CHAPTER



CAUSES OF CHANGE

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, CO₂, and water, H₂O.

START-UPACTIVITY

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

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

CONTENTS

SECTION 1 Energy Transfer

SECTION 2

Using Enthalpy

SECTION 3

Changes in Enthalpy During Reactions

SECTION 4 Order and Spontaneity



S E C T I O N

Energy Transfer

Key Terms

- heat
- enthalpy
- temperature

OBJECTIVES

- **Define** enthalpy.
- **Distinguish** between heat and temperature.
- **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.



heat

the energy transferred between objects that are at different temperatures

Figure 1

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









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.



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°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 K)? The atoms still move! However, the average and total kinetic energies of the atoms at 0.00 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 that make up a substance occur at 0.00 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.

b Change in Water Temperature on Heating



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

а

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 J/K•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 ΔT .

$$q = nC\Delta T$$

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.

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 H_2O can be determined by using the following equation. Also notice that Δt divided by ΔT is the inverse of the slope calculated above.

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



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 $27.8 \text{ J/K} \cdot \text{mol.}$

1 Gather information.

The amount of mercury is 10.0 mol. C for Hg = 27.8 J/K•mol ΔT = 7.5 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 2.1×10^3 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



- The molar heat capacity of tungsten is 24.2 J/K•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 1.7×10^2 J of energy as heat. Calculate the number of moles of NaCl if the molar heat capacity is 50.5 J/K•mol.
- 3 Calculate the energy as heat needed to increase the temperature of 0.80 mol of nitrogen, N₂, by 9.5 K. The molar heat capacity of nitrogen is 29.1 J/K•mol.

A 0.07 mol sample of octane, C_8H_{18} , absorbed 3.5×10^3 J of energy. Calculate the temperature increase of octane if the molar heat capacity of octane is 254.0 J/K •mol.

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.

PRACTICE HINT

| able i molar Heat Capacities of Elements and Compounds | | | | |
|--|-------------|--------------------------------|--------------|--|
| Element | C (J/K∙mol) | Compound | C (J/K •mol) | |
| Aluminum, Al(s) | 24.2 | Aluminum chloride, $AlCl_3(s)$ | 92.0 | |
| Argon, $Ar(g)$ | 20.8 | Barium chloride, $BaCl_2(s)$ | 75.1 | |
| Helium, He(g) | 20.8 | Cesium iodide, CsI(s) | 51.8 | |
| Iron, $Fe(s)$ | 25.1 | Octane, $C_8H_{18}(l)$ | 254.0 | |
| Mercury, $Hg(l)$ | 27.8 | Sodium chloride, NaCl(s) | 50.5 | |
| Nitrogen, $N_2(g)$ | 29.1 | Water, $H_2O(g)$ | 36.8 | |
| Silver, Ag(s) | 25.3 | Water, $H_2O(l)$ | 75.3 | |
| Tungsten W(s) | 24.2 | Water, $H_2O(s)$ | 37.4 | |

 Table 1
 Molar Heat Capacities of Elements and Compounds

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 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 $BaCl_2$ to be $C = 3 \times 25$ J/K•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 (g/mol) × c_p (J/K•g) = C (J/K•mol) (molar mass)(specific heat) = (molar heat capacity)



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.

O 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 1.0×10^2 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°C to 125°C.
- 10. Use the molar heat capacity for iron fromTable 1 to calculate the amount of energy needed to raise the temperature of 260.5 g of iron from 0°C to 125°C.

- 11. A sample of aluminum chloride increased in temperature by 3.5 K when the sample absorbed 1.67×10^2 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 2.5×10^2 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 1.0×10^2 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 PbS(s) and Ag₂S(s).
- **18.** Use **Table 1** to predict the molar heat capacity of $FeCl_3(s)$.
- **19.** Use your answer from item 18 to predict the specific heat of $\text{FeCl}_3(s)$.



Using Enthalpy

Key Terms

thermodynamics

OBJECTIVES

Define thermodynamics.

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 ΔH 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.

 $Fe(s, 300 \text{ K}) \longrightarrow Fe(s, 1100 \text{ K}) \quad \Delta H = 20.1 \text{ kJ/mol}$

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.



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.

molar enthalpy change = $C\Delta T$

molar enthalpy change = (molar heat capacity)(temperature change)

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 °C to -0.2 °C?

1 Gather information.

 $T_{\text{initial}} = -5.4 \text{ °C} = 267.8 \text{ K}$ and $T_{\text{final}} = -0.2 \text{ °C} = 273.0 \text{ K}$ For H₂O(s), C = 37.4 J/K • mol.

2 Plan your work.

3 Calculate.

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

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

PRACTICE HINT

Remember that molar enthalpy change has units of kJ/mol.

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

The molar enthalpy change is 0.19 kJ/mol.

4 Verify your results.

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

PRACTICE



Calculate the molar enthalpy change of $H_2O(l)$ when liquid water is heated from 41.7°C to 76.2°C.

- **2** Calculate the ΔH of NaCl when it is heated from 0.0°C to 100.0°C.
- **3** Calculate the molar enthalpy change when tungsten is heated by 15 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.

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

277 K - 292 K = -15 K

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

3 Calculate.

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

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

- 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.

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.

PRACTICE HINT

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



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 H₂ and Br₂. Or, the enthalpy of 2HBr is less than the enthalpy of H_2 and Br_2 , 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?

$$Fe(s, 300 \text{ K}) \longrightarrow Fe(s, 1100 \text{ K}) \quad \Delta H = 20.1 \text{ kJ/mol}$$

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.

 $H_2(g, 298 \text{ K}) + Br_2(l, 298 \text{ K}) \longrightarrow 2HBr(g, 298 \text{ K}) \quad \Delta H = -72.8 \text{ kJ}$

Notice that the enthalpy change for this reaction and other chemical reactions are written using the symbol ΔH . 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.



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° C to -10.1° C. Calculate the temperature change, ΔT , in degrees Celsius and in kelvins.
- **5.** Calculate the molar enthalpy change when a block of ice is heated from -8.4 °C to -5.2 °C.
- **6.** Calculate the molar enthalpy change when $H_2O(l)$ is cooled from 48.3°C to 25.2°C.

- 7. The molar heat capacity of benzene, $C_6H_6(l)$, is 136 J/K•mol. Calculate the molar enthalpy change when the temperature of $C_6H_6(l)$ changes from 19.7°C to 46.8°C.
- **8.** The molar heat capacity of diethyl ether, $(C_2H_5)_2O(l)$, is 172 J/K•mol. What is the temperature change if the molar enthalpy change equals -186.9 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?

S E C T I O N

Changes in Enthalpy During Chemical Reactions

Key Terms

- calorimetry
- calorimeter
- Hess's law



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

OBJECTIVES

- **Explain** the principles of calorimetry.
 - **Use** Hess's law and standard enthalpies of formation to calculate ΔH .

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.

$$\frac{1}{2}$$
H₂(g) + $\frac{1}{2}$ Br₂(l) \longrightarrow HBr(g) $\Delta H = -36.4$ kJ

This equation shows that when 0.5 mol of H_2 reacts with 0.5 mol of 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.





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

Chemical Calorimetry

For the H_2 and Br_2 reaction, in which ΔH 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 of 1.00 mol of carbon yields 393.5 kJ of energy.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$

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

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 342.3 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° C. The enthalpy change can be calculated and is shown below.

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l) \quad \Delta H = -2226 \text{ kJ}$$

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, PCl₅, when phosphorus is burned in excess chlorine.

$$P_4(s) + 10Cl_2(g) \longrightarrow 4PCl_5(g) \quad \Delta H = -1596 \text{ kJ}$$

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

Step 1:
$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(g) \quad \Delta H = -1224 \text{ kJ}$$

Step 2: $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g) \quad \Delta H = -93 \text{ kJ}$

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.

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(g) \quad \Delta H = -1224 \text{ kJ}$$
$$4PCl_3(g) + 4Cl_2(g) \longrightarrow 4PCl_5(g) \quad \Delta H = 4(-93 \text{ kJ}) = -372 \text{ kJ}$$

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, ΔH , for the two-step process is the same as the enthalpy change for the direct route of the formation of PCl₅. 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. If a quarterback drops back 5 yards and passes the ball a total of 10 yards, the net gain is 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_2 and solid carbon are reactants, is found using the equations below.

$$2C(s) + O_2(g) \longrightarrow 2CO(g) \quad \Delta H = -221 \text{ kJ}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393 \text{ kJ}$$

You cannot simply add these equations because CO_2 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.

$$-C(s) - O_2(g) \longrightarrow -CO_2(g) \quad \Delta H = -(-393 \text{ kJ})$$
$$CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta H = 393 \text{ kJ}$$

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_2 and C.

$$\frac{2C(s) + O_2(g) \longrightarrow 2CO(g) \quad \Delta H = -221 \text{ kJ}}{CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta H = 393 \text{ kJ}}$$
$$\frac{2C(s) + O_2(g) + CO_2(g) \longrightarrow 2CO(g) + C(s) + O_2(g) \quad \Delta H = 172 \text{ kJ}}{\Delta H = 172 \text{ kJ}}$$

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

$$C(s) + CO_2(g) \longrightarrow 2CO(g) \quad \Delta H = 172 \text{ kJ}$$

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, ΔH_f^0 . Many values of ΔH_f^0 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.

$$SO_2(g) + NO_2(g) \longrightarrow SO_3(g) + NO(g) \quad \Delta H = ?$$

Two of these steps convert the reactants into their elements. Notice that the reverse reactions for the formations of SO_2 and NO_2 are used. So, the standard enthalpies of formation for these reverse reactions are the negative of the standard enthalpies of formation for SO_2 and NO_2 .

$$SO_2(g) \longrightarrow \frac{1}{8}S_8(s) + O_2(g) \quad \Delta H = -\Delta H_f^0 = -(-296.8 \text{ kJ/mol})$$
$$NO_2(g) \longrightarrow \frac{1}{2}N_2(g) + O_2(g) \quad \Delta H = -\Delta H_f^0 = -(33.1 \text{ kJ/mol})$$

| adie 2 Stanuaru Entilarpies of Formation | | | | |
|--|---------------------------------|--------------------------|---------------------------------|--|
| Substance | ∆ <i>H^o</i> (kJ/mol) | Substance | ∆ <i>H^o(</i> kJ/mol) | |
| $Al_2O_3(s)$ | -1676.0 | $H_2O(g)$ | -241.8 | |
| $CaCO_3(s)$ | -1206.9 | $H_2O(l)$ | -285.8 | |
| CaO(s) | -634.9 | $\operatorname{Na}^+(g)$ | 609.4 | |
| $Ca(OH)_2(s)$ | -985.2 | NaBr(s) | -361.1 | |
| $C_2H_6(g)$ | -83.8 | $Na_2CO_3(s)$ | -1130.7 | |
| $CH_4(g)$ | -74.9 | NO(g) | 90.3 | |
| $\mathrm{CO}(g)$ | -110.5 | $NO_2(g)$ | 33.1 | |
| $CO_2(g)$ | -393.5 | Pb(s) | 0 | |
| $Fe_2O_3(s)$ | -825.5 | $SO_2(g)$ | -296.8 | |
| $H_2(g)$ | 0 | $SO_3(g)$ | -395.8 | |
| Hg(<i>l</i>) | 0 | ZnO(s) | -348.3 | |

Table 2 Standard Enthalpies of Formation

Refer to Appendix A for more standard enthalpies of formation.

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

$$\frac{1}{8}S_8(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g) \quad \Delta H_f^0 = -395.8 \text{ kJ/mol}$$
$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \quad \Delta H_f^0 = 90.3 \text{ kJ/mol}$$

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.

$$SO_2(g) + NO_2(g) \longrightarrow SO_3(g) + NO(g)$$
$$\Delta H = (\Delta H_{f, NO}^0 + \Delta H_{f, SO_3}^0) + (-\Delta H_{f, NO_2}^0 - \Delta H_{f, SO_2}^0)$$
$$\Delta H = (90.3 \text{ kJ/mol} - 395.8 \text{ kJ/mol}) + (-33.1 \text{ kJ/mol} + 296.8 \text{ kJ/mol}) = -41.8 \text{ kJ/mol}$$

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)
$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H_f^0 = -393.5 \text{ kJ/mol}$$

(2) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H_f^0 = -285.8 \text{ kJ/mol}$
(3) $C_5H_{12}(g) + 8O_2(g) \longrightarrow 5CO_2(g) + 6H_2O(l) \quad \Delta H = -3535.6 \text{ kJ/mol}$

Gather information.

The equation for the standard enthalpy of formation is

$$5C(s) + 6H_2(g) \longrightarrow C_5H_{12}(g) \quad \Delta H_f^0 = ?$$

Plan your work.

 C_5H_{12} is a product, so reverse the equation (3) and the sign of ΔH . Multiply equation (1) by 5 to give 5C as a reactant. Multiply equation (2) by 6 to give $6H_2$ as a reactant.

3 Calculate.

(1) $5C(s) + 5O_2(g) \longrightarrow 5CO_2(g) \quad \Delta H = 5(-393.5 \text{ kJ/mol})$ (2) $6H_2(g) + 3O_2(g) \longrightarrow 6H_2O(l) \quad \Delta H = 6(-285.8 \text{ kJ/mol})$ (3) $5CO_2(g) + 6H_2O(l) \longrightarrow C_5H_{12}(g) + 8O_2(g) \quad \Delta H = 3536.6 \text{ kJ/mol}$ $5C(s) + 6H_2(g) \longrightarrow C_5H_{12}(g) \quad \Delta H_f^0 = -145.7 \text{ kJ/mol}$

4 Verify your results.

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

PRACTICE



Calculate the enthalpy change for the following reaction.

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

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

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**.

 $2H_2(g) + 2CO_2(g) \longrightarrow 2H_2O(g) + 2CO(g)$

Then, state whether the reaction is exothermic or endothermic.

PRACTICE HINT

A positive ΔH means that the reaction has absorbed energy or that the reaction is endothermic. A negative ΔH means that the reaction has released energy or that the reaction is exothermic.

1 Gather information.

Standard enthalpies of formation for the products are as follows: For H₂O(*g*), $\Delta H_f^0 = -241.8$ kJ/mol. For CO(*g*), $\Delta H_f^0 = -110.5$ kJ/mol. Standard enthalpies of formation for the reactants are as follows: For H₂(*g*), $\Delta H_f^0 = 0$ kJ/mol. For CO₂(*g*), $\Delta H_f^0 = -393.5$ kJ/mol.

2 Plan your work.

The general rule is $\Delta H = \Delta H(\text{products}) - \Delta H(\text{reactants})$. So, $\Delta H = (\text{mol H}_2\text{O}(g)) \Delta H_f^0 (\text{for H}_2\text{O}(g)) + (\text{mol CO}(g)) \Delta H_f^0 (\text{for CO}(g)) - (\text{mol H}_2(g)) \Delta H_f^0 (\text{for H}_2(g)) - (\text{mol CO}_2(g)) \Delta H_f^0 (\text{for CO}_2(g)).$

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 kJ, is more negative than that of the products, -704.6 kJ, and shows that the total energy of the reaction increases by 82.4 kJ.

PRACTICE

1 Use data from **Table 2** to calculate ΔH for the following reaction.

$$C_2H_6(g) + \frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

2 The exothermic reaction known as lime slaking is $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$. Calculate ΔH from the data in **Table 2.**

PRACTICE HINT

Always be sure to check the states of matter when you use standard enthalpy of formation data. $H_2O(g)$ and $H_2O(l)$ have different values.



Section Review

UNDERSTANDING KEY IDEAS

- **1.** What is the standard thermodynamic temperature?
- 2. Why are no elements listed in Table 2?
- **3.** How do bomb calorimetry and adiabatic calorimetry differ?

PRACTICE PROBLEMS

4. Use **Table 2** to calculate ΔH for the decomposition of calcium carbonate into

calcium oxide and carbon dioxide.

5. What enthalpy change accompanies the reaction $2Al(s) + 3H_2O(l) \rightarrow$

 $Al_2O_3(s) + 3H_2(g)?$

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?

S E C T I O N



Order and Spontaneity

Key Terms

- entropy
- Gibbs energy

internet connect

Topic: Entropy SciLinks code: HW4053

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INKS Teachers Assess

a measure of the randomness or disorder of a system

d by the

OBJECTIVES

- **Define** *entropy*, and discuss the factors that influence the sign and magnitude of ΔS for a chemical reaction.
- **Describe** Gibbs energy, and discuss the factors that influence the sign and magnitude of ΔG .
- **Indicate** whether ΔG values describe spontaneous or nonspontaneous reactions.

Entropy Some reset

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 ΔH 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, ΔS is positive.

Figure 11

entropy

a Crystals of potassium permanganate, KMnO₄, are dropped into a beaker of water and dissolve to produce the $K^+(aq)$ and $MnO^-_4(aq)$ ions.





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