C}$  to  $46.8^\circ\text{C}$ .
8. The molar heat capacity of diethyl ether,  $(\text{C}_2\text{H}_5)_2\text{O}(l)$ , is  $172 \text{ J/K}\cdot\text{mol}$ . What is the temperature change if the molar enthalpy change equals  $-186.9 \text{ J/mol}$ ?
9. If the enthalpy of 1 mol of a compound decreases by 428 J when the temperature decreases by 10.0 K, what is the compound's molar heat capacity?

### CRITICAL THINKING

10. Under what circumstances could the enthalpy of a system be increased without the temperature rising?
11. What approximate enthalpy increase would you expect if you heated one mole of a solid metal by 40 K?

# Changes in Enthalpy During Chemical Reactions

## KEY TERMS

- calorimetry
- calorimeter
- Hess's law

## OBJECTIVES

- 1 Explain the principles of calorimetry.
- 2 Use Hess's law and standard enthalpies of formation to calculate  $\Delta H$ .

### Topic Link

Refer to the "Science of Chemistry" chapter for a discussion of endothermic and exothermic reactions.

## Changes in Enthalpy Accompany Reactions

Changes in enthalpy occur during reactions. A change in enthalpy during a reaction depends on many variables, but temperature is one of the most important variables. To standardize the enthalpies of reactions, data are often presented for reactions in which both reactants and products have the *standard thermodynamic temperature* of 25.00°C or 298.15 K.

Chemists usually present a thermodynamic value for a chemical reaction by using the chemical equation, as in the example below.



This equation shows that when 0.5 mol of  $\text{H}_2$  reacts with 0.5 mol of  $\text{Br}_2$  to produce 1 mol HBr and all have a temperature of 298.15 K, the enthalpy decreases by 36.4 kJ.

Remember that reactions that have negative enthalpy changes are exothermic, and reactions that have positive enthalpy changes are endothermic.

**Figure 7**

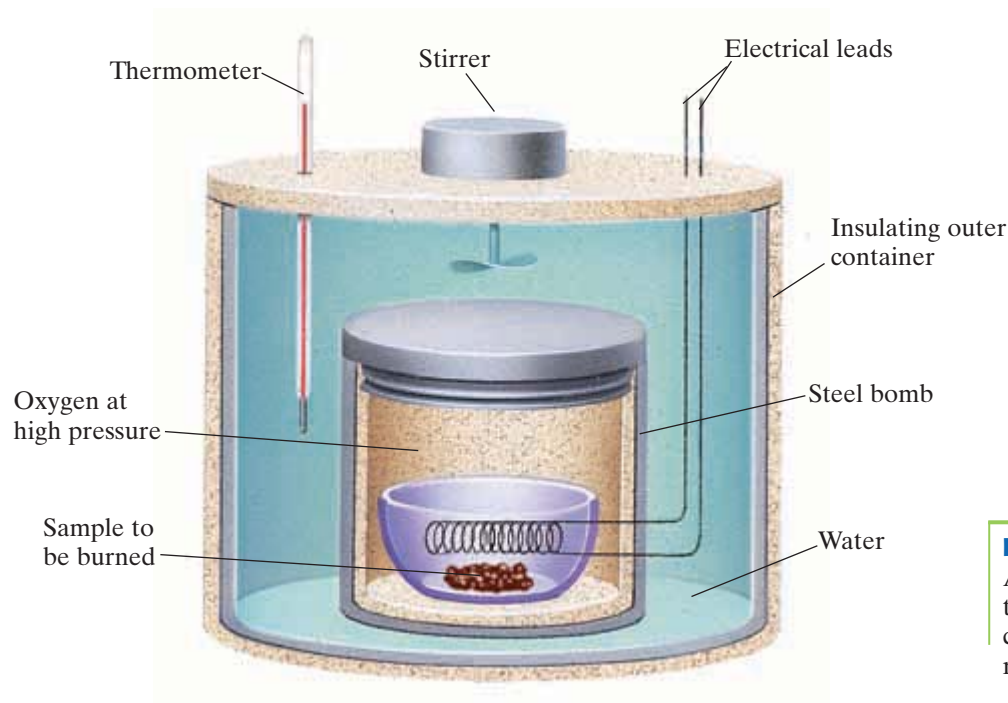
The combustion of charcoal generates energy as heat and cooks the food on the grill.



internet connect

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 Topic: Endothermic and Exothermic Reactions  
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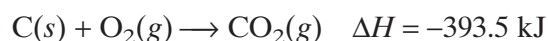


**Figure 8**  
A bomb calorimeter is used to measure enthalpy changes caused by combustion reactions.

## Chemical Calorimetry

For the  $\text{H}_2$  and  $\text{Br}_2$  reaction, in which  $\Delta H$  is negative, the total energy of the reaction decreases. Energy cannot disappear, so what happens to the energy? The energy is released as heat by the system. If the reaction was endothermic, energy in the form of heat would be absorbed by the system and the enthalpy would increase.

The experimental measurement of an enthalpy change for a reaction is called **calorimetry**. Combustion reactions, such as the reaction in **Figure 7**, are always exothermic. The enthalpy changes of combustion reactions are determined using a bomb **calorimeter**, such as the one shown in **Figure 8**. This instrument is a sturdy, steel vessel in which the sample is ignited electrically in the presence of high-pressure oxygen. The energy from the combustion is absorbed by a surrounding water bath and by other parts of the calorimeter. The water and the other parts of the calorimeter have known specific heats. So, a measured temperature increase can be used to calculate the energy released in the combustion reaction and then the enthalpy change. In **Figure 7**, the combustion of 1.00 mol of carbon yields 393.5 kJ of energy.



## Nutritionists Use Bomb Calorimetry

Inside the pressurized oxygen atmosphere of a bomb calorimeter, most organic matter, including food, fabrics, and plastics, will ignite easily and burn rapidly. Some samples of matter may even explode, but the strong walls of the calorimeter contain the explosions. Sample sizes are chosen so that there is excess oxygen during the combustion reactions. Under these conditions, the reactions go to completion and produce carbon dioxide, water, and possibly other compounds.

### calorimetry

the measurement of heat-related constants, such as specific heat or latent heat

### calorimeter

a device used to measure the heat absorbed or released in a chemical or physical change



### Figure 9

Nutritionists work with bomb-calorimeter data for a recipe's ingredients to determine the food-energy content of meals.



Nutritionists, such as the nutritionist shown in **Figure 9**, use bomb calorimetry to measure the energy content of foods. To measure the energy, nutritionists assume that all the combustion energy is available to the body as we digest food. For example, consider table sugar,  $C_{12}H_{22}O_{11}$ , also known as sucrose. Its molar mass is 342.3 g/mol. When 3.423 grams of sugar are burned in a bomb calorimeter, the 1.505 kg of the calorimeter's water bath increased in temperature by  $3.524^{\circ}C$ . The enthalpy change can be calculated and is shown below.



When enthalpy changes are reported in this way, a coefficient in the chemical equation indicates the number of moles of a substance. So, the equation above describes the enthalpy change when 1 mol of sucrose reacts with 12 mol of oxygen to produce 12 mol of carbon dioxide and 11 mol of liquid water, at 298.15 K.

Calorimetric measurements can be made with very high precision. In fact, most thermodynamic quantities are known to many significant figures.

### Adiabatic Calorimetry Is Another Strategy

Instead of using a water bath to absorb the energy generated by a chemical reaction, *adiabatic calorimetry* uses an insulating vessel. The word *adiabatic* means “not allowing energy to pass through.” So, no energy can enter or escape this type of vessel. As a result, the reaction mixture increases in temperature if the reaction is exothermic or decreases in temperature if the reaction is endothermic. If the system's specific heat is known, the reaction enthalpy can be calculated. Adiabatic calorimetry is used for reactions that are not ignited, such as for reactions in aqueous solution.



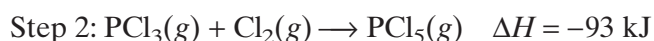
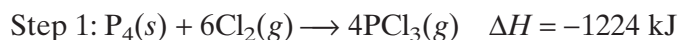
## Hess's Law

Any two processes that both start with the same reactants in the same state and finish with the same products in the same state will have the same enthalpy change. This statement is the basis for **Hess's law**, which states that the overall enthalpy change in a reaction is equal to the sum of the enthalpy changes for the individual steps in the process.

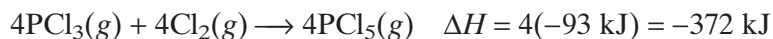
Consider the following reaction, the synthesis of 4 mol of phosphorus pentachloride,  $\text{PCl}_5$ , when phosphorus is burned in excess chlorine.



Phosphorus pentachloride may also be prepared in a two-step process.



However, the second reaction must take place four times for each occurrence of the first reaction in the two-step process. This two-step process is more accurately described by the following equations.



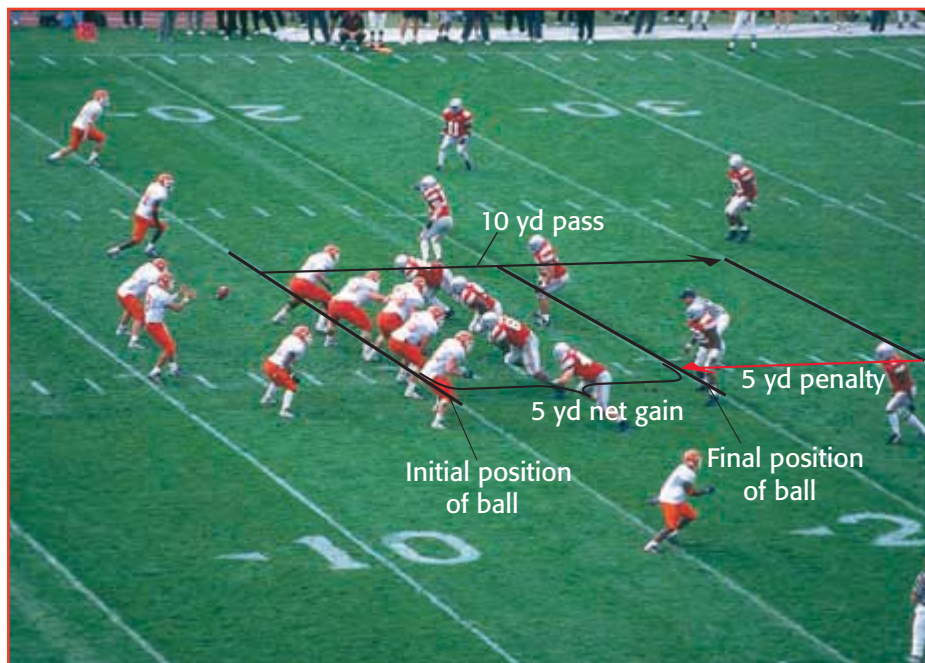
So, the total change in enthalpy by the two-step process is as follows:

$$(-1224 \text{ kJ}) + (-372 \text{ kJ}) = -1596 \text{ kJ}$$

This enthalpy change,  $\Delta H$ , for the two-step process is the same as the enthalpy change for the direct route of the formation of  $\text{PCl}_5$ . This example is in agreement with Hess's law.

### Hess's law

the law that states that the amount of heat released or absorbed in a chemical reaction does not depend on the number of steps in the reaction



**Figure 10**

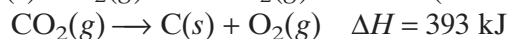
In football, as in Hess's law, only the initial and final conditions matter. A team that gains 10 yards on a pass play but has a five-yard penalty, has the same net gain as the team that gained only 5 yards.

## Using Hess's Law and Algebra

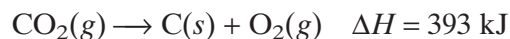
Chemical equations can be manipulated using rules of algebra to get a desired equation. When equations are added or subtracted, enthalpy changes must be added or subtracted. And when equations are multiplied by a constant, the enthalpy changes must also be multiplied by that constant. For example, the enthalpy of the formation of CO, when CO<sub>2</sub> and solid carbon are reactants, is found using the equations below.



You cannot simply add these equations because CO<sub>2</sub> would not be a reactant. But if you subtract or reverse the second equation, carbon dioxide will be on the correct side of the equation. This process is shown below.



So, reversing an equation causes the enthalpy of the new reaction to be the negative of the enthalpy of the original reaction. Now add the two equations to get the equation for the formation of CO by using CO<sub>2</sub> and C.



Oxygen and carbon that appear on both sides of the equation can be canceled. So, the final equation is as shown below.



## Standard Enthalpies of Formation

The enthalpy change in forming 1 mol of a substance from elements in their standard states is called the *standard enthalpy of formation* of the substance,  $\Delta H_f^\circ$ . Many values of  $\Delta H_f^\circ$  are listed in **Table 2**. Note that the values of the standard enthalpies of formation for elements are 0. From a list of standard enthalpies of formation, the enthalpy change of any reaction for which data is available can be calculated. For example, the following reaction can be considered to take place in four steps.



Two of these steps convert the reactants into their elements. Notice that the reverse reactions for the formations of SO<sub>2</sub> and NO<sub>2</sub> are used. So, the standard enthalpies of formation for these reverse reactions are the negative of the standard enthalpies of formation for SO<sub>2</sub> and NO<sub>2</sub>.

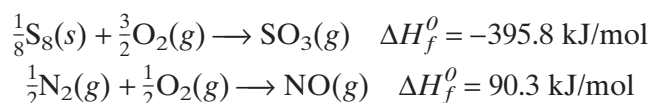


**Table 2 Standard Enthalpies of Formation**

Substance	$\Delta H_f^\circ$ (kJ/mol)	Substance	$\Delta H_f^\circ$ (kJ/mol)
$\text{Al}_2\text{O}_3(s)$	-1676.0	$\text{H}_2\text{O}(g)$	-241.8
$\text{CaCO}_3(s)$	-1206.9	$\text{H}_2\text{O}(l)$	-285.8
$\text{CaO}(s)$	-634.9	$\text{Na}^+(g)$	609.4
$\text{Ca}(\text{OH})_2(s)$	-985.2	$\text{NaBr}(s)$	-361.1
$\text{C}_2\text{H}_6(g)$	-83.8	$\text{Na}_2\text{CO}_3(s)$	-1130.7
$\text{CH}_4(g)$	-74.9	$\text{NO}(g)$	90.3
$\text{CO}(g)$	-110.5	$\text{NO}_2(g)$	33.1
$\text{CO}_2(g)$	-393.5	$\text{Pb}(s)$	0
$\text{Fe}_2\text{O}_3(s)$	-825.5	$\text{SO}_2(g)$	-296.8
$\text{H}_2(g)$	0	$\text{SO}_3(g)$	-395.8
$\text{Hg}(l)$	0	$\text{ZnO}(s)$	-348.3

Refer to Appendix A for more standard enthalpies of formation.

The two other steps, which are listed below reform those elements into the products.



In fact, the enthalpy change of any reaction can be determined in the same way—the reactants can be converted to their elements, and the elements can be recombined into the products. Why? Hess's law states that the overall enthalpy change of a reaction is the same, whether for a single-step process or a multiple step one. If you apply this rule, the exothermic reaction that forms sulfur trioxide and nitrogen oxide has the enthalpy change listed below.

$$\text{SO}_2(g) + \text{NO}_2(g) \longrightarrow \text{SO}_3(g) + \text{NO}(g)$$

$$\Delta H = (\Delta H_{f, \text{NO}}^\circ + \Delta H_{f, \text{SO}_3}^\circ) + (-\Delta H_{f, \text{NO}_2}^\circ - \Delta H_{f, \text{SO}_2}^\circ)$$

$$\Delta H = (90.3 \text{ kJ/mol} - 395.8 \text{ kJ/mol}) + (-33.1 \text{ kJ/mol} + 296.8 \text{ kJ/mol}) = -41.8 \text{ kJ/mol}$$

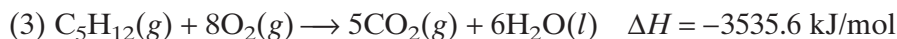
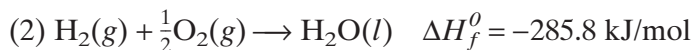
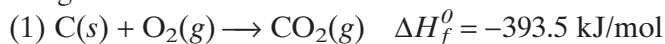
When using standard enthalpies of formation to determine the enthalpy change of a chemical reaction, remember the following equation.

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

## SAMPLE PROBLEM D

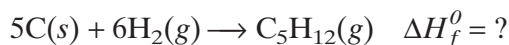
### Calculating a Standard Enthalpy of Formation

Calculate the standard enthalpy of formation of pentane,  $C_5H_{12}$ , using the given information.



#### 1 Gather information.

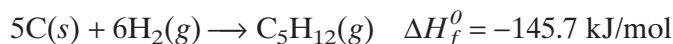
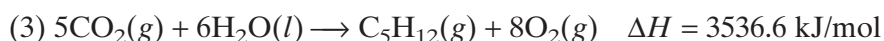
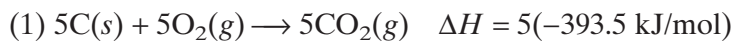
The equation for the standard enthalpy of formation is



#### 2 Plan your work.

$C_5H_{12}$  is a product, so reverse the equation (3) and the sign of  $\Delta H$ . Multiply equation (1) by 5 to give 5C as a reactant. Multiply equation (2) by 6 to give 6H<sub>2</sub> as a reactant.

#### 3 Calculate.



#### 4 Verify your results.

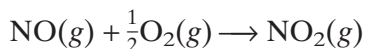
The unnecessary reactants and products cancel to give the correct equation.

### PRACTICE HINT

A positive  $\Delta H$  means that the reaction has absorbed energy or that the reaction is endothermic. A negative  $\Delta H$  means that the reaction has released energy or that the reaction is exothermic.

### PRACTICE

#### 1 Calculate the enthalpy change for the following reaction.



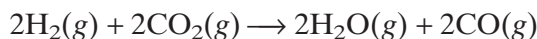
#### 2 Calculate the enthalpy change for the combustion of methane gas, $CH_4$ , to form $CO_2(g)$ and $H_2O(l)$ .

**PROBLEM SOLVING SKILL**

## SAMPLE PROBLEM E

### Calculating a Reaction's Change in Enthalpy

Calculate the change in enthalpy for the reaction below by using data from **Table 2**.



Then, state whether the reaction is exothermic or endothermic.

### 1 Gather information.

Standard enthalpies of formation for the products are as follows:  
For  $\text{H}_2\text{O}(g)$ ,  $\Delta H_f^\circ = -241.8 \text{ kJ/mol}$ . For  $\text{CO}(g)$ ,  $\Delta H_f^\circ = -110.5 \text{ kJ/mol}$ .  
Standard enthalpies of formation for the reactants are as follows:  
For  $\text{H}_2(g)$ ,  $\Delta H_f^\circ = 0 \text{ kJ/mol}$ . For  $\text{CO}_2(g)$ ,  $\Delta H_f^\circ = -393.5 \text{ kJ/mol}$ .

### 2 Plan your work.

The general rule is  $\Delta H = \Delta H(\text{products}) - \Delta H(\text{reactants})$ . So,  
 $\Delta H = (\text{mol H}_2\text{O}(g)) \Delta H_f^\circ (\text{for H}_2\text{O}(g)) + (\text{mol CO}(g)) \Delta H_f^\circ (\text{for CO}(g)) -$   
 $(\text{mol H}_2(g)) \Delta H_f^\circ (\text{for H}_2(g)) - (\text{mol CO}_2(g)) \Delta H_f^\circ (\text{for CO}_2(g))$ .

### 3 Calculate.

$$\Delta H = (2 \text{ mol})(-241.8 \text{ kJ/mol}) + (2 \text{ mol})(-110.5 \text{ kJ/mol}) -$$
$$(2 \text{ mol})(0 \text{ kJ/mol}) - (2 \text{ mol})(-393.5 \text{ kJ/mol}) = 82.4 \text{ kJ}$$

Because the enthalpy change is positive, the reaction is endothermic.

### 4 Verify your results.

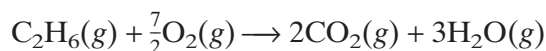
The enthalpy of the reactants,  $-787 \text{ kJ}$ , is more negative than that of the products,  $-704.6 \text{ kJ}$ , and shows that the total energy of the reaction increases by  $82.4 \text{ kJ}$ .

### PRACTICE HINT

Always be sure to check the states of matter when you use standard enthalpy of formation data.  $\text{H}_2\text{O}(g)$  and  $\text{H}_2\text{O}(l)$  have different values.

### PRACTICE

- 1 Use data from **Table 2** to calculate  $\Delta H$  for the following reaction.



- 2 The exothermic reaction known as lime slaking is  $\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s)$ . Calculate  $\Delta H$  from the data in **Table 2**.



## 3

## Section Review

### UNDERSTANDING KEY IDEAS

1. What is the standard thermodynamic temperature?
2. Why does  $\Delta H_f^\circ = 0$  for elements, as listed in **Table 2**?
3. How do bomb calorimetry and adiabatic calorimetry differ?

### PRACTICE PROBLEMS

4. Use **Table 2** to calculate  $\Delta H$  for the

decomposition of calcium carbonate into calcium oxide and carbon dioxide.

5. What enthalpy change accompanies the reaction  $2\text{Al}(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{H}_2(g)$ ?

### CRITICAL THINKING

6. **Table 2** includes two entries for water. What does the difference between the two values represent?
7. What general conclusion can you draw from observing that most standard enthalpies of formation are negative?

# Order and Spontaneity

## KEY TERMS

- entropy
- Gibbs energy

## OBJECTIVES

- 1 **Define** *entropy*, and discuss the factors that influence the sign and magnitude of  $\Delta S$  for a chemical reaction.
- 2 **Describe** *Gibbs energy*, and discuss the factors that influence the sign and magnitude of  $\Delta G$ .
- 3 **Indicate** whether  $\Delta G$  values describe spontaneous or nonspontaneous reactions.



## entropy

a measure of the randomness or disorder of a system

## Entropy

Some reactions happen easily, but others do not. For example, sodium and chlorine react when they are brought together. However, nitrogen and oxygen coexist in the air you breathe without forming poisonous nitrogen monoxide, NO. One factor you can use to predict whether reactions will occur is enthalpy. A reaction is more likely to occur if it is accompanied by a *decrease in enthalpy* or if  $\Delta H$  is negative.

But a few processes that are endothermic can occur easily. Why? Another factor known as entropy can determine if a process will occur. **Entropy**,  $S$ , is a measure of the disorder in a system and is a thermodynamic property. Entropy is not a form of energy and has the units joules per kelvin, J/K. A process is more likely to occur if it is accompanied by an *increase in entropy*; that is,  $\Delta S$  is positive.

**Figure 11**

**a** Crystals of potassium permanganate,  $\text{KMnO}_4$ , are dropped into a beaker of water and dissolve to produce the  $\text{K}^+(\text{aq})$  and  $\text{MnO}_4^-(\text{aq})$  ions.



**b** Diffusion causes entropy to increase and leads to a uniform solution.

**Table 3** Standard Entropy Changes for Some Reactions

Reaction	Entropy change, $\Delta S$ (J/K)
$\text{CaCO}_3(s) + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{CO}_2(g) + 3\text{H}_2\text{O}(l)$	138
$\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$	43
$\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$	25
$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$	-5
$2\text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\text{NaCl}(s)$	-181
$2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$	-176

### Factors That Affect Entropy

If you scatter a handful of seeds, you have dispersed them. You have created a more disordered arrangement. In the same way, as molecules or ions become dispersed, their disorder increases and their entropy increases. In **Figure 11**, the intensely violet permanganate ions,  $\text{MnO}_4^-(aq)$  are initially found only in a small volume of solution. But they gradually spread until they occupy the whole beaker. You can't see the potassium  $\text{K}^+(aq)$  ions because these ions are colorless, but they too have dispersed. This process of dispersion is called *diffusion* and causes the increase in entropy.

Entropy also increases as solutions become more dilute or when the pressure of a gas is reduced. In both cases, the molecules fill larger spaces and so become more disordered. Entropies also increase with temperature, but this effect is not great unless a phase change occurs.

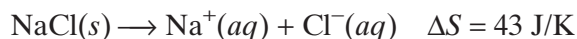
The entropy can change during a reaction. The entropy of a system can increase when the total number of moles of product is greater than the total number of moles of reactant. Entropy can increase in a system when the total number of particles in the system increases. Entropy also increases when a reaction produces more gas particles, because gases are more disordered than liquids or solids.

**Table 3** lists the entropy changes of some familiar chemical reactions. Notice that entropy decreases as sodium chloride forms: 2 mol of sodium combine with 1 mol of chlorine to form 2 mol of sodium chloride.



This decrease in entropy is because of the order present in crystalline sodium chloride.

Also notice that the entropy increases when 1 mol of sodium chloride dissolves in water to form 1 mol of aqueous sodium ions and 1 mol of aqueous chlorine ions.



This increase in entropy is because of the order lost when a crystalline solid dissociates to form ions.



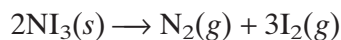


**Figure 12**

The decomposition of nitrogen triiodide to form nitrogen and iodine has a large entropy increase.

### Hess's Law Also Applies to Entropy

The decomposition of nitrogen triiodide to form nitrogen and iodine in **Figure 12** creates 4 mol of gas from 2 mol of a solid.



This reaction has such a large entropy increase that the reaction proceeds once the reaction is initiated by a mechanical shock.

Molar entropy has the same unit, J/K•mol, as molar heat capacity. In fact, molar entropies can be calculated from molar heat capacity data.

Entropies can also be calculated by using Hess's law and entropy data for other reactions. This statement means that you can manipulate chemical equations using rules of algebra to get a desired equation. But remember that when equations are added or subtracted, entropy changes must be added or subtracted. And when equations are multiplied by a constant, the entropy changes must also be multiplied by that constant. Finally, atoms and molecules that appear on both sides of the equation can be canceled.

The *standard entropy* is represented by the symbol  $S^{\circ}$  and some standard entropies are listed in **Table 4**. The standard entropy of the substance is the entropy of 1 mol of a substance at a standard temperature, 298.15 K. Unlike having standard enthalpies of formation equal to 0, elements can have standard entropies that have values other than zero. You should also know that most standard entropies are positive; this is not true of standard enthalpies of formation.

The entropy change of a reaction can be calculated by using the following equation.

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

**Table 4 Standard Entropies of Some Substances**

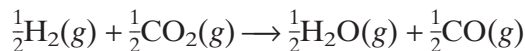
Substance	$S^{\circ}$ (J/K•mol)
C(s) (graphite)	5.7
CO(g)	197.6
CO <sub>2</sub> (g)	213.8
H <sub>2</sub> (g)	130.7
H <sub>2</sub> O(g)	188.7
H <sub>2</sub> O(l)	70.0
Na <sub>2</sub> CO <sub>3</sub> (s)	135.0
O <sub>2</sub> (g)	205.1

Refer to Appendix A for more standard entropies.

## SAMPLE PROBLEM F

### Hess's Law and Entropy

Use **Table 4** to calculate the entropy change that accompanies the following reaction.



#### 1 Gather information.

Products:  $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$

Reactants:  $\text{H}_2(\text{g}) + \text{CO}_2(\text{g})$

#### 2 Plan your work.

The general rule is  $\Delta S = \Delta S(\text{products}) - \Delta S(\text{reactants})$ .

So,  $\Delta S = (\text{mol H}_2\text{O}(\text{g})) S^\circ (\text{for H}_2\text{O}(\text{g})) + (\text{mol CO}(\text{g})) S^\circ$

(for  $\text{CO}(\text{g})$ )  $- (\text{mol H}_2(\text{g})) S^\circ (\text{for H}_2(\text{g})) - (\text{mol CO}_2(\text{g})) S^\circ (\text{for CO}_2(\text{g}))$ .

The standard entropies from **Table 4** are as follows:

For  $\text{H}_2\text{O}$ ,  $S^\circ = 188.7 \text{ J/K}\cdot\text{mol}$ . For  $\text{CO}$ ,  $S^\circ = 197.6 \text{ J/K}\cdot\text{mol}$ .

For  $\text{H}_2$ ,  $S^\circ = 130.7 \text{ J/K}\cdot\text{mol}$ . For  $\text{CO}_2$ ,  $S^\circ = 213.8 \text{ J/K}\cdot\text{mol}$ .

#### 3 Calculate.

Substitute the values into the equation for  $\Delta S$ .

$$\begin{aligned} \Delta S &= \left[ \left( \frac{1}{2} \text{ mol} \right) (188.7 \text{ J/K}\cdot\text{mol}) + \left( \frac{1}{2} \text{ mol} \right) (197.6 \text{ J/K}\cdot\text{mol}) - \right. \\ &\left. \left( \frac{1}{2} \text{ mol} \right) (130.7 \text{ J/K}\cdot\text{mol}) - \left( \frac{1}{2} \text{ mol} \right) (213.8 \text{ J/K}\cdot\text{mol}) \right] = 94.35 \text{ J/K} + \\ &98.8 \text{ J/K} - 65.35 \text{ J/K} - 106.9 \text{ J/K} = 193.1 \text{ J/K} - 172.2 \text{ J/K} = 20.9 \text{ J/K} \end{aligned}$$

#### 4 Verify your results.

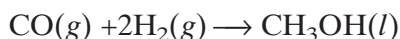
The sum of the standard entropies of gaseous water and carbon monoxide is larger than the sum of the standard entropies of gaseous hydrogen and carbon dioxide. So, the  $\Delta S$  for this reaction should be positive.

### PRACTICE HINT

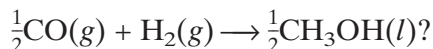
Always check the signs of entropy values. Standard entropies are almost always positive, while standard entropies of formation are positive and negative.

### PRACTICE

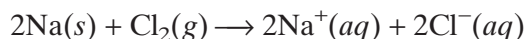
- 1 Find the change in entropy for the reaction below by using **Table 4** and that  $S^\circ$  for  $\text{CH}_3\text{OH}(\text{l})$  is  $126.8 \text{ J/K}\cdot\text{mol}$ .



- 2 What is the entropy change for



- 3 Use data from **Table 3** to calculate the entropy change for the following reaction:



## Gibbs Energy

You have learned that the tendency for a reaction to occur depends on both  $\Delta H$  and  $\Delta S$ . If  $\Delta H$  is negative and  $\Delta S$  is positive for a reaction, the reaction will likely occur. If  $\Delta H$  is positive and  $\Delta S$  is negative for a reaction, the reaction will *not* occur. How can you predict what will happen if  $\Delta H$  and  $\Delta S$  are both positive or both negative?

Josiah Willard Gibbs, a professor at Yale University, answered that question by proposing another thermodynamic quantity, which now bears his name. **Gibbs energy** is represented by the symbol  $G$  and is defined by the following equation.

$$G = H - TS$$

Another name for Gibbs energy is *free energy*.

### Gibbs Energy Determines Spontaneity

When the term *spontaneous* is used to describe reactions, it has a different meaning than the meaning that we use to describe other events. A spontaneous reaction is one that does occur or is likely to occur without continuous outside assistance, such as input of energy. A nonspontaneous reaction will never occur without assistance. The avalanche shown in **Figure 13** is a good example of a spontaneous process. On mountains during the winter, an avalanche may or may not occur, but it always *can* occur. The return of the snow from the bottom of the mountain to the mountaintop is a nonspontaneous event, because this event will not happen without aid.

A reaction is spontaneous if the Gibbs energy change is negative. If a reaction has a  $\Delta G$  greater than 0, the reaction is nonspontaneous. If a reaction has a  $\Delta G$  of exactly zero, the reaction is at equilibrium.

#### Gibbs energy

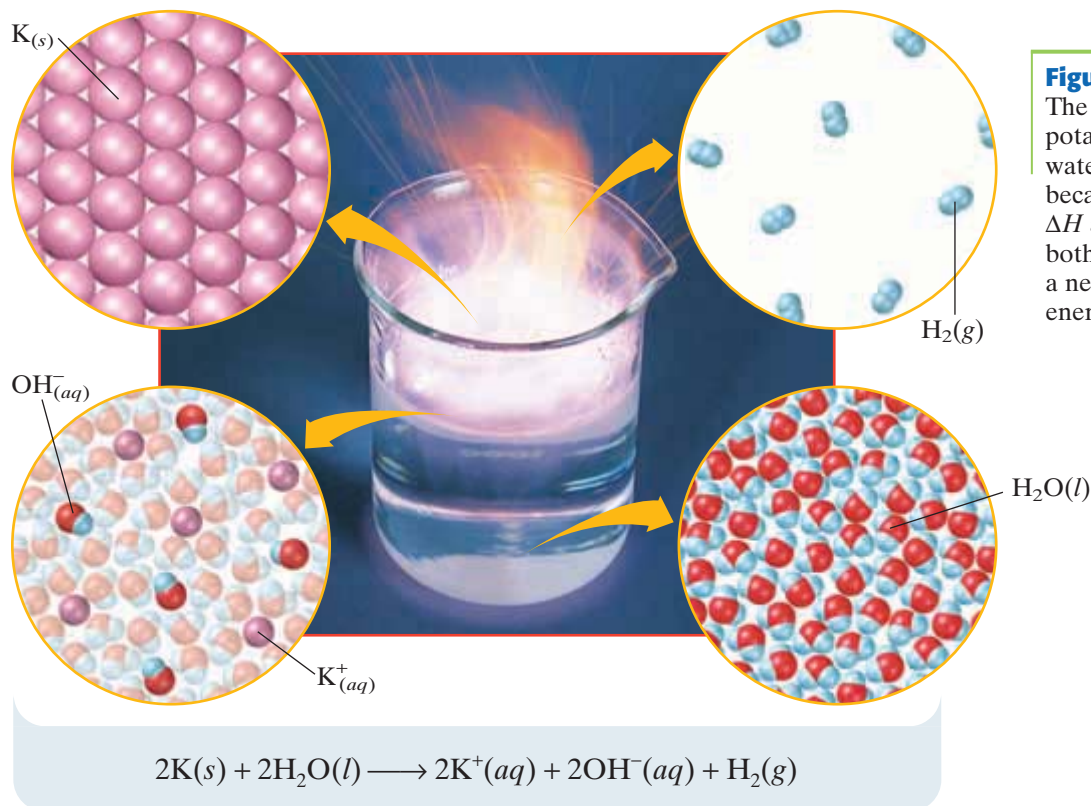
the energy in a system that is available for work

#### Figure 13

An avalanche is a spontaneous process driven by an increase in disorder and a decrease in energy.



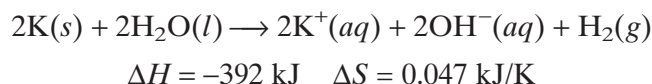
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**Figure 14**  
The reaction of potassium metal with water is spontaneous because a negative  $\Delta H$  and a positive  $\Delta S$  both contribute to a negative Gibbs energy change.

## Entropy and Enthalpy Determine Gibbs Energy

Reactions that have large negative  $\Delta G$  values often release energy and increase disorder. The vigorous reaction of potassium metal and water shown in **Figure 14** is an example of this type of reaction. The reaction is described by the following equation.



The change in Gibbs energy for the reaction above is calculated below.

$$\Delta G = \Delta H - T\Delta S =$$

$$-392 \text{ kJ} - (298.15 \text{ K})(0.047 \text{ kJ/K}) = -406 \text{ kJ}$$

Notice that the reaction of potassium and water releases energy and increases disorder. This example and **Sample Problem G** show how to determine  $\Delta G$  values at  $25^\circ\text{C}$  by using  $\Delta H$  and  $\Delta S$  data. However, you can calculate  $\Delta G$  in another way because lists of standard Gibbs energies of formation exist, such as **Table 5**.

The standard Gibbs energy of formation,  $\Delta G_f^\circ$ , of a substance is the change in energy that accompanies the formation of 1 mol of the substance from its elements at 298.15 K. These standard Gibbs energies of formation can be used to find the  $\Delta G$  for any reaction in exactly the same way that  $\Delta H_f^\circ$  data were used to calculate the enthalpy change for any reaction. Hess's law also applies when calculating  $\Delta G$ .

$$\Delta G_{\text{reaction}} = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$$

**Table 5 Standard Gibbs Energies of Formation**

Substance	$\Delta G_f^\circ$ (kJ/mol)
Ca(s)	0
CaCO <sub>3</sub> (s)	-1128.8
CaO(s)	-604.0
CaCl <sub>2</sub> (s)	-748.1
CH <sub>4</sub> (g)	-50.7
CO <sub>2</sub> (g)	-394.4
CO(g)	-137.2
H <sub>2</sub> (g)	0
H <sub>2</sub> O(g)	-228.6
H <sub>2</sub> O(l)	-237.2

**Refer to Appendix A for more standard Gibbs energies of formation.**

## SAMPLE PROBLEM G

### Calculating a Change in Gibbs Energy from $\Delta H$ and $\Delta S$

Given that the changes in enthalpy and entropy are  $-139 \text{ kJ}$  and  $277 \text{ J/K}$  respectively for the reaction given below, calculate the change in Gibbs energy. Then, state whether the reaction is spontaneous at  $25^\circ\text{C}$ .



This reaction represents the fermentation of glucose into ethanol and carbon dioxide, which occurs in the presence of enzymes provided by yeast cells. This reaction is used in baking.

#### 1 Gather information.

$$\Delta H = -139 \text{ kJ}$$

$$\Delta S = 277 \text{ J/K}$$

$$T = 25^\circ\text{C} = (25 + 273.15) \text{ K} = 298 \text{ K}$$

$$\Delta G = ?$$

#### 2 Plan your work.

The equation  $\Delta G = \Delta H - T\Delta S$  may be used to find  $\Delta G$ .

If  $\Delta G$  is positive, the reaction is nonspontaneous. If  $\Delta G$  is negative, the reaction is spontaneous.

#### 3 Calculate.

$$\Delta G = \Delta H - T\Delta S = (-139 \text{ kJ}) - (298 \text{ K})(277 \text{ J/K})$$

$$= (-139 \text{ kJ}) - (298 \text{ K})(0.277 \text{ kJ/K})$$

$$= (-139 \text{ kJ}) - (83 \text{ kJ}) = -222 \text{ kJ}$$

The negative sign of  $\Delta G$  shows that the reaction is spontaneous.

#### 4 Verify your results.

The calculation was not necessary to prove the reaction is spontaneous, because each requirement for spontaneity—a negative  $\Delta H$  and a positive  $\Delta S$ —was met. In addition, the reaction occurs in nature without a source of energy, so the reaction must be spontaneous.

### PRACTICE HINT

Enthalpies and Gibbs energies are generally expressed in kilojoules, but entropies are usually stated in joules (not kilojoules) per kelvin. Remember to divide all entropy values expressed in joules by 1000.

### PRACTICE

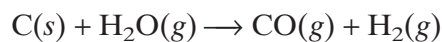
- 1 A reaction has a  $\Delta H$  of  $-76 \text{ kJ}$  and a  $\Delta S$  of  $-117 \text{ J/K}$ . Is the reaction spontaneous at  $298.15 \text{ K}$ ?
- 2 A reaction has a  $\Delta H$  of  $11 \text{ kJ}$  and a  $\Delta S$  of  $49 \text{ J/K}$ . Calculate  $\Delta G$  at  $298.15 \text{ K}$ . Is the reaction spontaneous?
- 3 The gas-phase reaction of  $\text{H}_2$  with  $\text{CO}_2$  to produce  $\text{H}_2\text{O}$  and  $\text{CO}$  has a  $\Delta H = 11 \text{ kJ}$  and a  $\Delta S = 41 \text{ J/K}$ . Is the reaction spontaneous at  $298.15 \text{ K}$ ? What is  $\Delta G$ ?



## SAMPLE PROBLEM H

### Calculating a Gibbs Energy Change Using $\Delta G_f^\circ$ Values

Use **Table 5** to calculate  $\Delta G$  for the following water-gas reaction.



Is this reaction spontaneous?

#### 1 Gather information.

For  $\text{H}_2\text{O}(g)$ ,  $\Delta G_f^\circ = -228.6 \text{ kJ/mol}$ .

For  $\text{CO}(g)$ ,  $\Delta G_f^\circ = -137.2 \text{ kJ/mol}$ .

For  $\text{H}_2(g)$ ,  $\Delta G_f^\circ = 0 \text{ kJ/mol}$ .

For  $\text{C}(s)$  (graphite),  $\Delta G_f^\circ = 0 \text{ kJ/mol}$ .

#### 2 Plan your work.

The following simple relation may be used to find the total change in Gibbs energy.

$$\Delta G = \Delta G(\text{products}) - \Delta G(\text{reactants})$$

If  $\Delta G$  is positive, the reaction is nonspontaneous. If  $\Delta G$  is negative, the reaction is spontaneous.

#### 3 Calculate.

$$\begin{aligned} \Delta G &= \Delta G(\text{products}) - \Delta G(\text{reactants}) = \\ &[(\text{mol CO}(g))(\Delta G_f^\circ \text{ for CO}(g)) + (\text{mol H}_2(g))(\Delta G_f^\circ \text{ for H}_2(g))] - \\ &[(\text{mol C}(s))(\Delta G_f^\circ \text{ for C}(s)) + (\text{mol H}_2\text{O}(g))(\Delta G_f^\circ \text{ for H}_2\text{O}(g))] = \\ &[(1 \text{ mol})(-137.2 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) - \\ &(1 \text{ mol})(-228.6 \text{ kJ/mol})] = (-137.2 + 228.6) \text{ kJ} = 91.4 \text{ kJ} \end{aligned}$$

The reaction is nonspontaneous under standard conditions.

#### 4 Verify your results.

The  $\Delta G_f^\circ$  values in this problem show that water has a Gibbs energy that is 91.4 kJ lower than the Gibbs energy of carbon monoxide. Therefore, the reaction would increase the Gibbs energy by 91.4 kJ. Processes that lead to an increase in Gibbs energy never occur spontaneously.

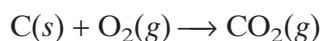
### PRACTICE HINT

Because many thermodynamic data are negative, it is easy to use the incorrect signs while performing calculations. Pay attention to signs, and check them frequently.

The  $\Delta G_f^\circ$  values for elements are always zero.

### PRACTICE

- 1 Use **Table 5** to calculate the Gibbs energy change that accompanies the following reaction.



Is the reaction spontaneous?

- 2 Use **Table 5** to calculate the Gibbs energy change that accompanies the following reaction.



Is the reaction spontaneous?



**Table 6** Relating Enthalpy and Entropy Changes to Spontaneity

$\Delta H$	$\Delta S$	$\Delta G$	Is the reaction spontaneous?
Negative	positive	negative	yes, at all temperatures
Negative	negative	either positive or negative	only if $T < \Delta H/\Delta S$
Positive	positive	either positive or negative	only if $T > \Delta H/\Delta S$
Positive	negative	positive	never

### Predicting Spontaneity

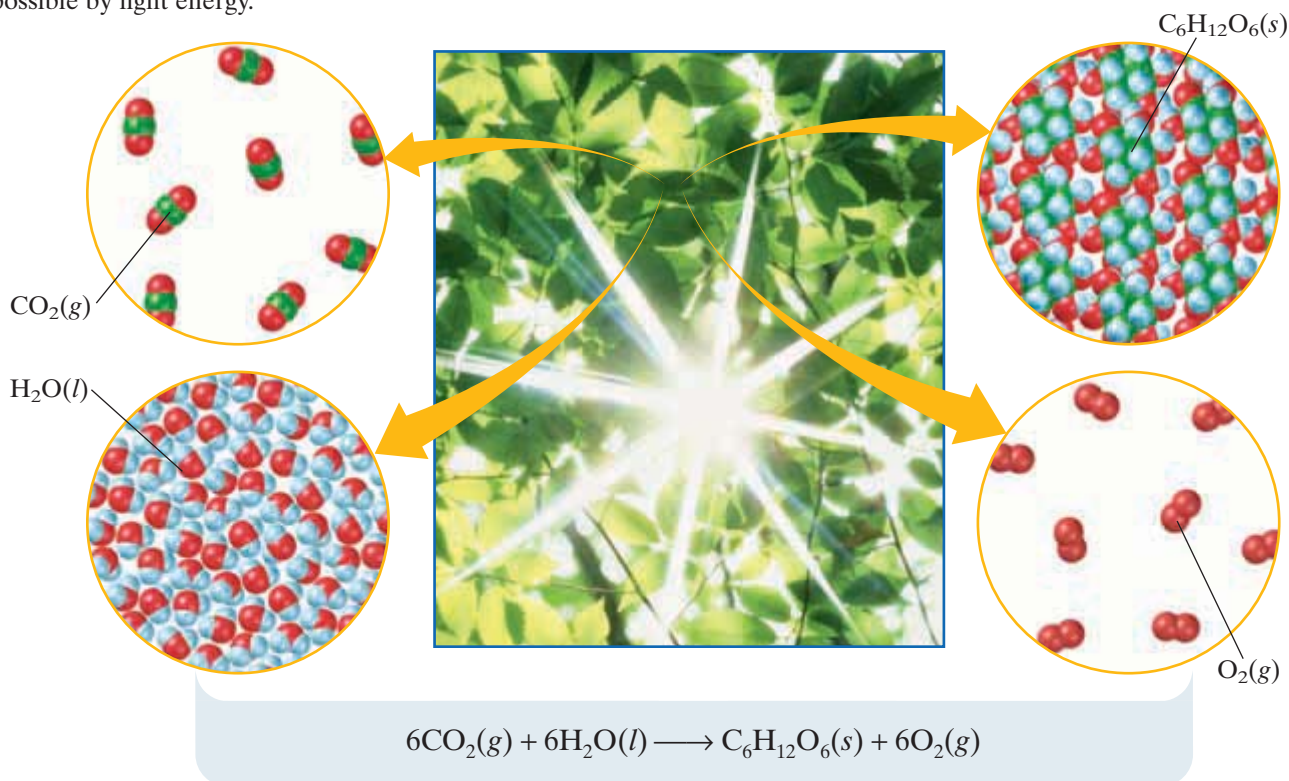
Does temperature affect spontaneity? Consider the equation for  $\Delta G$ .

$$\Delta G = \Delta H - T\Delta S$$

The terms  $\Delta H$  and  $\Delta S$  change very little as temperature changes, but the presence of  $T$  in the equation for  $\Delta G$  indicates that temperature may greatly affect  $\Delta G$ . **Table 6** summarizes the four possible combinations of enthalpy and entropy changes for any chemical reaction. Suppose a reaction has both a positive  $\Delta H$  value and a positive  $\Delta S$  value. If the reaction occurs at a low temperature, the value for  $T\Delta S$  will be small and will have little impact on the value of  $\Delta G$ . The value of  $\Delta G$  will be similar to the value of  $\Delta H$  and will have a positive value. But when the same reaction proceeds at a high enough temperature,  $T\Delta S$  will be larger than  $\Delta H$  and  $\Delta G$  will be negative. So, increasing the temperature of a reaction can make a nonspontaneous reaction spontaneous.

**Figure 15**

Photosynthesis, the non-spontaneous conversion of carbon dioxide and water into carbohydrate and oxygen, is made possible by light energy.



Can a nonspontaneous reaction ever occur? A nonspontaneous reaction cannot occur unless some form of energy is added to the system. **Figure 15** shows that the nonspontaneous reaction of photosynthesis occurs with outside assistance. During photosynthesis, light energy from the sun is used to drive the nonspontaneous process. This reaction is described by the equation below.



## 4

# Section Review

### UNDERSTANDING KEY IDEAS

1. What aspect of a substance contributes to a high or a low entropy?
2. What is diffusion? Give an example.
3. Name three thermodynamic properties, and give the relationship between them.
4. What signs of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  favor spontaneity?
5. What signs of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  favor nonspontaneity?
6. How can the Gibbs energy change of a reaction can be calculated?

### PRACTICE PROBLEMS

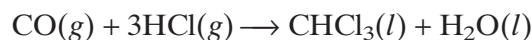
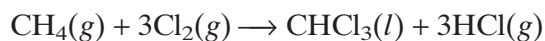
7. The standard entropies for the following substances are  $210.8 \text{ J/K}\cdot\text{mol}$  for  $\text{NO}(g)$ ,  $240.1 \text{ J/K}\cdot\text{mol}$  for  $\text{NO}_2(g)$ , and  $205.1 \text{ J/K}\cdot\text{mol}$  for  $\text{O}_2(g)$ . Determine the entropy for the reaction below.
 
$$2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$$
8. Suppose  $\text{X}(s) + 2\text{Y}_2(g) \rightarrow \text{XY}_4(g)$  has a  $\Delta H = -74.8 \text{ kJ}$  and a  $\Delta S = -80.8 \text{ J/K}$ . Calculate  $\Delta G$  for this reaction at  $298.15 \text{ K}$ .
9. Use **Table 5** to determine whether the reaction below is spontaneous.
 
$$\text{CaCl}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{CaO}(s) + 2\text{HCl}(g)$$

The standard Gibbs energy of formation for  $\text{HCl}(g)$  is  $-95.3 \text{ kJ/mol}$ .

10. Calculate the Gibbs energy change for the reaction  $2\text{CO}(g) \rightarrow \text{C}(s) + \text{CO}_2(g)$ . Is the reaction spontaneous?
11. Calculate the Gibbs energy change for the reaction  $\text{CO}(g) \rightarrow \frac{1}{2}\text{C}(s) + \frac{1}{2}\text{CO}_2(g)$ ? How does this result differ from the result in item 10?

### CRITICAL THINKING

12. A reaction is endothermic and has a  $\Delta H = 8 \text{ kJ}$ . This reaction occurs spontaneously at  $25^\circ\text{C}$ . What must be true about the entropy change?
13. You are looking for a method of making chloroform,  $\text{CHCl}_3(l)$ . The standard Gibbs energy of formation for  $\text{HCl}(g)$  is  $-95.3 \text{ kJ/mol}$  and the standard Gibbs energy of formation for  $\text{CHCl}_3(l)$  is  $-73.66 \text{ kJ/mol}$ . Use **Table 5** to decide which of the following reactions should be investigated.



14. If the reaction  $\text{X} \rightarrow \text{Y}$  is spontaneous, what can be said about the reaction  $\text{Y} \rightarrow \text{X}$ ?
15. At equilibrium, what is the relationship between  $\Delta H$  and  $\Delta S$ ?
16. If both  $\Delta H$  and  $\Delta S$  are negative, how does temperature affect spontaneity?





# SCIENCE AND TECHNOLOGY

## CAREER APPLICATION



### Engineer

Engineers design, construct, or maintain equipment, buildings, other structures, and transportation. In fact, engineers helped to develop hydrogen-powered cars and the fuel cells. Engineers have also designed and built transportation, such as space shuttles and space stations. And engineers have built structures that you encounter every day, such as your school, your home, and the bridge you cross to get home from school. Most engineers study chemistry in college. There is even a branch of engineering called *chemical engineering*. Some engineers only use computers and paper to create or improve things. Other engineers actually build and maintain equipment or structures. However, the goal of all engineers is to produce items that people use.

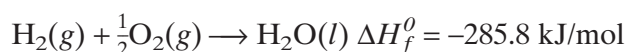


## Hydrogen-Powered Cars

Fuel cells that use hydrogen are used to power cars, such as the car in the photo.

### Hydrogen As Fuel

When you think of fuel, you probably think of gasoline or nuclear fuel. But did you know that scientists have been studying ways to use the energy generated by the following reaction?



Engineers use fuel cells that drive an electrochemical reaction, which converts hydrogen or hydrogen-containing materials and oxygen into water, electrical energy, and energy as heat. Fuel cells have already been used by NASA to provide space crews with electrical energy and drinking water. In the future, electrical energy for buildings, ships, submarines, and vehicles may be obtained using the reaction of hydrogen and oxygen to form water.

### Cars That Are Powered by Hydrogen Fuel Cells

Many car manufacturers are researching ways to mass produce vehicles that are powered by hydrogen fuel cells. Some hydrogen-powered cars that manufacturers have already developed can reach speeds of over 150 km/h (90 mi/h). These types of cars will also travel 400 to 640 km (250 to 400 mi) before refueling.

These cars have many benefits. Fuel cells have an efficiency of 50 to 60%, which is about twice as efficient as internal combustion engines. These cells are also safe for the environment because they can produce only water as a by product. Unfortunately, fuel cells are expensive because they contain expensive materials, such as platinum.

### Questions

1. Research electrical energy and its sources. Which source is the most environmentally safe? Which source is the cheapest? Which source is the most efficient?
2. Research your favorite type of car. How does this car run? How far can this car travel before refueling? What pollutants does this car produce?

# CHAPTER HIGHLIGHTS

# 10

## KEY TERMS

heat  
enthalpy  
temperature

thermodynamics

calorimetry  
calorimeter  
Hess's law

entropy  
Gibbs energy

## KEY IDEAS

### SECTION ONE Energy Transfer

- Heat is energy transferred from a region at one temperature to a region at a lower temperature.
- Temperature depends on the average kinetic energy of the atoms.
- The molar heat capacity of an element or compound is the energy as heat needed to increase the temperature of 1 mol by 1 K.

### SECTION TWO Using Enthalpy

- The enthalpy of a system can be its total energy.
- When *only* temperature changes, the change in molar enthalpy is represented by  $\Delta H = C\Delta T$ .

### SECTION THREE Changes in Enthalpy During Reactions

- Calorimetry measures the enthalpy change, which is represented by  $\Delta H$ , during a chemical reaction.
- Reactions that have positive  $\Delta H$  are endothermic; reactions that have negative  $\Delta H$  are exothermic.
- Hess's law indicates that the thermodynamic changes for any particular process are the same, whether the changes are treated as a single reaction or a series of steps.

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

### SECTION FOUR Order and Spontaneity

- The entropy of a system reflects the system's disorder.
- Gibbs energy is defined by  $G = H - TS$ .
- The sign of  $\Delta G$  determines spontaneity.

$$\Delta G_{\text{reaction}} = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$$

## KEY SKILLS

**Calculating the Molar Heat Capacity of a Sample**  
Sample Problem A p. 342

**Calculating Molar Enthalpy Change for Heating**  
Sample Problem B p. 346

**Calculating the Molar Enthalpy Change for Cooling**  
Sample Problem C p. 347

**Calculating a Standard Enthalpy of Formation**  
Sample Problem D p. 356

**Calculating a Reaction's Change in Enthalpy**  
Sample Problem E p. 356

**Hess's Law and Entropy**  
Sample Problem F p. 361

**Calculating Changes in Gibbs Energy**  
Sample Problem G p. 364  
Sample Problem H p. 365



# Physical Setting/Chemistry

## REGENTS EXAM PRACTICE

### PART A

For each item, write on a separate piece of paper the number of the word, expression, or statement that best answers the item.

- Energy is measured in units called
  - kelvins.
  - Celsius.
  - joules.
  - degrees.
- A solid at  $100^{\circ}\text{C}$  is placed in a liquid at  $25^{\circ}\text{C}$ . Which statement describes the energy transferred as heat between the solid and the liquid?
  - The solid absorbs energy as heat, and the liquid releases energy as heat.
  - The solid releases energy as heat, and the liquid absorbs energy as heat.
  - Both the solid and liquid absorb energy as heat.
  - Both the solid and liquid release energy as heat.
- Which property of a system is measured by its temperature?
  - total kinetic energy
  - entropy
  - average kinetic energy
  - molar heat capacity
- Which best describes the total energy content of a system?
  - heat
  - enthalpy
  - temperature
  - standard entropy
- Which value is negative for any exothermic process?
  - $\Delta G$
  - $\Delta S$
  - $\Delta V$
  - $\Delta H$
- Which symbol represents the change in Gibbs energy for any chemical reaction in any system?
  - $\Delta G$
  - $\Delta S$
  - $\Delta T$
  - $\Delta H$
- In a chemical reaction, which value is most likely to be determined by using an adiabatic calorimeter?
  - $\Delta G$
  - $\Delta S$
  - $\Delta H$
  - $\Delta V$
- Which combination of units is most often used in thermodynamic calculations?
  - energy as heat in calories, temperature in Celsius degrees
  - energy as heat in calories, temperature in kelvins
  - energy as heat in joules, temperature in Celsius degrees
  - energy as heat in joules, temperature in kelvins
- Which symbol represents the enthalpy change for an endothermic reaction?
  - $-\Delta H$
  - $\Delta T$
  - $\Delta H$
  - $C$
- Photosynthesis is a nonspontaneous reaction, as reflected by
  - $\Delta H > 0$ .
  - $\Delta H < 0$ .
  - $\Delta G < 0$ .
  - $\Delta G > 0$ .

### Regents Test-Taking Tip

Test questions are not necessarily arranged in order of increasing difficulty. If you are unable to answer a question, mark it and move on to other questions.



## PART B-1

For each item, write on a separate piece of paper the number of the word, expression, or statement that best answers the item.

11. Consider the following equation.



What is the standard molar enthalpy of formation of solid water?

- (1)  $-560 \text{ kJ}$                       (3)  $-280 \text{ kJ}$   
(2)  $560 \text{ kJ}$                         (4)  $280 \text{ kJ}$

12. How is  $\Delta H$  calculated?

- (1)  $H_{\text{products}} - H_{\text{reactants}}$   
(2)  $H_{\text{products}} \times H_{\text{reactants}}$   
(3)  $H_{\text{products}} + H_{\text{reactants}}$   
(4)  $\frac{H_{\text{products}}}{H_{\text{reactants}}}$

13. What quantity of energy is absorbed when the temperature of 100 grams of water is raised from  $15^\circ\text{C}$  to  $20^\circ\text{C}$ ?

- (1) 500 joules                      (3) 2.09 joules  
(2) 0.500 joules                  (4)  $2.09 \times 10^3$  joules

14. The temperature of 15 grams of water was increased to  $100^\circ\text{C}$  by the addition of 1254 joules of energy. What was the initial temperature of the water?

- (1)  $10^\circ\text{C}$                               (3)  $80^\circ\text{C}$   
(2)  $20^\circ\text{C}$                               (4)  $120^\circ\text{C}$

15. What is the enthalpy change associated with formation of one mole of HI?

- (1)  $-26.5 \text{ kJ}$                       (3)  $-53.0 \text{ kJ}$   
(2)  $+26.5 \text{ kJ}$                       (4)  $+53.0 \text{ kJ}$

16. Which applies to any reaction that has a Gibbs energy change of  $-0.8 \text{ kJ}$  at  $298 \text{ K}$ ?

- (1) The reaction has no entropy.  
(2) The reaction has no Gibbs energy.  
(3) The reaction is spontaneous.  
(4) The reaction is nonspontaneous.

17. Which symbol is used to represent the change of entropy in any reaction in a system?

- (1)  $\Delta G$                               (3)  $\Delta T$   
(2)  $\Delta S$                               (4)  $\Delta H$

18. According to the Gibbs energy equation

$$\Delta G = \Delta H - T\Delta S,$$

$\Delta G$  is negative at any temperature when

- (1)  $\Delta H$  is positive, and  $\Delta S$  is positive.  
(2)  $\Delta H$  is positive, and  $\Delta S$  is negative.  
(3)  $\Delta H$  is negative, and  $\Delta S$  is negative.  
(4)  $\Delta H$  is negative, and  $\Delta S$  is positive.

19. Which reaction shows an increase in entropy?

- (1)  $2\text{C}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_2(\text{g})$   
(2)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$   
(3)  $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow$   
 $3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$   
(4)  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$

20. What is the  $\Delta H$  for the following reaction?



- (1)  $+53.0 \text{ kJ}$                       (3)  $+26.5 \text{ kJ}$   
(2)  $-53.0 \text{ kJ}$                       (4)  $-26.5 \text{ kJ}$

21. Which set of conditions always favors a spontaneous reaction at any temperature?

- (1) an increase in entropy and a decrease in enthalpy  
(2) a decrease in entropy and a decrease in enthalpy  
(3) a decrease in entropy and an increase in enthalpy  
(4) an increase in entropy and an increase in enthalpy

22. Decreasing the temperature can turn a non-spontaneous reaction into a spontaneous reaction when

- (1)  $\Delta H > 0$  and  $\Delta S > 0$ .  
(2)  $\Delta H > 0$  and  $\Delta S < 0$ .  
(3)  $\Delta H < 0$  and  $\Delta S > 0$ .  
(4)  $\Delta H < 0$  and  $\Delta S < 0$ .



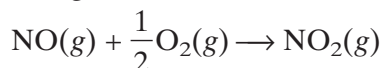
## PART B-2

Answer the following items.

- 23.** The diagram below represents two metals. Answer the questions that follow the diagram based on your knowledge of chemistry.



- a.** How is energy as heat transferred when the two metals are placed in direct contact with one another?
- b.** Which metal has the higher average kinetic energy? Explain.
- 24.** Lead has a molar heat capacity of 26.4 J/mol•K. What molar enthalpy change occurs when lead is heated from 90°C to 100°C?
- 25.** Calculate the quantity of energy as heat required to change 100 grams of liquid water to steam at 373 K.
- 26.** Using the standard molar enthalpies of formation as shown below, calculate the  $\Delta H$  for the following reaction.

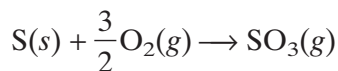


$$\text{NO}(g) \Delta H_f^\circ = +90.3 \text{ kJ/mol}$$

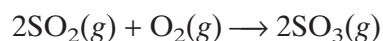
$$\text{O}_2(g) \Delta H_f^\circ = 0$$

$$\text{NO}_2(g) \Delta H_f^\circ = +33.1 \text{ kJ/mol}$$

- 27.** The molar heat capacity of tungsten is 24.2 J/mol•K. Calculate the energy as heat needed to increase the temperature of 0.50 mol of tungsten by 20°C.
- 28.** Using the equations below, calculate the enthalpy of formation for sulfur dioxide,  $\text{SO}_2$ , from its elements, sulfur and oxygen as shown by the following equation.

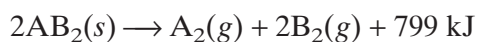


$$\Delta H = -395.2 \text{ kJ/mol}$$



$$\Delta H = -198.2 \text{ kJ/mol}$$

- 29.** Predict whether the following reaction is spontaneous or nonspontaneous. Explain your prediction in terms of the changes in enthalpy and entropy of the reaction.





30. Consider the following reaction whose  $\Delta S$  is  $+0.00300 \text{ kJ/mol}\cdot\text{K}$  at  $298.15 \text{ K}$ .



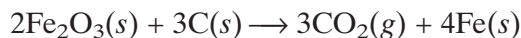
- Is this reaction endothermic or exothermic?
  - Calculate  $\Delta G$  for this reaction.
  - Is this reaction spontaneous at  $298.15 \text{ K}$ ? Explain.
31. A reaction has a  $\Delta H$  value of  $-356 \text{ kJ}$  and a  $\Delta S$  value of  $-36 \text{ J/K}$ . Calculate  $\Delta G$  at  $25^\circ\text{C}$  to confirm that this reaction is spontaneous.
32. Using the following values, compute the  $\Delta G$  value for each reaction and predict whether they will occur spontaneously.

Reaction	$\Delta H$ (kJ)	Temperature	$\Delta S$ (J/K)
1	+125	293 K	+35
2	-85.2	127 K	+125
3	-275	$500^\circ\text{C}$	+45

## PART C

Answer the following items.

33. A basketball player places an ice bag on his injured leg.
- Is the melting of ice endothermic or exothermic? Explain.
  - Indicate the direction of energy transfer between the injured leg and the ice bag.
34. In a calorimetry experiment, a student obtained the following data.
- Mass of calorimeter = 215 g  
Mass of calorimeter and water = 265 g  
Initial temperature of the water =  $23^\circ\text{C}$   
Final temperature of the water =  $58^\circ\text{C}$
- Calculate the change in temperature ( $\Delta T$ ) of the water.
  - Calculate the volume of water used in the experiment. (density of water =  $1.00 \text{ g/mL}$ ).
  - How much energy as heat is absorbed by the water in the experiment?
35. The production of iron involves the following reaction.



Use  $\Delta H_f^\circ$  values to calculate the energy as heat liberated during the production of 1 mol of iron.



**36.** Glucose,  $C_6H_{12}O_6$ , is a primary energy source for many organisms. Calculate the enthalpy change when 1 mol of glucose reacts with oxygen to form  $CO_2(g)$  and  $H_2O(l)$ . For glucose,  $\Delta H_f^\circ = -1263$  kJ/mol.

**37.** Photosynthesis is the production of carbohydrates from carbon dioxide and water, using sunlight as a source of energy. The photosynthesis reaction is shown below.



- What is the value for  $\Delta H$  for this reaction?
- Calculate  $\Delta G$  at 297 K if  $\Delta S = 259$  J/K.
- Is photosynthesis spontaneous? Explain your answer.

**38.** Hydrogen gas can be prepared for use in cars in several ways, such as by the decomposition of water or hydrogen chloride.



Use the following data to determine whether these reactions can occur spontaneously at 25°C. Assume that  $\Delta H$  and  $\Delta S$  are constant.

Substance	$H_f^\circ$ (kJ/mol)	$S^\circ$ (J/K·mol)
$H_2O(l)$	-285.8	+70.0
$H_2(g)$	0	+130.7
$O_2(g)$	0	+205.1
$HCl(g)$	-95.3	+186.9
$Cl_2(g)$	0	+223.1

**39.** In an experiment, 32 joules of energy as heat was required to change the temperature of a 4.0 g sample of glass from 274 K to 314 K.

- What is the specific heat of this type of glass?
- How much energy will the same sample of glass gain when it is heated from 314 K to 344 K?

**40.** Why are the specific heats of  $F_2(g)$  and  $Br_2(g)$  very different, whereas their molar heat capacities are very similar?

**41.** Why are most entries in Table 2 negative?

**42.** Why are most entries in Table 4 negative?

**43.** Give examples of situations in which (a) the entropy is low; (b) the entropy is high.

**44.** Under what circumstances might a nonspontaneous reaction occur?

## FOCUS ON GRAPHING

Study the graph below, and answer the questions that follow.  
For help in interpreting graphs, see Appendix B, “Study Skills for Chemistry.”

45. How would the slope differ if you were to cool the water at the same rate that graph shows the water was heated?
46. What would a slope of zero indicate about the temperature of water during heating?
47. Calculate the slope given the following data.

$$y_2 = 3.3 \text{ K} \qquad x_2 = 50 \text{ s}$$

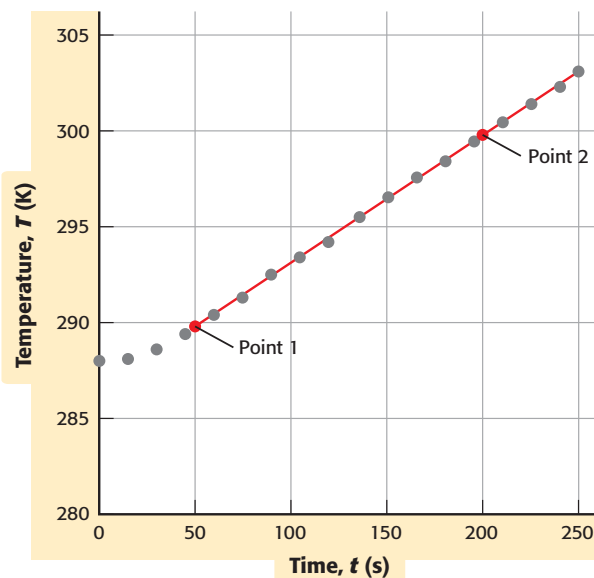
$$y_1 = 5.6 \text{ K} \qquad x_1 = 30 \text{ s}$$

48. Calculate the slope give the following data.

$$y_2 = 63.7 \text{ mL} \qquad x_2 = 5 \text{ s}$$

$$y_1 = 43.5 \text{ mL} \qquad x_1 = 2 \text{ s}$$

### Change in Water Temperature on Heating



## TECHNOLOGY AND LEARNING

### 49. Graphing Calculator

#### *Calculating the Gibbs-Energy Change*

The graphing calculator can run a program that calculates the Gibbs-energy change, given the temperature,  $T$ , change in enthalpy,  $\Delta H$ , and change in entropy,  $\Delta S$ . Given that the temperature is 298 K, the change in enthalpy is 131.3 kJ/mol, and the change in entropy is 0.134 kJ/(mol $\cdot$ K), you can calculate Gibbs-energy change in kilojoules per mole. Then use the program to make calculations.

**Go to Appendix C.** If you are using a TI-83 Plus, you can download the program ENERGY data and run the application as directed. If you are using another

calculator, your teacher will provide you with keystrokes and data sets to use. After you have run the program, answer the following questions.

- What is the Gibbs-energy change given a temperature of 300 K, a change in enthalpy of 132 kJ/mol, and a change in entropy of 0.086 kJ/(mol $\cdot$ K)?
- What is the Gibbs-energy change given a temperature of 288 K, a change in enthalpy of 115 kJ/mol, and a change in entropy of 0.113 kJ/(mol $\cdot$ K)?
- What is the Gibbs-energy change given a temperature of 298 K, a change in enthalpy of 181 kJ/mol, and a change in entropy of 0.135 kJ/(mol $\cdot$ K)?