

# 5

# THERMOCHEMISTRY

## 5.1 | The Nature of Chemical Energy



The study of energy and its transformations is known as **thermodynamics** (Greek: *thérme-*, “heat”; *dy’namis*, “power”). This area of study began during the Industrial Revolution in order to develop the relationships among heat, work, and fuels. These were used in steam engines, such as the beam engine pictured here. Here, we will examine the relationships between chemical reactions and energy changes that involve heat. This portion of thermodynamics is called **thermochemistry**. We will discuss additional aspects of thermodynamics in Chapter 19.

## WHAT'S AHEAD

- 5.1 ► The Nature of Chemical Energy
- 5.2 ► The First Law of Thermodynamics
- 5.3 ► Enthalpy
- 5.4 ► Enthalpies of Reaction
- 5.5 ► Calorimetry
- 5.6 ► Hess’s Law
- 5.7 ► Enthalpies of Formation
- 5.8 ► Bond Enthalpies
- 5.9 ► Foods and Fuels

By the end of this section, you should be able to

- Understand the relationship between energy and the making or breaking of chemical bonds

As we learned in Chapter 1 (Section 1.4), energy is defined as the capacity to do work or transfer heat. Anyone who has sat by a fire or used a propane grill has witnessed chemical reactions that release heat [**Figure 5.1(a)**]. Some chemical reactions also absorb heat, such as those that occur when you cook. Chemical reactions can also do work in various ways. Recall the definition of work from Chapter 1:

$$w = F \times d \quad [5.1]$$

For example, the combustion reaction between fuel and oxygen produces gases that expand and in the process do work that can be used to power a car. Champagne is made when yeasts use chemical reactions to ferment sugars into ethanol and carbon dioxide. By carrying out the last stages of fermentation in a corked bottle, pressure from the generated CO<sub>2</sub> builds up and can be used to do work when the cork is popped [**Figure 5.1(b)**]. Yet another example is a battery, where redox reactions produce electrical energy that can be used to do work.

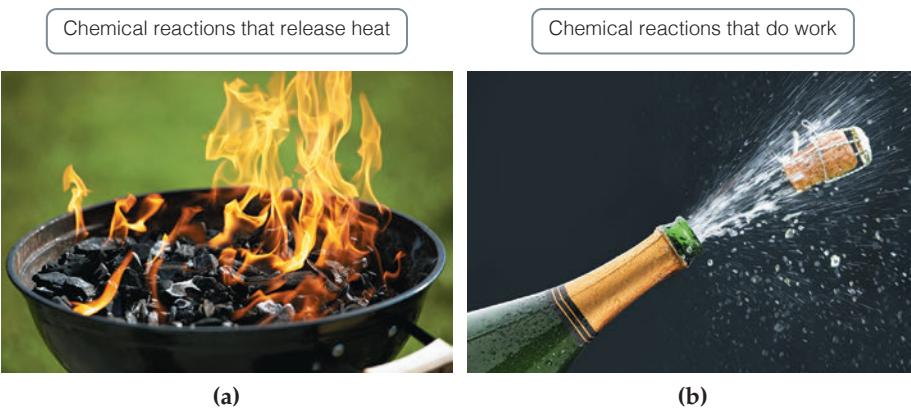
All forms of energy can be classified as either kinetic or potential energy. The energy that originates from chemical reactions is associated mainly with changes in potential energy. This energy results from electrostatic interactions at the atomic level. Thus, if we are to understand the energy associated with chemical reactions, we must first understand electrostatic potential energy, which arises from the interactions between charged particles.

The electrostatic potential energy,  $E_{\text{el}}$ , associated with two charged particles is proportional to their electrical charges,  $Q_1$  and  $Q_2$ , and is inversely proportional to the distance,  $d$ , separating them:

$$E_{\text{el}} = \frac{\kappa Q_1 Q_2}{d} \quad [5.2]$$

where  $\kappa$  is a proportionality constant whose value is  $8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$ .\* Recall from Chapter 1 that the units used to measure energy are joules, where  $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$ . At the atomic level, the charges  $Q_1$  and  $Q_2$  are typically on the order of magnitude of the charge of an electron ( $1.60 \times 10^{-19} \text{ C}$ ), while distances range from tenths to tens of nanometers ( $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ ).

Inspection of Equation 5.2 shows that electrostatic potential energy goes to zero as  $d$  becomes infinite. Thus, zero electrostatic potential energy is defined as infinite

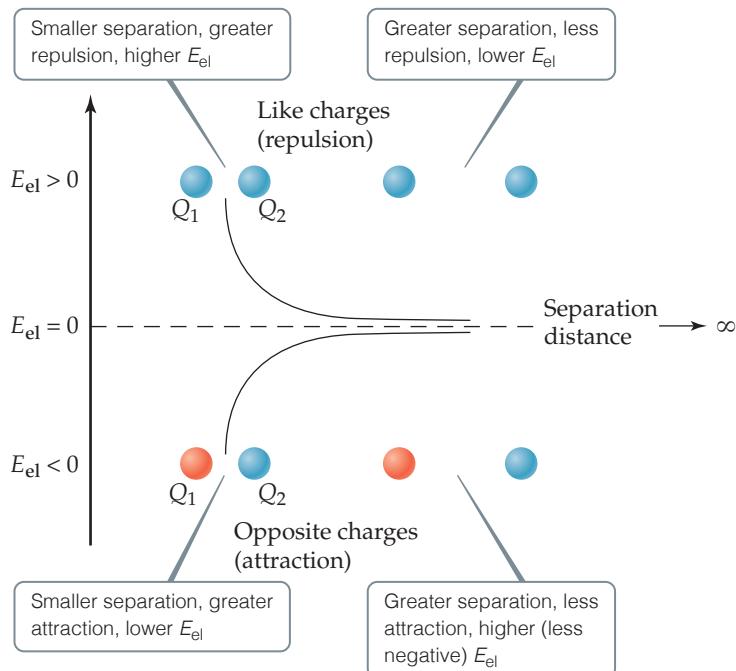


**▲ Figure 5.1 Chemical reactions and energy.** Energy changes in chemical reactions can be used to transfer heat or do work.

\*We read the combined units J·m/C<sup>2</sup> as joule-meters per coulomb squared. You may see combinations of units such as J·m/C<sup>2</sup> expressed with dots separating units instead of short dashes, J·m/C<sup>2</sup>, or with dashes and dots totally absent, J m/C<sup>2</sup>.

**Go Figure**

A positively charged particle and a negatively charged particle are initially far apart. What happens to their electrostatic potential energy as they are brought closer together?



**▲ Figure 5.2 Electrostatic potential energy.** At finite separation distances the electrostatic potential energy,  $E_{el}$ , is positive for objects with like charges, and negative for objects that are oppositely charged. As the particles move farther apart, their electrostatic potential energy approaches zero.

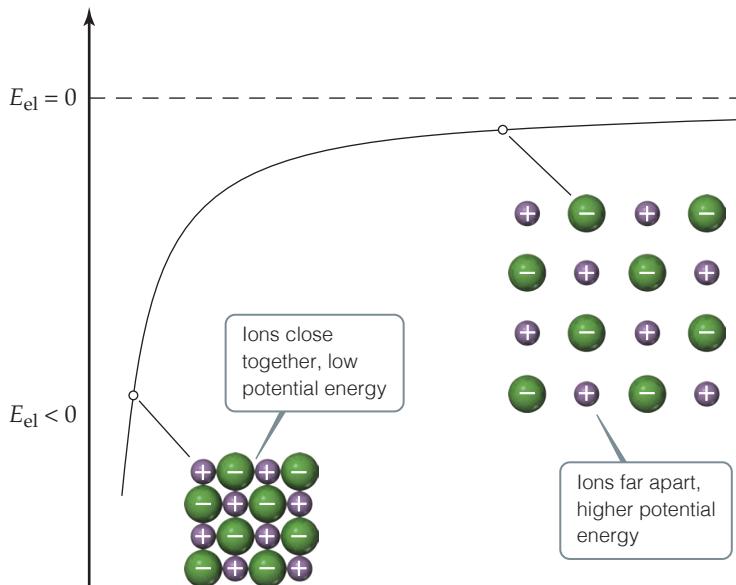
separation of the charged particles. **Figure 5.2** illustrates how  $E_{el}$  behaves as the distance between two charges is varied. When  $Q_1$  and  $Q_2$  have the same sign (for example, both are positive), the two charged particles repel each other, and a repulsive force pushes them apart. In order to bring two positively charged objects close together, one would have to do work to overcome the repulsive force that exists between the two. Upon releasing them, they would move away from each other as potential energy is converted to kinetic energy. In this case,  $E_{el}$  is positive, and the potential energy decreases as the distance between particles increases. When  $Q_1$  and  $Q_2$  have opposite signs, the particles attract each other, and an attractive force pulls them toward each other. In this case  $E_{el}$  is negative, and the potential energy increases (becomes less negative) as the particles move apart.

To understand the relationship between electrostatic potential energy and the energy stored in chemical bonds, it is instructive to consider an ionic compound like NaCl. The  $\text{Na}^+$  cations and  $\text{Cl}^-$  anions are held together by the electrostatic attraction between the oppositely charged ions. In chemistry we refer to this force as ionic bonding. We'll go into the details of ionic bonding in Chapter 8, but for now it is sufficient to understand that the ionic bonds that hold sodium and chloride ions together are based on the electrostatic attraction between cations and anions. To separate the ions, we must overcome, or break, the ionic bonds between  $\text{Na}^+$  and  $\text{Cl}^-$ , increasing the potential energy, as illustrated in **Figure 5.3**. The energy to do this must come from some other source. The reverse process where ions separated by a large distance are allowed to come together to form ionic bonds lowers the potential energy and therefore releases energy. This illustrates a fundamental principle of thermochemistry:

*Energy is released when chemical bonds are formed;  
energy is consumed when chemical bonds are broken.*

 Go Figure

If the ions in the figure on the right were released and allowed to move, would they move closer together or farther apart?



**▲ Figure 5.3 Electrostatic potential energy and ionic bonding.** As the separation between ions increases, the electrostatic potential energy increases (becomes less negative). As the distance separating the ions goes toward infinity, the electrostatic potential energy goes to zero. In real compounds, repulsions between core electrons place a lower limit on how closely the ions can approach each other.

You may be wondering how these same principles apply to molecular substances such as water, H<sub>2</sub>O, and methane, CH<sub>4</sub>, that do not contain cations and anions. As we will learn in Chapters 8 and 9, the atoms in a molecule are held together by covalent bonds. While the link to electrostatic potential energy is less obvious, the forces that underlie covalent bonds are also electrostatic in nature. Just like ionic bonds, energy must be provided to break covalent bonds and is released when they form.

## Self-Assessment Exercise

- 5.1 Which solid would have the lower (more negative) potential energy?

(a) NaCl

(b) CaO

## Exercises

- 5.2 (a) What is the electrostatic potential energy (in joules) between an electron and a proton that are separated by 230 pm?  
 (b) What is the change in potential energy if the distance separating the electron and proton is increased to 1.0 nm?  
 (c) Does the potential energy of the two particles increase or decrease when the distance is increased to 1.0 nm?
- 5.3 A sodium ion, Na<sup>+</sup>, with a charge of  $1.6 \times 10^{-19}$  C and a chloride ion, Cl<sup>-</sup>, with charge of  $-1.6 \times 10^{-19}$  C, are separated by

a distance of 0.50 nm. How much work would be required to increase the separation of the two ions to an infinite distance?

- 5.4 Identify the force present and explain whether work is being performed in the following cases: (a) You lift a book off the top of a desk. (b) Air is compressed in a bicycle pump.

5.1 (b)



## 5.2 | The First Law of Thermodynamics



With the exception of the energy from the Sun, most of the energy used in our daily lives comes from chemical reactions. The combustion of fuel, the production of electricity from coal, the heating of homes by natural gas, and the use of batteries to power electronic devices are all examples of how chemical reactions are used to produce energy. But that's only the beginning. Chemical reactions provide the energy that sustains living systems. Plants use solar energy to carry out photosynthesis, allowing them to grow. In the process, they store a portion of the Sun's energy in the chemical bonds of the molecules that are produced during photosynthesis. When animals eat and digest plants, they derive the energy needed to move, maintain body temperature, and carry out all other bodily functions from that same chemical energy.

Energy comes in many different forms, including kinetic energy, which we encountered in Chapter 1, and various types of potential energy. You don't have to look far to find processes that involve conversions from one form of energy to another. Dropping a stone down a deep well converts gravitational potential energy into kinetic energy. Heating your house by reacting natural gas with oxygen converts chemical energy into heat. In both cases—and every other one you can imagine—*energy can be converted from one form to another, but it is neither created nor destroyed*. This observation, one of the most important in all of science, is known as the **first law of thermodynamics**. To apply this law quantitatively we need to divide the universe into a finite system of interest to us, and define the energy of that system more precisely. We explore these concepts next.

### System and Surroundings

When analyzing energy changes, we need to focus on a limited and well-defined part of the universe to keep track of the energy changes that occur. The portion we single out for study is called the **system**; everything else is called the **surroundings**. When we study the energy change that accompanies a chemical reaction in a laboratory, the reactants and products constitute the system. The container and everything beyond it are considered the surroundings.

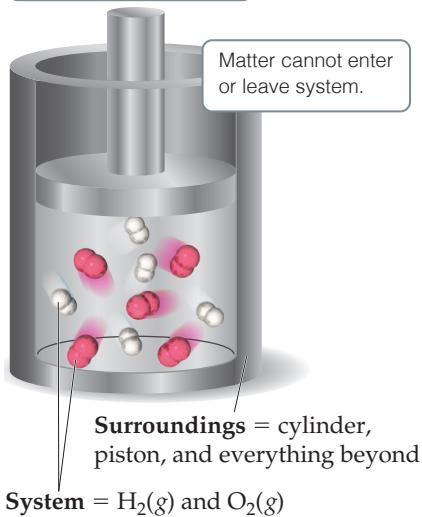
Systems may be open, closed, or isolated. An *open system* is one in which matter and energy can be exchanged with the surroundings. An uncovered pot of boiling water on a stove is an open system: Heat comes into the system from the stove, and water is released to the surroundings as steam.

The systems we can most readily study in thermochemistry are called *closed systems*—systems that can exchange energy but not matter with their surroundings. For example, consider a mixture of hydrogen gas, H<sub>2</sub>, and oxygen gas, O<sub>2</sub>, in a cylinder fitted


**Go Figure**

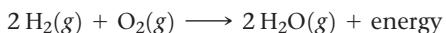
If the H<sub>2</sub> and O<sub>2</sub> molecules in the cylinder react to form H<sub>2</sub>O, will the number of molecules in the cylinder change? Will the mass in the cylinder change?

Energy can enter or leave system as heat or as work done on piston.



▲ Figure 5.4 A closed system.

with a piston (Figure 5.4). The system is just the hydrogen and oxygen; the cylinder, piston, and everything beyond them (including us) are the surroundings. If the gases react to form water, energy is liberated:



Although the chemical form of the hydrogen and oxygen atoms in the system is changed by this reaction, the system has not lost or gained mass, which means it has not exchanged any matter with its surroundings. However, it can exchange energy with its surroundings in the form of *work* and *heat*.

An *isolated* system is one in which neither energy nor matter can be exchanged with the surroundings. An insulated thermos containing hot coffee approximates an isolated system. We know, however, that the coffee eventually cools, so it is not perfectly isolated.

### Internal Energy

The **internal energy**, *E*, of a system is the sum of *all* the kinetic and potential energies of the components of the system. For the system in Figure 5.4, for example, the internal energy includes not only the motions and interactions of the H<sub>2</sub> and O<sub>2</sub> molecules but also the motions and interactions of their component nuclei and electrons. We generally do not know the numerical value of a system's internal energy. In thermodynamics, we are mainly concerned with the *change* in *E* (and, as we shall see, changes in other quantities as well) that accompanies a change in the system.

Imagine that we start with a system with an initial internal energy *E*<sub>initial</sub>. The system then undergoes a change, which might involve work being done or heat being transferred. After the change, the final internal energy of the system is *E*<sub>final</sub>. We define the *change* in internal energy, denoted  $\Delta E$  (read “delta *E*”),\* as the difference between *E*<sub>final</sub> and *E*<sub>initial</sub>:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} \quad [5.3]$$

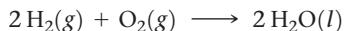
We generally cannot determine the actual values of *E*<sub>final</sub> and *E*<sub>initial</sub> for any system of practical interest. Nevertheless, we can determine the value of  $\Delta E$  experimentally by applying the first law of thermodynamics.

Thermodynamic quantities such as  $\Delta E$  have three parts:

1. a number
2. a unit
3. a sign

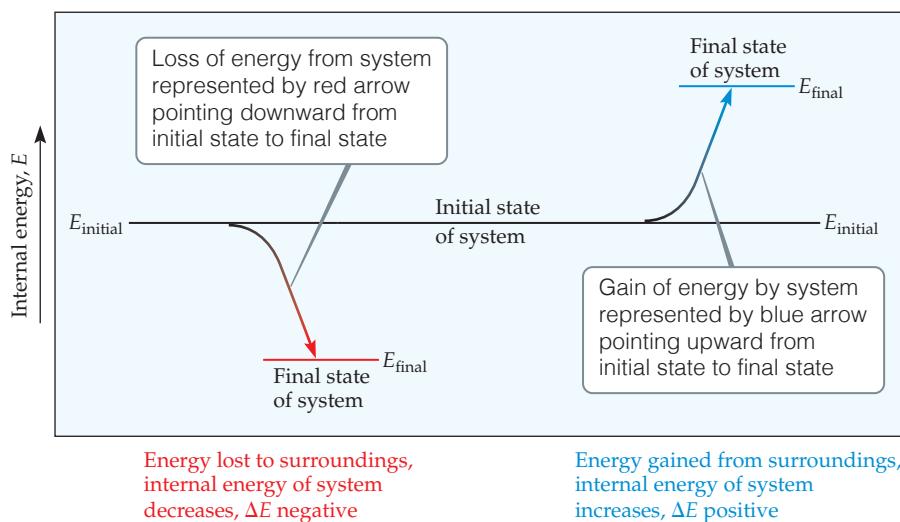
(1) and (2) together give the magnitude of the change, while (3) gives the direction. A *positive* value of  $\Delta E$  results when *E*<sub>final</sub> > *E*<sub>initial</sub>, indicating that the system has gained energy from its surroundings. A *negative* value of  $\Delta E$  results when *E*<sub>final</sub> < *E*<sub>initial</sub>, indicating that the system has lost energy to its surroundings. Notice that we are taking the point of view of the system rather than that of the surroundings in discussing the energy changes. We need to remember, however, that any increase in the energy of the system is accompanied by a decrease in the energy of the surroundings, and vice versa. These features of energy changes are summarized in Figure 5.5.

In a chemical reaction, the initial state of the system refers to the reactants and the final state refers to the products. In the reaction



for instance, the initial state is 2 H<sub>2</sub>(g) + O<sub>2</sub>(g) and the final state is 2 H<sub>2</sub>O(l). When hydrogen and oxygen form water at a given temperature, the system loses energy to the surroundings. Because energy is lost from the system, the internal energy of the products (final state) is less than that of the reactants (initial state), and  $\Delta E$  for the process is negative. Thus, the *energy diagram* in Figure 5.6 shows that the internal energy of the mixture of H<sub>2</sub> and O<sub>2</sub> is greater than that of the H<sub>2</sub>O produced in the reaction.

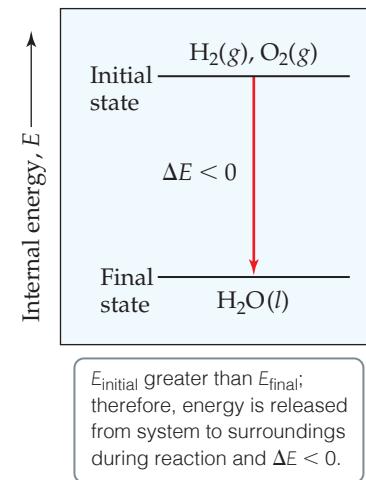
\*The symbol  $\Delta$  is commonly used to denote *change*. For example, a change in height, *h*, can be represented by  $\Delta h$ .

**Go Figure**What is the value of  $\Delta E$  if  $E_{\text{final}}$  equals  $E_{\text{initial}}$ ?

▲ Figure 5.5 Changes in internal energy.

**Go Figure**

Sketch the energy diagram representing the reaction  $\text{MgCl}_2(s) \rightarrow \text{Mg}(s) + \text{Cl}_2(g)$  knowing that the internal energy for a mixture of  $\text{Mg}(s)$  and  $\text{Cl}_2(g)$  is larger than that of  $\text{MgCl}_2(s)$ .

▲ Figure 5.6 Energy diagram for the reaction  $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l)$ .**Relating  $\Delta E$  to Heat and Work**

As we noted in Section 5.1, a system may exchange energy with its surroundings in two general ways: as heat or as work. The internal energy of a system changes in magnitude as heat is added to or removed from the system or as work is done on or by the system. If we think of internal energy as the system's bank account of energy, we see that deposits or withdrawals can be made in the form of either heat or work. Deposits increase the energy of the system (positive  $\Delta E$ ), whereas withdrawals decrease the energy of the system (negative  $\Delta E$ ).

We can use these ideas to write a useful algebraic expression of the first law of thermodynamics. When a system undergoes any chemical or physical change, the accompanying change in internal energy,  $\Delta E$ , is the sum of the heat added to or liberated from the system,  $q$ , and the work done on or by the system,  $w$ :

$$\Delta E = q + w \quad [5.4]$$

When heat is added to a system or work is done on a system, its internal energy increases. Therefore, when heat is transferred to the system from the surroundings,  $q$  has a positive value. Adding heat to the system is like making a deposit to the energy account—the energy of the system increases (Figure 5.7). Likewise, when work is done on the system by the surroundings,  $w$  has a positive value. Conversely, both the heat lost by the system to the surroundings and the work done by the system on the surroundings have negative values; that is, they lower the internal energy of the system. They are energy withdrawals and lower the amount of energy in the system's account.

The sign conventions for  $q$ ,  $w$ , and  $\Delta E$  are summarized in Table 5.1. Notice that any energy entering the system as either heat or work carries a positive sign.

**Sample Exercise 5.1****Relating Heat and Work to Changes of Internal Energy**

Gases A(g) and B(g) are confined in a cylinder-and-piston arrangement like that in Figure 5.4 and react to form a solid product C(s):  $\text{A}(g) + \text{B}(g) \rightarrow \text{C}(s)$ . As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

Continued

**SOLUTION**

**Analyze** The question asks us to determine  $\Delta E$ , given information about  $q$  and  $w$ .

**Plan** We first determine the signs of  $q$  and  $w$  (Table 5.1) and then use Equation 5.4,  $\Delta E = q + w$ , to calculate  $\Delta E$ .

**Solve** Heat is transferred from the system to the surroundings, and work is done on the system by the surroundings, so  $q$  is negative and  $w$  is positive:  $q = -1150\text{ J}$  and  $w = 480\text{ J}$ . Thus,

$$\Delta E = q + w = (-1150\text{ J}) + (480\text{ J}) = -670\text{ J}$$

The negative value of  $\Delta E$  tells us that a net quantity of 670 J of energy has been transferred from the system to the surroundings.

**Comment** You can think of this change as a decrease of 670 J in the net value of the system's energy bank account (hence, the negative sign); 1150 J is withdrawn in the form of heat, while 480 J is deposited in the form of work. Notice that as the volume of the gases decreases, work is being done *on* the system *by* the surroundings, resulting in a deposit of energy.

**► Practice Exercise**

A mixture of gases  $A_2$  and  $B_2$  are introduced to a slender metal cylinder that has one end closed and the other fitted with a piston that makes a gas-tight seal so that the gases are a closed system. The cylinder is submerged in a large beaker of water whose temperature is  $25^\circ\text{C}$ , and a spark is used to trigger a reaction in the cylinder. At the completion of the reaction, the piston has moved downward, and the temperature of the water bath has increased to  $28^\circ\text{C}$ . If we define the system as the gases inside the cylinder, which of the following best describes the signs of  $q$ ,  $w$ , and  $\Delta E$  for this reaction?

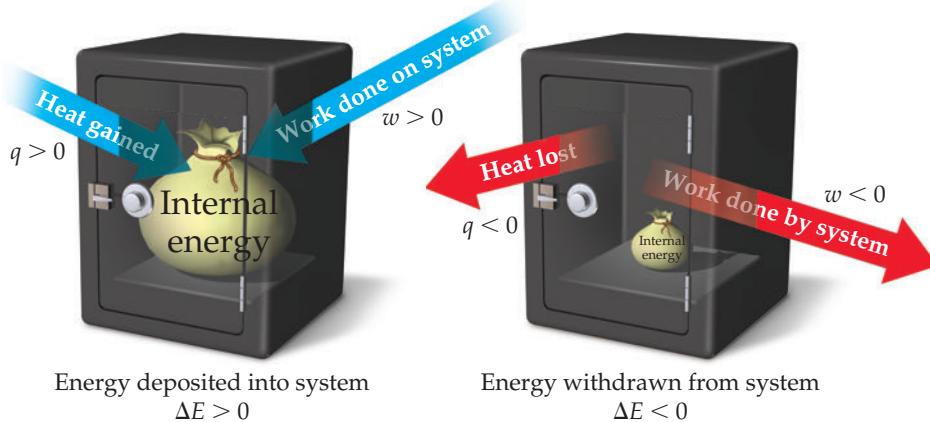
- (a)  $q < 0$ ,  $w < 0$ ,  $\Delta E < 0$
- (b)  $q < 0$ ,  $w > 0$ ,  $\Delta E < 0$
- (c)  $q < 0$ ,  $w > 0$ , the sign of  $\Delta E$  cannot be determined from the information given
- (d)  $q > 0$ ,  $w > 0$ ,  $\Delta E > 0$
- (e)  $q > 0$ ,  $w < 0$ , the sign of  $\Delta E$  cannot be determined from the information given

**Go Figure**

Suppose a system receives a “deposit” of 50 J of work from the surroundings and loses a “withdrawal” of 85 J of heat to the surroundings. What is the magnitude and the sign of  $\Delta E$  for this process?



System is interior of vault



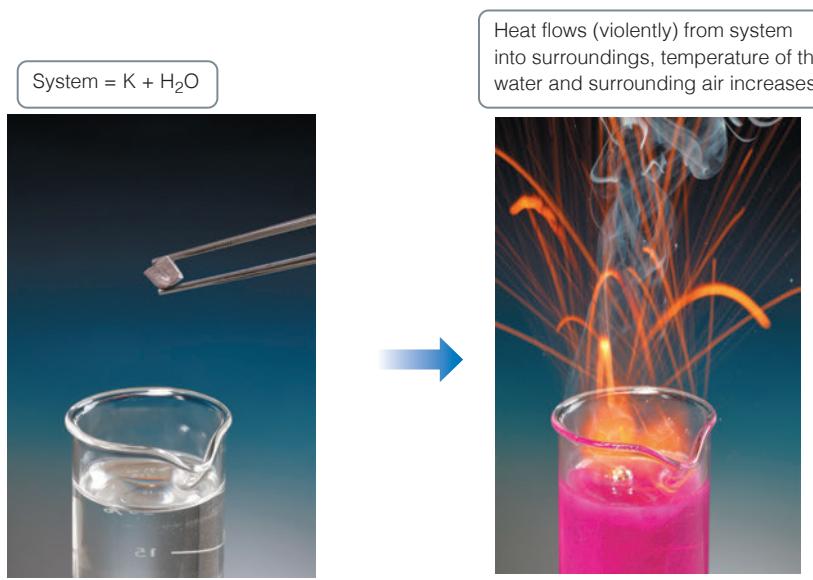
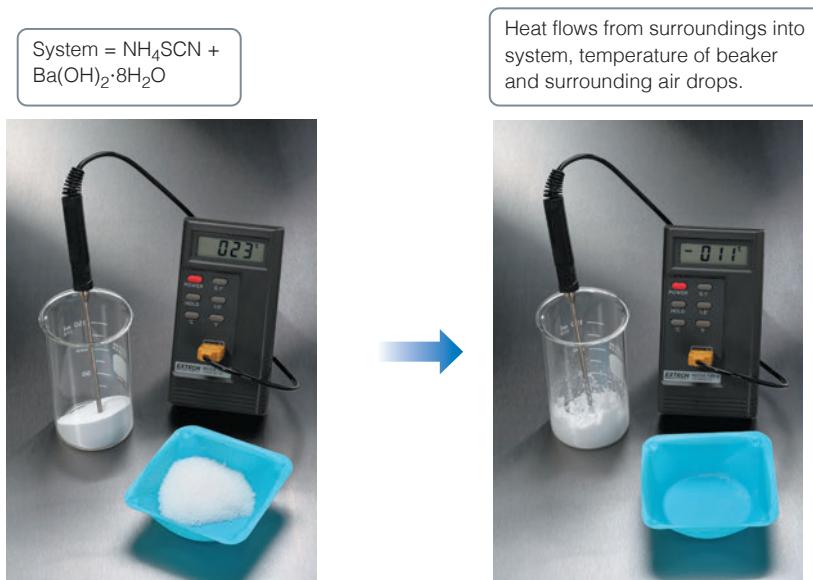
**▲ Figure 5.7** Sign conventions for heat and work. Heat,  $q$ , transferred into a system and work,  $w$ , done on a system are both positive quantities, corresponding to “deposits” of internal energy into the system. Conversely, heat transferred out of a system to the surroundings and work done by the system on the surroundings are both “withdrawals” of internal energy from the system.

**TABLE 5.1 Sign Conventions for  $q$ ,  $w$ , and  $\Delta E$** 

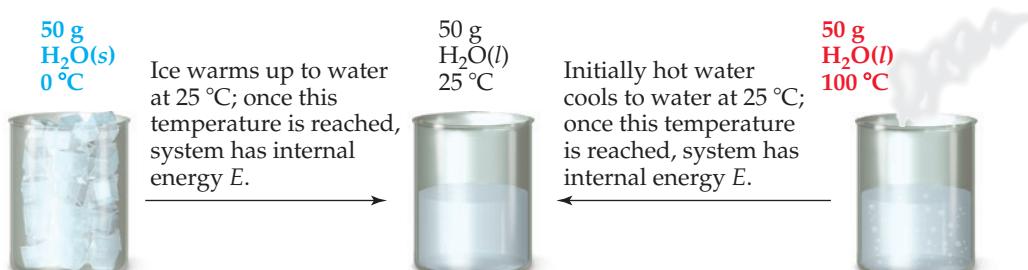
For $q$	+ means system <i>gains</i> heat	- means system <i>loses</i> heat
For $w$	+ means work done <i>on</i> system	- means work done <i>by</i> system
For $\Delta E$	+ means <i>net gain</i> of energy by system	- means <i>net loss</i> of energy by system

## Endothermic and Exothermic Processes

Because transfer of heat to and from the system is central to our discussion in this chapter, we have some special terminology to indicate the direction of transfer. When a process occurs in which the system absorbs heat, the process is called **endothermic** (*endo-* means “into”). During an endothermic process, such as the melting of ice, heat flows *into* the system from its surroundings [Figure 5.8(a)]. If we, as part of the surroundings, touch a container in which ice is melting, the container feels cold to us because heat has passed from our hand to the container.



◀ **Figure 5.8** Endothermic and exothermic reactions. In both instances, the system is defined as the reactants and products, while surroundings are the containers and everything else in the universe.



▲ **Figure 5.9 Internal energy,  $E$ , a state function.** Any state function depends only on the present state of the system and not on the path by which the system arrived at that state.

A process in which the system loses heat is called **exothermic** (*exo-* means “out of”). During an exothermic process, such as the combustion of gas, heat *exits* or flows *out of* the system into the surroundings [Figure 5.8(b)].

### State Functions

Although we usually have no way of knowing the precise value of the internal energy of a system,  $E$ , it does have a fixed value for a given set of conditions. The conditions that influence internal energy include the temperature and pressure. Furthermore, the internal energy of a system is proportional to the total quantity of matter in the system because energy is an extensive property.

Suppose we define our system as 50 g of water at 25 °C (Figure 5.9). The system could have reached this state by cooling 50 g of water from 100 to 25 °C or by melting 50 g of ice and subsequently warming the water to 25 °C. The internal energy of the water at 25 °C is the same in either case. Internal energy is an example of a **state function**, a property of a system that is determined by specifying the system’s condition, or state (in terms of temperature, pressure, and so forth). *The value of a state function depends only on the present state of the system, not on the path the system took to reach that state.* Because  $E$  is a state function,  $\Delta E$  depends only on the initial and final states of the system, not on how the change occurs.

An analogy may help you understand the difference between quantities that are state functions and those that are not. Suppose you drive from one city, which is 180 m above sea level, to another city, which is 1610 m above sea level. No matter which route you take, the altitude change is 1430 m. The distance you travel, however, depends on your route. Altitude is analogous to a state function because the change in altitude is independent of the path taken. Distance traveled is not a state function.

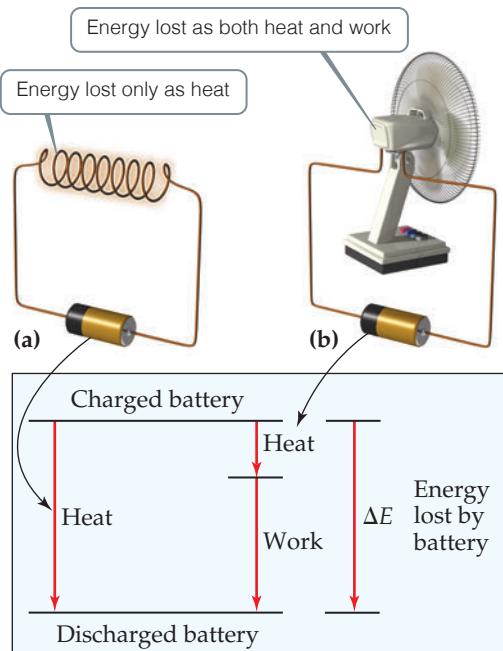
Some thermodynamic quantities, such as  $E$ , are state functions. Other quantities, such as  $q$  and  $w$ , are not. This means that, although  $\Delta E = q + w$  does not depend on how the change occurs, the specific amounts of heat and work depend on the way in which the change occurs. Thus, if changing the path by which a system goes from an initial state to a final state increases the value of  $q$ , that path change will also decrease the value of  $w$  by exactly the same amount. The result is that  $\Delta E$  is the same for the two paths.

We can illustrate this principle using a battery as our system. As the battery is discharged, its internal energy decreases as the energy stored in the battery is released to the surroundings. In Figure 5.10, we consider two possible ways of discharging the battery at constant temperature. In Figure 5.10(a), a wire shorts out the battery and no work is accomplished because nothing is moved against a force. All the energy lost from the battery is in the form of heat. (The wire gets warmer and releases heat to the surroundings.) In Figure 5.10(b), the battery is used to make a motor turn and the discharge produces work. Some heat is released, but not as much as when the battery is shorted out. We see that the magnitudes of  $q$  and  $w$  must be different for these two cases. If the initial and final states of the battery are identical in the two cases, however, then  $\Delta E = q + w$  must be the same in both cases because  $E$  is a state function. *Remember:  $\Delta E$  depends only on the initial and final states of the system, not on the specific path taken from the initial to the final state.*



### Go Figure

If the battery is defined as the system, what is the sign of  $w$  in part (b)?



▲ **Figure 5.10** Internal energy is a state function, but heat and work are not. (a) A battery shorted out by a wire loses energy to the surroundings only as heat; no work is performed. (b) A battery discharged through a motor loses energy as work (to make the fan turn) and also loses some energy as heat. The value of  $\Delta E$  is the same for both processes even though the values of  $q$  and  $w$  in (a) are different from those in (b).

## Self-Assessment Exercise

- 5.5 An aluminum can of a soft drink is placed in a freezer. Later, you find that the can is split open and its contents have frozen. Work was done on the can in splitting it open. Where did the energy for this work come from?

- (a) Freezing of water releases energy  
 (b) The cold temperature in the freezer provided the energy

## Exercises

- 5.6 (a) Which of the following cannot leave or enter a closed system: heat, work, or matter? (b) Which cannot leave or enter an isolated system? (c) What do we call the part of the universe that is not part of the system?
- 5.7 (a) According to the first law of thermodynamics, what quantity is conserved? (b) What is meant by the *internal energy* of a system? (c) By what means can the internal energy of a closed system increase?
- 5.8 Calculate  $\Delta E$  and determine whether the process is endothermic or exothermic for the following cases: (a)  $q = 0.763 \text{ kJ}$  and  $w = -840 \text{ J}$ . (b) A system releases  $66.1 \text{ kJ}$  of heat to its surroundings while the surroundings do  $44.0 \text{ kJ}$  of work on the system.
- 5.9 A gas is confined to a cylinder fitted with a piston and an electrical heater, as shown here:



Suppose that current is supplied to the heater so that 100 J of energy is added. Consider two different situations. In case (1) the piston is allowed to move as the energy is added. In case (2) the piston is fixed so that it cannot move. (a) In which case does the gas have the higher temperature after addition of the electrical energy? (b) Identify the sign (positive,

negative, or zero) of  $q$  and  $w$  in each case? (c) In which case is  $\Delta E$  for the system (the gas in the cylinder) larger?

- 5.10** (a) What is meant by the term *state function*? (b) Give an example of a quantity that is a state function and one that is not. (c) Is the volume of a system a state function? Why or why not?

5.4 (a)

ANSWERS TO SELF-ASSESSMENT EXERCISE



## 5.3 | Enthalpy



The reaction between aluminum metal and iron oxide produces aluminum oxide and iron metal. It also generates enough heat to melt the iron metal formed in the reaction. It can be used for welding railway lines and provides a convenient method of generating molten iron without the need of high temperature blow torches. The thermite reaction is a dramatic illustration of how potential energy stored in chemical bonds can be converted to heat.

By the end of this section, you should be able to

- Understand the relationship between enthalpy and heat in a chemical reaction.

The chemical and physical changes that occur around us, such as photosynthesis in the leaves of a plant, evaporation of water from a lake, or a reaction in an open beaker in a laboratory, occur under the essentially constant pressure of Earth's atmosphere.\* These changes can result in the release or absorption of heat and can be accompanied by work done by or on the system. In exploring these changes, it is useful to have a thermodynamic function that is a state function and relates mainly to heat flow. Under conditions of constant pressure, a thermodynamic quantity called **enthalpy** (from the Greek *enthalpein*, "to warm") provides such a function.

**Enthalpy**, which we denote by the symbol  $H$ , is defined as the internal energy plus the product of the *pressure*,  $P$ , and *volume*,  $V$ , of the system:

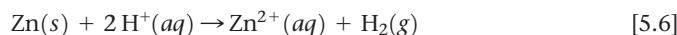
$$H = E + PV \quad [5.5]$$

\*You are probably familiar with the notion of atmospheric pressure from a previous course in chemistry. We will discuss it in detail in Chapter 10. Here we need realize only that the atmosphere exerts a pressure on the surface of Earth that is nearly constant.

Like internal energy  $E$ , both  $P$  and  $V$  are state functions—they depend only on the current state of the system and not on the path taken to that state. Because energy, pressure, and volume are all state functions, enthalpy is also a state function.

### Pressure–Volume Work

To better understand the significance of enthalpy, recall from Equation 5.4 that  $\Delta E$  involves not only the heat  $q$  added to or removed from the system but also the work  $w$  done by or on the system. Most commonly, the only kind of work produced by chemical or physical changes open to the atmosphere is the mechanical work associated with a change in volume. For example, when the reaction of zinc metal with hydrochloric acid solution



is run at constant pressure in the apparatus illustrated in **Figure 5.11**, the piston moves up or down to maintain a constant pressure in the vessel. If we assume for simplicity that the piston has no mass, the pressure in the apparatus is the same as atmospheric pressure. As the reaction proceeds,  $\text{H}_2$  gas forms, and the piston rises. The gas within the flask is thus doing work on the surroundings by lifting the piston against the force of atmospheric pressure.

The work involved in the expansion or compression of gases is called **pressure-volume work** ( $P\text{-}V$  work). When pressure is constant in a process, as in our preceding example, the sign and magnitude of the pressure–volume work are given by

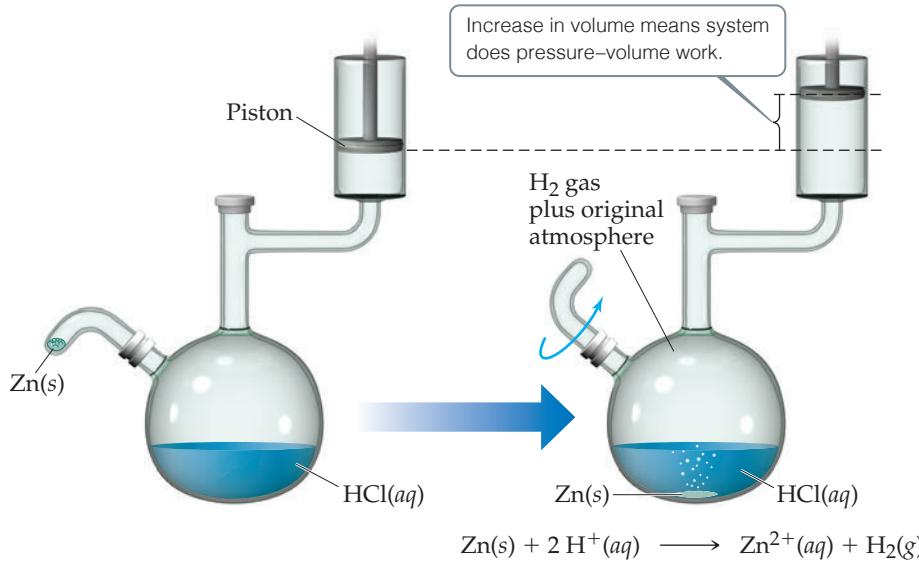
$$w = -P \Delta V \quad [5.7]$$

where  $P$  is pressure and  $\Delta V = V_{\text{final}} - V_{\text{initial}}$  is the change in volume of the system. The pressure  $P$  is always either a positive number or zero. If the volume of the system expands, then  $\Delta V$  is positive as well. The negative sign in Equation 5.7 is necessary to conform to the sign convention for  $w$  (Table 5.1). When a gas expands, the system does work on the surroundings, as indicated by a negative value of  $w$ . (The negative sign  $\times$  positive  $P \times$  positive  $\Delta V$  results in a negative number for  $w$ .) On the other hand, if the gas is compressed,  $\Delta V$  is negative (the volume decreases), and Equation 5.7 indicates that  $w$  is therefore positive, meaning work is done on the system by the surroundings. The box “A Closer Look: Energy, Enthalpy, and  $P\text{-}V$  Work” discusses pressure–volume work in detail, but all you need to keep in mind for now is Equation 5.7, which applies to processes occurring at constant pressure.



### Go Figure

If we define the system as the reactants and products, what is the sign of work in this process, positive or negative?



▲ **Figure 5.11** A system that does work on its surroundings.

The units of work obtained by using Equation 5.7 will be those of pressure (usually kPa) multiplied by those of volume (usually L). To express the work in the more familiar unit of joules, we use the conversion factor 1 L-kPa = 1 J.



## Sample Exercise 5.2

### Calculating Pressure-Volume Work

A fuel is burned in a cylinder equipped with a piston. The initial volume of the cylinder is 0.250 L, and the final volume is 0.980 L. If the piston expands against a constant pressure of 136.8 kPa, how much work (in J) is done?

#### SOLUTION

**Analyze** We are given an initial volume and a final volume from which we can calculate  $\Delta V$ . We are also given the pressure,  $P$ . We are asked to calculate work,  $w$ .

**Plan** The equation  $w = -P\Delta V$  allows us to calculate the work done by the system from the given information.

**Solve** The volume change is

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 0.980 \text{ L} - 0.250 \text{ L} = 0.730 \text{ L}$$

Thus, the quantity of work is

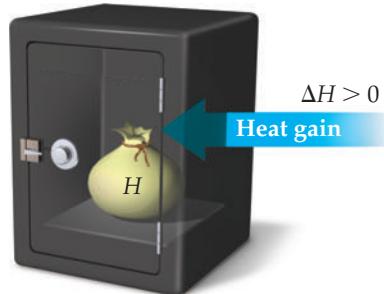
$$\begin{aligned} w &= -P\Delta V = -(136.8 \text{ kPa})(0.730 \text{ L}) = 99.8 \text{ L-kPa} \\ &= -99.8 \text{ J} \end{aligned}$$

**Check** The significant figures are correct (3), and the units are the requested ones for energy (J). The negative sign is consistent with an expanding gas doing work on its surroundings.

#### ► Practice Exercise

Calculate the work, in J, if the volume of a system contracts from 1.55 to 0.85 L at a constant pressure of 99.8 kPa.

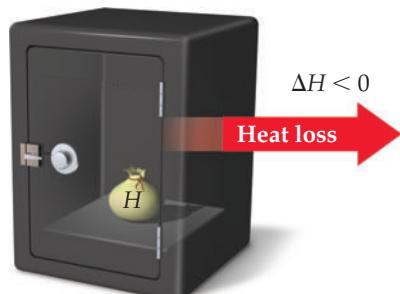
Constant pressure maintained in system



(a) An endothermic reaction

$$\Delta H > 0$$

Heat gain



(b) An exothermic reaction

$$\Delta H < 0$$

Heat loss

$\Delta H$  is amount of heat that flows into or out of system under constant pressure.

▲ **Figure 5.12** Endothermic and exothermic processes. (a) An endothermic process ( $\Delta H > 0$ ) deposits heat into the system. (b) An exothermic process ( $\Delta H < 0$ ) withdraws heat from the system.

## Enthalpy Change

Let's now return to our discussion of enthalpy. When a change occurs at constant pressure, the change in enthalpy,  $\Delta H$ , is given by the relationship

$$\begin{aligned} \Delta H &= \Delta(E + PV) \\ &= \Delta E + P\Delta V \quad (\text{constant pressure}) \end{aligned} \quad [5.8]$$

That is, the change in enthalpy equals the change in internal energy plus the product of the constant pressure and the change in volume.

Recall that  $\Delta E = q + w$  (Equation 5.4) and that the work involved in the expansion or compression of a gas is  $w = -P\Delta V$  (at constant pressure). Substituting  $-w$  for  $P\Delta V$  and  $q + w$  for  $\Delta E$  into Equation 5.8, we have

$$\Delta H = \Delta E + P\Delta V = (q_P + w) - w = q_P \quad [5.9]$$

The subscript  $P$  on  $q$  indicates that the process occurs at constant pressure. Thus, the equations show:

*The change in enthalpy equals the heat  $q_P$  gained or lost at constant pressure.*

Because  $q_P$  is something we can either measure or calculate and because so many physical and chemical changes of interest to us occur at constant pressure, enthalpy is a more useful function for most reactions than is internal energy. In addition, for most reactions the difference in  $\Delta H$  and  $\Delta E$  is small because  $P\Delta V$  is small.

When  $\Delta H$  is positive (that is, when  $q_P$  is positive), the system has gained heat from the surroundings (Table 5.1), which means the process is endothermic. When  $\Delta H$  is negative, the system has released heat to the surroundings, which means the process is exothermic. To continue the bank analogy of Figure 5.7, under constant pressure, an endothermic process deposits energy in the system in the form of heat and an exothermic process withdraws energy in the form of heat (Figure 5.12).

Because  $H$  is a state function,  $\Delta H$  (which equals  $q_P$ ) depends only on the initial and final states of the system, not on how the change occurs. At first glance this statement might seem to contradict our discussion in Section 5.2, in which we said that  $q$  is *not* a state function. There is no contradiction, however, because the relationship between  $\Delta H$  and  $q_P$  has special limitations that only  $P\text{-}V$  work is involved and that the pressure is constant.



## Sample Exercise 5.3

### Determining the Sign of $\Delta H$

Indicate the sign of the enthalpy change,  $\Delta H$ , in the following processes carried out under atmospheric pressure and indicate whether each process is endothermic or exothermic: (a) An ice cube melts; (b) 1 g of butane ( $C_4H_{10}$ ) is combusted in sufficient oxygen to give complete combustion to  $CO_2$  and  $H_2O$ .

### SOLUTION

**Analyze** Our goal is to determine whether  $\Delta H$  is positive or negative for each process. Because each process occurs at constant pressure, the enthalpy change equals the quantity of heat absorbed or released,  $\Delta H = q_p$ .

**Plan** We must predict whether heat is absorbed or released by the system in each process. Processes in which heat is absorbed are endothermic and have a positive sign for  $\Delta H$ ; those in which heat is released are exothermic and have a negative sign for  $\Delta H$ .

**Solve** In (a) the water that makes up the ice cube is the system. The ice cube absorbs heat from the surroundings as it melts, so  $\Delta H$  is

positive and the process is endothermic. In (b) the system is the 1 g of butane and the oxygen required to combust it. The combustion of butane in oxygen gives off heat, so  $\Delta H$  is negative and the process is exothermic.

### ► Practice Exercise

A chemical reaction that gives off heat to its surroundings is said to be \_\_\_\_\_ and has a \_\_\_\_\_ value of  $\Delta H$ .

- (a) endothermic, positive
- (b) endothermic, negative
- (c) exothermic, positive
- (d) exothermic, negative

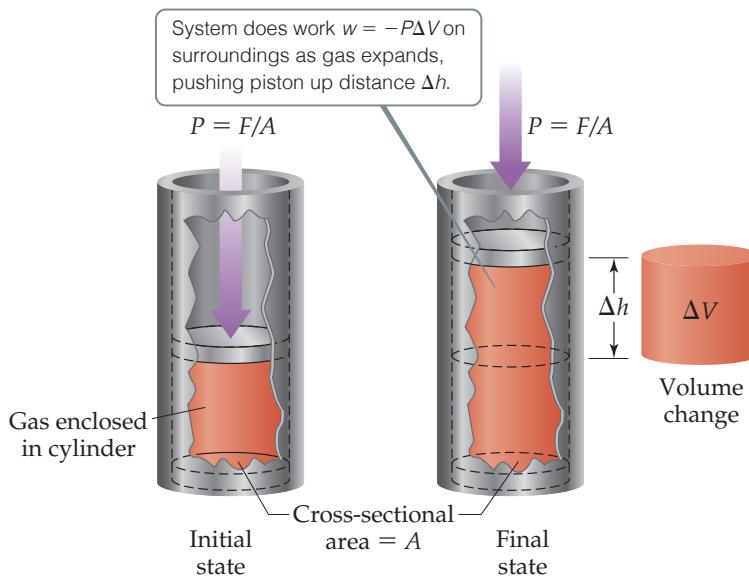
## A CLOSER LOOK Energy, Enthalpy, and P-V Work

In chemistry we are interested mainly in two types of work: electrical work and mechanical work done by expanding gases. We focus here on the latter, called pressure-volume, or *P-V*, work. Expanding gases in the cylinder of an automobile engine do *P-V* work on the piston; this work eventually turns the wheels. Expanding gases from an open reaction vessel do *P-V* work on the atmosphere. This work accomplishes nothing in a practical sense, but we must keep track of all work, useful or not, when monitoring energy changes in a system.

Let's consider a gas confined to a cylinder with a movable piston of cross-sectional area  $A$  (Figure 5.13). A downward force  $F$  acts on the piston. The pressure,  $P$ , on the gas is the force per area:  $P = F/A$ . We assume that the piston is massless and that the only pressure acting on it is the *atmospheric pressure* that is due to Earth's atmosphere, which we assume to be constant.

Suppose the gas expands and the piston moves a distance  $\Delta h$ . From Equation 5.1, the magnitude of the work done by the system is

$$\text{Magnitude of work} = \text{force} \times \text{distance} = F \times \Delta h \quad [5.10]$$



▲ Figure 5.13 Pressure-volume work. The amount of work done by the system on the surroundings is  $w = -P\Delta V$ .

We can rearrange the definition of pressure,  $P = F/A$ , to  $F = P \times A$ . The volume change,  $\Delta V$ , resulting from the movement of the piston is the product of the cross-sectional area of the piston and the distance it moves:  $\Delta V = A \times \Delta h$ . Substituting into Equation 5.10 gives

$$\begin{aligned} \text{Magnitude of work} &= F \times \Delta h = P \times A \times \Delta h \\ &= P \times \Delta V \end{aligned}$$

Because the system (the confined gas) does work on the surroundings, the work is a negative quantity:

$$w = -P\Delta V \quad [5.11]$$

Now, if *P-V* work is the only work that can be done, we can substitute Equation 5.11 into Equation 5.4 to give

$$\Delta E = q + w = q - P\Delta V \quad [5.12]$$

When a reaction is carried out in a constant-volume container ( $\Delta V = 0$ ), the heat transferred equals the change in internal energy:

$$\Delta E = q - P\Delta V = q - P(0) = q_V \quad (\text{constant volume}) \quad [5.13]$$

The subscript *V* indicates that the volume is constant.

Most reactions are run under constant pressure, so that Equation 5.12 becomes

$$\begin{aligned} \Delta E &= q_p - P\Delta V \\ q_p &= \Delta E + P\Delta V \quad (\text{constant pressure}) \end{aligned} \quad [5.14]$$

We see from Equation 5.8 that the right side of Equation 5.14 is the enthalpy change under constant-pressure conditions. Thus,  $\Delta H = q_p$ , as we saw in Equation 5.9.

In summary, the change in internal energy is equal to the heat gained or lost at constant volume, and the change in enthalpy is equal to the heat gained or lost at constant pressure. The difference between  $\Delta E$  and  $\Delta H$  is the amount of *P-V* work done by the system when the process occurs at constant pressure,  $-P\Delta V$ . The volume change accompanying many reactions is close to zero, which makes  $P\Delta V$  and, therefore, the difference between  $\Delta E$  and  $\Delta H$  small. Under most circumstances, it is generally satisfactory to use  $\Delta H$  as the measure of energy changes during most chemical processes.

**Related Exercises: 5.15, 5.73–5.75**

## Self-Assessment Exercise

**5.11** Enthalpy can be measured from heat flow under which of the following conditions?

- (a) constant pressure
- (b) constant volume

## Exercises

**5.12** During a deep breath, our lungs expand about 2.0 L against an external pressure of 101.3 kPa. How much work is involved in this process (in J)?

**5.13** (a) Why is the change in internal energy  $\Delta E$  usually harder to measure than the change in enthalpy  $\Delta H$ ? (b)  $E$  is a state

function, but  $q$  is not a state function. Explain. (c) For a given process at constant pressure,  $\Delta H$  is negative. Is the process endothermic or exothermic?

5.11 (a)

Answers to Self-Assessment Exercise

## 5.4 | Enthalpies of Reaction



The thermite reaction is spectacular as a lot of heat is generated from small quantities of solid reactants. In this section, we start to focus on the energy changes that accompany a chemical reaction and this provides us with an additional depth of understanding of the process under study.

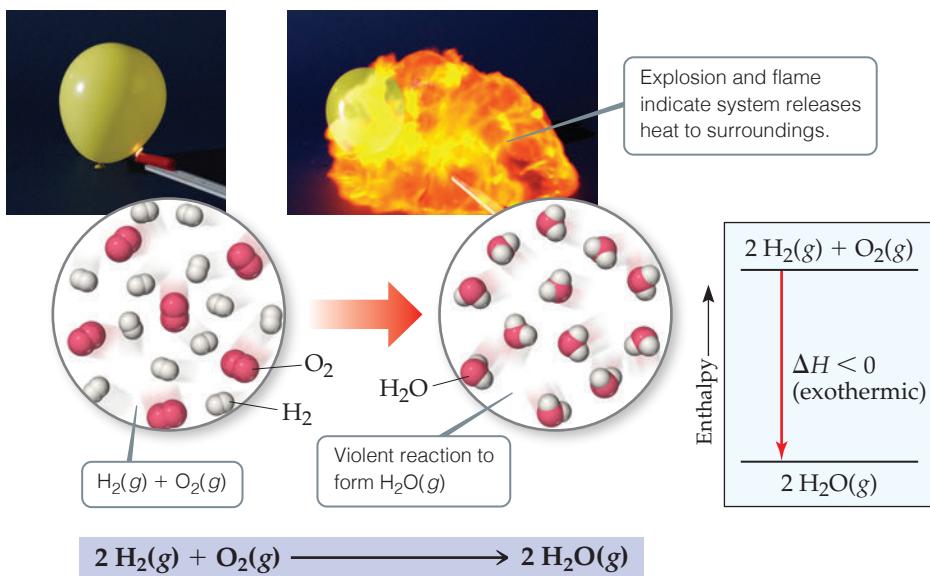
By the end of this section, you should be able to

- Use thermochemical equations to relate the amount of heat energy transferred in reactions at constant pressure  $\Delta H$  to the amount of substance involved in the reaction.

Because  $\Delta H = H_{\text{final}} - H_{\text{initial}}$ , the enthalpy change for a chemical reaction is given by

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad [5.15]$$

The enthalpy change that accompanies a reaction is called either the **enthalpy of reaction** or the *heat of reaction* and is sometimes written  $\Delta H_{\text{rxn}}$ , where “rxn” is a commonly used abbreviation for “reaction.”



When we give a numerical value for  $\Delta H_{\text{rxn}}$ , we must specify the reaction involved. For example, when 2 mol  $\text{H}_2(\text{g})$  burn to form 2 mol  $\text{H}_2\text{O}(\text{g})$  at a constant pressure, the system releases 483.6 kJ of heat. We can summarize this information as

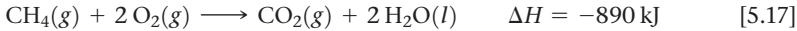


The negative sign for  $\Delta H$  tells us that this reaction is exothermic. Notice that  $\Delta H$  is reported at the end of the balanced equation, without explicitly specifying the amounts of chemicals involved. In such cases the coefficients in the balanced equation represent the number of moles of reactants and products producing the associated enthalpy change. Balanced chemical equations that show the associated enthalpy change in this way are called *thermochemical equations*.

The exothermic nature of this reaction is also shown in the *enthalpy diagram* in Figure 5.14. Notice that the enthalpy of the reactants is greater (more positive) than the enthalpy of the products. Thus,  $\Delta H = H_{\text{products}} - H_{\text{reactants}}$  is negative.

The following guidelines are helpful when using thermochemical equations and enthalpy diagrams:

- 1. Enthalpy is an extensive property.** The magnitude of  $\Delta H$  is proportional to the amount of reactant consumed in the process. For example, 890 kJ of heat is produced when 1 mol of  $\text{CH}_4$  is burned in a constant-pressure system:



Because the combustion of 1 mol of  $\text{CH}_4$  with 2 mol of  $\text{O}_2$  releases 890 kJ of heat, the combustion of 2 mol of  $\text{CH}_4$  with 4 mol of  $\text{O}_2$  releases twice as much heat, 1780 kJ. Although chemical equations are usually written with whole-number coefficients, thermochemical equations sometimes utilize fractions, as in the preceding Give It Some Thought question.

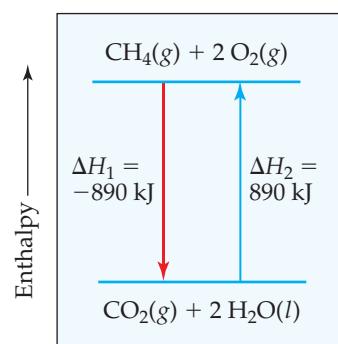
- 2. The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to  $\Delta H$  for the reverse reaction.** For example,  $\Delta H$  for the reverse of Equation 5.17 is +890 kJ:



When we reverse a reaction, we reverse the roles of the products and the reactants. From Equation 5.15, we see that reversing the products and reactants leads to the same magnitude of  $\Delta H$ , but a change in sign (Figure 5.15).

- 3. The enthalpy change for a reaction depends on the states of the reactants and products.** If the product in Equation 5.17 were  $\text{H}_2\text{O}(\text{g})$  instead of  $\text{H}_2\text{O}(\text{l})$ ,  $\Delta H_{\text{rxn}}$  would be  $-802 \text{ kJ}$  instead of  $-890 \text{ kJ}$ . Less heat would be available for

◀ **Figure 5.14** Exothermic reaction of hydrogen with oxygen. When a mixture of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is ignited to form  $\text{H}_2\text{O}(\text{g})$ , the resultant explosion produces a ball of flame. Because the system releases heat to the surroundings, the reaction is exothermic as indicated in the enthalpy diagram.



▲ **Figure 5.15**  $\Delta H$  for a reverse reaction. Reversing a reaction changes the sign but not the magnitude of the enthalpy change:  $\Delta H_2 = -\Delta H_1$ .

transfer to the surroundings because the enthalpy of  $\text{H}_2\text{O}(g)$  is greater than that of  $\text{H}_2\text{O}(l)$ . One way to see this is to imagine that the product is initially liquid water. The liquid water must be converted to water vapor, and the conversion of 2 mol  $\text{H}_2\text{O}(l)$  to 2 mol  $\text{H}_2\text{O}(g)$  is an endothermic process that absorbs 88 kJ:



Thus, it is important to specify the states of the reactants and products in thermochemical equations. In addition, we will generally assume that the reactants and products are both at the same temperature, 25 °C, unless otherwise indicated.

## Sample Exercise 5.4

### Relating $\Delta H$ to Quantities of Reactants and Products

How much heat is released when 4.50 g of methane gas is burned in a constant-pressure system? (Use the information given in Equation 5.17.)

#### SOLUTION

**Analyze** Our goal is to use a thermochemical equation to calculate the heat produced when a specific amount of methane gas is combusted. According to Equation 5.17, 890 kJ is released by the system when 1 mol  $\text{CH}_4$  is burned at constant pressure.

#### Solve

The conversion sequence is:



By adding the atomic weights of C and 4 H, we have

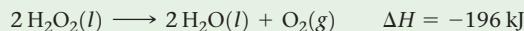
1 mol  $\text{CH}_4$  = 16.0  $\text{CH}_4$ . We can use the appropriate conversion factors to convert grams of  $\text{CH}_4$  to moles of  $\text{CH}_4$  to kilojoules:

$$\text{Heat} = (4.50 \text{ g } \text{CH}_4) \left( \frac{1 \text{ mol } \text{CH}_4}{16.0 \text{ g } \text{CH}_4} \right) \left( \frac{-890 \text{ kJ}}{1 \text{ mol } \text{CH}_4} \right) = -250 \text{ kJ}$$

The negative sign indicates that the system released 250 kJ into the surroundings.

#### ► Practice Exercise

Hydrogen peroxide can decompose to water and oxygen by the reaction



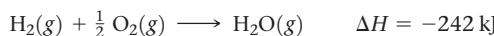
Calculate the quantity of heat released when 5.00 g of  $\text{H}_2\text{O}_2(l)$  decomposes at constant pressure.

## A CLOSER LOOK Using Enthalpy as a Guide

If you hold a brick in the air and let it go, you know what happens: It falls as the force of gravity pulls it toward Earth. A process that is thermodynamically favored to happen, such as a brick falling to the ground, is called a *spontaneous* process. A spontaneous process can be either fast or slow; the rate at which processes occur is not governed by thermodynamics.

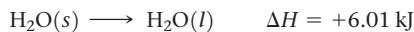
Chemical processes can be thermodynamically favored, or spontaneous, too. By spontaneous, however, we do not mean that the reaction will form products without any intervention. That can be the case, but often some energy must be imparted to get the process started. Just as it is spontaneous for a rock to roll down the side of a hill once started, so too can it be spontaneous for chemical reactions to proceed once enough energy is imparted to initiate the

reaction (Figure 5.16). The enthalpy change in a reaction gives one indication as to whether the reaction is likely to be spontaneous. The combustion of  $\text{H}_2(g)$  and  $\text{O}_2(g)$ , for example, is highly exothermic:



Hydrogen gas and oxygen gas can exist together in a volume indefinitely without noticeable reaction occurring. Once the reaction is initiated, however, energy is rapidly transferred from the system (the reactants) to the surroundings as heat. The system thus loses enthalpy by transferring the heat to the surroundings. (Recall that the first law of thermodynamics tells us that the total energy of the system plus the surroundings does not change; energy is conserved.)

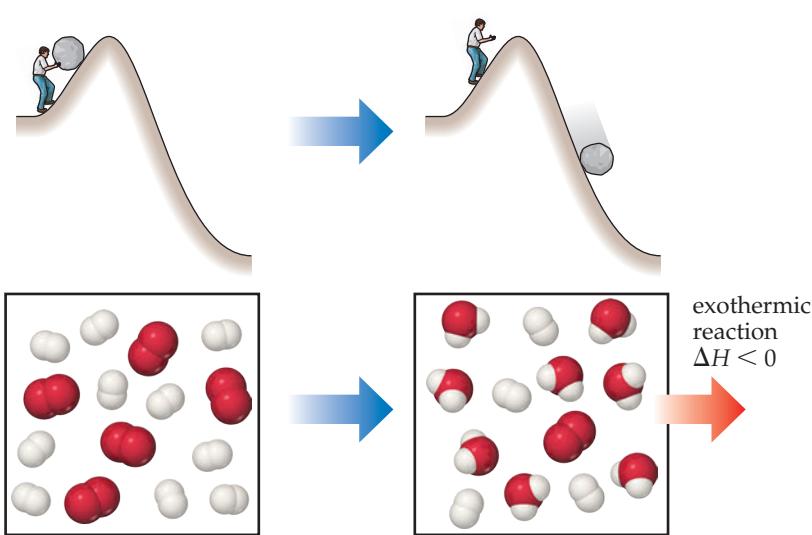
Enthalpy change is not the only consideration in the spontaneity of reactions, nor is it a foolproof guide. For example, even though ice melting is an endothermic process,



this process is spontaneous at temperatures above the freezing point of water ( $0^\circ\text{C}$ ). The reverse process, water freezing, is spontaneous at temperatures below  $0^\circ\text{C}$ . Thus, we know that ice at room temperature melts and water put into a freezer at  $-20^\circ\text{C}$  turns into ice. Both processes are spontaneous under different conditions even though they are the reverse of one another. In Chapter 19, we will address the spontaneity of processes more fully. We will see why a process can be spontaneous at one temperature but not at another, as is the case for the conversion of water to ice.

Despite these complicating factors, you should pay attention to the enthalpy changes in reactions. As a general observation, when the enthalpy change is large, it is the dominant factor in determining spontaneity. Thus, reactions for which  $\Delta H$  is *large* (about 100 kJ or more) and *negative* tend to be spontaneous. Reactions for which  $\Delta H$  is *large* and *positive* tend to be spontaneous only in the reverse direction.

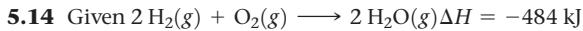
**Related Exercises:** 5.20, 5.80



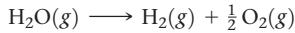
**▲ Figure 5.16 Exothermic reactions and spontaneity.** Chemical reactions that are highly exothermic ( $\Delta H$  much less than 0) usually occur spontaneously. Such reactions often need some input of energy to get started, just like it can take a push to get a boulder rolling down a hill to a spot of lower potential energy. However, once they get started, such reactions spontaneously proceed to form the products, which have lower potential energy.

In many situations, we will find it valuable to know the sign and magnitude of the enthalpy change associated with a given chemical process. As we see in the following sections,  $\Delta H$  can be either determined directly by experiment or calculated from known enthalpy changes of other reactions.

## Self-Assessment Exercise



What is the enthalpy change for the formation of hydrogen and oxygen from one mole of steam?



(a)  $\Delta H = +242 \text{ kJ}$

(b)  $\Delta H = +484 \text{ kJ}$

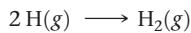
(c)  $\Delta H = +968 \text{ kJ}$

## Exercises

**5.15** A gas is confined to a cylinder under constant atmospheric pressure, as illustrated in Figure 5.4. When the gas undergoes a particular chemical reaction, it absorbs 824 J of heat from its surroundings and has 0.65 kJ of  $PV$  work done on it by its surroundings. What are the values of  $\Delta H$  and  $\Delta E$  for this process?

**5.16** The complete combustion of methane,  $\text{CH}_4(g)$ , to form  $\text{H}_2\text{O}(l)$  and  $\text{CO}_2(g)$  at constant pressure releases 890 kJ of heat per mole of  $\text{CH}_4$ . (a) Write a balanced thermochemical equation for this reaction. (b) Draw an enthalpy diagram for the reaction.

**5.17** Atomic hydrogen ( $\text{H}$ ) is used in welding (AHW). The atoms recombine to hydrogen molecules with a large release of heat according to the following reaction:



(a) Using the thermodynamic data in Appendix C, calculate the enthalpy change for this reaction per mole of  $\text{H}_2$ .

(b) Which has the higher enthalpy under these conditions,  $2 \text{H}(g)$  or  $\text{H}_2(g)$ ?

**5.18** Consider the following reaction:



(a) Is this reaction exothermic or endothermic?

(b) Calculate the amount of heat transferred when 3.55 g of  $\text{Mg}(s)$  reacts at constant pressure.

(c) How many grams of  $\text{MgO}$  are produced during an enthalpy change of  $-234 \text{ kJ}$ ?

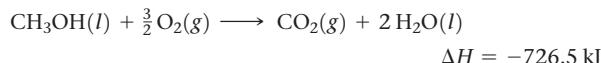
(d) How many kilojoules of heat are absorbed when 40.3 g of  $\text{MgO}(s)$  is decomposed into  $\text{Mg}(s)$  and  $\text{O}_2(g)$  at constant pressure?

- 5.19** When solutions containing silver ions and chloride ions are mixed, silver chloride precipitates



(a) Calculate  $\Delta H$  for the production of 0.450 mol of AgCl by this reaction. (b) Calculate  $\Delta H$  for the production of 9.00 g of AgCl. (c) Calculate  $\Delta H$  when  $9.25 \times 10^{-4}$  mol of AgCl dissolves in water.

- 5.20** Consider the combustion of liquid methanol,  $\text{CH}_3\text{OH}(l)$ :



- (a) What is the enthalpy change for the reverse reaction? (b) Balance the forward reaction with whole-number coefficients. What is  $\Delta H$  for the reaction represented by this equation? (c) Which is more likely to be thermodynamically favored, the forward reaction or the reverse reaction? (d) If the reaction were written to produce  $\text{H}_2\text{O}(g)$  instead of  $\text{H}_2\text{O}(l)$ , would you expect the magnitude of  $\Delta H$  to increase, decrease, or stay the same? Explain.

5.14 (a)

Answers to Self-Assessment Exercise



## 5.5 | Calorimetry



The word *thermometer* comes from the Greek words ‘thermos’ meaning hot, and ‘metron’ meaning measure. Early instruments that attempted to measure temperature utilized an air bubble trapped in a glass tube closed at one end and dipped into water at the other end. As the temperature changed, the volume of the trapped air changed. However, this was also subject to changes in atmospheric pressure. The first reliable thermometer was invented in 1714 by Daniel Gabriel Fahrenheit, who employed a sealed tube—to avoid the effects of changing atmospheric pressures—and the high coefficient of expansion of mercury to translate temperature changes to the visible movement of the mercury along the tube. Fahrenheit is remembered with a monument in the city of his birth, Gdansk, Poland, but lived most of his life in the Dutch Republic. He also suggested a scale for temperature, which bears his name.

Nowadays, we have many different devices that measure temperature and the use of mercury in thermometers is diminishing. While the use of the Celsius scale is widespread, it is not yet universal with some countries still recording, for example, weather temperatures in Fahrenheit.

By the end of this section, you should be able to

- Calculate the heat transferred in a process from temperature measurements together with heat capacities or specific heats

The value of  $\Delta H$  can be determined experimentally by measuring the heat flow accompanying a reaction at constant pressure. Typically, we can determine the magnitude of the heat flow by measuring the magnitude of the temperature change the heat flow produces. The measurement of heat flow is **calorimetry**; a device used to measure heat flow is a **calorimeter**.

## Heat Capacity and Specific Heat

The more heat an object gains, the hotter it gets. All substances change temperature when they are heated, but the magnitude of the temperature change produced by a given quantity of heat varies from substance to substance. The temperature change experienced by an object when it absorbs a certain amount of heat is determined by its **heat capacity**, denoted  $C$ . The heat capacity of an object is the amount of heat required to raise its temperature by 1 K (or 1 °C). The greater the heat capacity, the greater the heat required to produce a given increase in temperature.

For pure substances the heat capacity is usually given for a specified amount of the substance. The heat capacity of one mole of a substance is called its **molar heat capacity**,  $C_m$ . The heat capacity of one gram of a substance is called its *specific heat capacity*, or merely its **specific heat**,  $c$ . The specific heat,  $c$ , of a substance can be determined experimentally by measuring the temperature change,  $\Delta T$ , that a known mass  $m$  of the substance undergoes when it gains or loses a specific quantity of heat  $q$ :

$$\text{Specific heat} = \frac{\text{(quantity of heat transferred)}}{\text{(grams of substance)} \times \text{(temperature change)}}$$

$$c = \frac{q}{m \times \Delta T} \quad [5.20]$$

For example, 209 J is required to increase the temperature of 50.0 g of water by 1.00 K. Thus, the specific heat of water is

$$c = \frac{209 \text{ J}}{(50.0 \text{ g})(1.00 \text{ K})} = 4.18 \text{ J/g K}$$

Notice how the units combine in the calculation. A temperature change in kelvins is equal in magnitude to the temperature change in degrees Celsius:  $\Delta T$  in K =  $\Delta T$  in °C. Therefore, this specific heat for water can also be reported as 4.18 J/g °C, where the unit is pronounced “Joules per gram-degree Celsius.”

Because the specific heat values for a given substance can vary slightly with temperature, the temperature is often precisely specified. The 4.18 J/g K value we use here for water, for instance, is for water initially at 14.5 °C (Figure 5.17). Water’s specific heat at this temperature is used to define the calorie: 1 cal = 4.184 J exactly.

When a sample absorbs heat (positive  $q$ ), its temperature increases (positive  $\Delta T$ ). Rearranging Equation 5.20, we get

$$q = C_s \times m \times \Delta T \quad [5.21]$$

Thus, we can calculate the quantity of heat a substance gains or loses by using its specific heat together with its measured mass and temperature change.

**Table 5.2** lists the specific heats of several substances. Notice that the specific heat of liquid water is higher than those of the other substances listed. The high specific heat of water affects Earth’s climate because it makes the temperatures of the oceans relatively resistant to change.

**TABLE 5.2 Specific Heats of Some Substances at 298 K**

Elements		Compounds	
Substance	Specific Heat (J/g K)	Substance	Specific Heat (J/g K)
N <sub>2</sub> (g)	1.04	H <sub>2</sub> O(l)	4.18
Al(s)	0.90	CH <sub>4</sub> (g)	2.20
Fe(s)	0.45	CO <sub>2</sub> (g)	0.84
Hg(l)	0.14	CaCO <sub>3</sub> (s)	0.82

### Go Figure

Is the process shown in the figure endothermic or exothermic?

1.000 g H<sub>2</sub>O(l)  
 $T_{\text{final}} = 15.5 \text{ }^{\circ}\text{C}$

+ 4.184 J (1 cal)  
of heat

1.000 g H<sub>2</sub>O(l)  
 $T_{\text{initial}} = 14.5 \text{ }^{\circ}\text{C}$

▲ Figure 5.17 Specific heat of water.



## Sample Exercise 5.5

### Relating Heat, Temperature Change, and Heat Capacity

- (a) How much heat is needed to warm 250 g of water (about 1 cup) from 22 °C (about room temperature) to 98 °C (near its boiling point)? (b) What is the molar heat capacity of water?

#### SOLUTION

**Analyze** In part (a) we must find the quantity of heat ( $q$ ) needed to warm the water, given the mass of water ( $m$ ), its temperature change ( $\Delta T$ ), and its specific heat ( $c$ ). In part (b) we must calculate the molar heat capacity (heat capacity per mole,  $C_m$ ) of water from its specific heat (heat capacity per gram).

#### Solve

- (a) The water undergoes a temperature change of:

**Plan** (a) Given  $c$ ,  $m$ , and  $\Delta T$ , we can calculate the quantity of heat,  $q$ , using Equation 5.21. (b) We can use the molar mass of water and dimensional analysis to convert from heat capacity per gram to heat capacity per mole.

Using Equation 5.21, we have:

$$\Delta T = 98^\circ\text{C} - 22^\circ\text{C} = 76^\circ\text{C} = 76\text{ K}$$

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

$$= (4.18\text{ J/g K})(250\text{ g})(76\text{ K}) = 7.9 \times 10^4\text{ J}$$

- (b) The molar heat capacity is the heat capacity of one mole of substance. Using the atomic weights of hydrogen and oxygen, we have:

$$1\text{ mol H}_2\text{O} = 18.0\text{ g H}_2\text{O}$$

From the specific heat used in part (a), we have:

$$C_m = \left(4.18 \frac{\text{J}}{\text{g K}}\right) \left(\frac{18.0\text{ g}}{1\text{ mol}}\right) = 75.2\text{ J/mol-K}$$

#### ► Practice Exercise

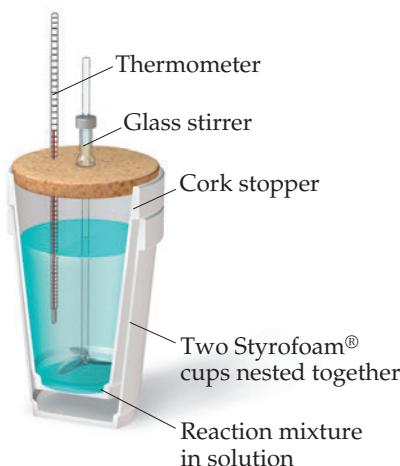
- (a) Large beds of rocks are used in some solar-heated homes to store heat. Assume that the specific heat of the rocks is 0.82 J/g K. Calculate the quantity of heat absorbed by

50.0 kg of rocks if their temperature increases by 12.0 °C.

- (b) What temperature change would these rocks undergo if they emitted 450 kJ of heat?

#### Go Figure

Why do you think two Styrofoam® cups are often used instead of just one.



**▲ Figure 5.18** Coffee-cup calorimeter.  
This simple apparatus is used to measure temperature changes of reactions at constant pressure.

### Constant-Pressure Calorimetry

The techniques and equipment employed in calorimetry depend on the nature of the process being studied. For many reactions, such as those occurring in solution, it is easy to control pressure so that  $\Delta H$  is measured directly. Although the calorimeters used for highly accurate work are precision instruments, a simple “coffee-cup” calorimeter (Figure 5.18) is often used in general chemistry laboratories to illustrate the principles of calorimetry. Because the calorimeter is not sealed, the reaction occurs under the essentially constant pressure of the atmosphere.

Imagine adding two aqueous solutions, each containing a reactant, to a coffee-cup calorimeter. Once mixed, a reaction occurs. In this case, there is no physical boundary between the system and the surroundings. The reactants and products of the reaction are the system, and the water in which they are dissolved is part of the surroundings. (The calorimeter apparatus is also part of the surroundings.) If we assume that the calorimeter is perfectly insulated, then any heat released or absorbed by the reaction will raise or lower the temperature of the water in the solution. Thus, we measure the temperature change of the solution and assume that any changes are due to heat transferred from the reaction to the water (for an exothermic process) or transferred from the water to the reaction (endothermic). In other words, by monitoring the temperature of the solution, we are seeing the flow of heat between the system (the reactants and products in the solution) and the surroundings (the water that forms the bulk of the solution).

For an exothermic reaction, heat is “lost” by the reaction and “gained” by the water in the solution, so the temperature of the solution rises. The opposite occurs for an

endothermic reaction: Heat is gained by the reaction and lost by the water in the solution, and the temperature of the solution decreases. The heat gained or lost by the solution,  $q_{\text{soln}}$ , is therefore equal in magnitude but opposite in sign to the heat absorbed or released by the reaction,  $q_{\text{rxn}}$ , in mathematical terms  $q_{\text{soln}} = -q_{\text{rxn}}$ . The value of  $q_{\text{soln}}$  is readily calculated from the mass of the solution, its specific heat, and the temperature change:

$$q_{\text{soln}} = (\text{specific heat of solution}) \times (\text{grams of solution}) \times \Delta T = -q_{\text{rxn}} \quad [5.22]$$

For dilute aqueous solutions we usually assume that the specific heat of the solution is the same as that of water, 4.18 J/g K.

Equation 5.22 makes it possible to calculate  $q_{\text{rxn}}$  from the temperature change of the solution in which the reaction occurs. A temperature increase ( $\Delta T > 0$ ) means the reaction is exothermic ( $q_{\text{rxn}} < 0$ ).

## Sample Exercise 5.6

### Measuring $\Delta H$ Using a Coffee-Cup Calorimeter



When a student mixes 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 to 27.5 °C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/mL, and that its specific heat is 4.18 J/g K.

### SOLUTION

**Analyze** Mixing solutions of HCl and NaOH results in an acid-base reaction:



We need to calculate the heat produced per mole of HCl, given the temperature increase of the solution, the number of moles of HCl and NaOH involved, and the density and specific heat of the solution.

**Plan** The total heat produced can be calculated using Equation 5.22. The number of moles of HCl consumed in the reaction must be calculated from the volume and molarity of this substance, and this amount is then used to determine the heat produced per mol HCl.

### Solve

Because the total volume of the solution is 100 mL, its mass is:

$$(100 \text{ mL})(1.0 \text{ g/mL}) = 100 \text{ g}$$

The temperature change is:

$$\Delta T = 27.5^\circ\text{C} - 21.0^\circ\text{C} = 6.5^\circ\text{C} = 6.5 \text{ K}$$

Using Equation 5.22, we have:

$$q_{\text{rxn}} = -c \times m \times \Delta T$$

$$= -(4.18 \text{ J/g K})(100 \text{ g})(6.5 \text{ K}) = -2.7 \times 10^3 \text{ J} = -2.7 \text{ kJ}$$

Because the process occurs at constant pressure,

$$\Delta H = q_p = -2.7 \text{ kJ}$$

To express the enthalpy change on a molar basis, we use the fact that the number of moles of HCl is given by the product of the volume (50 mL = 0.050 L) and concentration (1.0 M = 1.0 mol/L) of the HCl solution:

$$(0.050 \text{ L})(1.0 \text{ mol/L}) = 0.050 \text{ mol}$$

Thus, the enthalpy change per mole of HCl is:

$$\Delta H = -2.7 \text{ kJ}/0.050 \text{ mol} = -54 \text{ kJ/mol}$$

**Check**  $\Delta H$  is negative (exothermic), as evidenced by the observed increase in the temperature. The magnitude of the molar enthalpy change seems reasonable.

of the mixture increases from 22.30 to 23.11 °C. The temperature increase is caused by the following reaction:



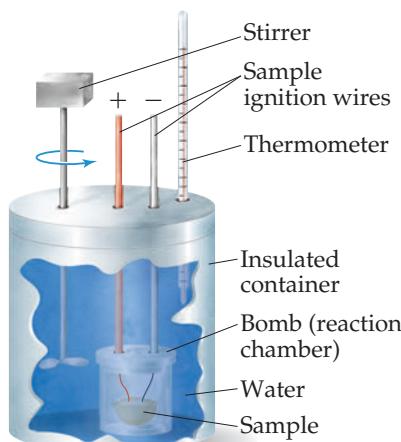
When 50.0 mL of 0.100 M AgNO<sub>3</sub> and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature

Calculate  $\Delta H$  for this reaction in kJ/mol AgNO<sub>3</sub>, assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g·°C.

### ► Practice Exercise

 Go Figure

Is the water surrounding the reaction chamber part of the system or the surroundings?



▲ Figure 5.19 Bomb calorimeter.

## Bomb Calorimetry (Constant-Volume Calorimetry)

An important type of reaction studied using calorimetry is combustion, in which a compound reacts completely with excess oxygen. (Section 3.2) Combustion reactions are most accurately studied using a **bomb calorimeter** (Figure 5.19). The substance to be studied is placed in a small cup within an insulated sealed vessel called a *bomb*. The bomb, which is designed to withstand high pressures, has an inlet valve for adding oxygen and electrical leads for initiating the reaction. After the sample has been placed in the bomb, the bomb is sealed and pressurized with oxygen. It is then placed in the calorimeter and covered with an accurately measured quantity of water. The combustion reaction is initiated by passing an electrical current through a fine wire in contact with the sample. When the wire becomes sufficiently hot, the sample ignites.

The heat released when combustion occurs is absorbed by the water and the various components of the calorimeter (which all together make up the surroundings), causing the water temperature to rise. The change in water temperature caused by the reaction is measured very precisely.

To calculate the heat of combustion from the measured temperature increase, we must know the total heat capacity of the calorimeter,  $C_{\text{cal}}$ . This quantity is determined by combusting a sample that releases a known quantity of heat and measuring the temperature change. For example, combustion of exactly 1 g of benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , in a bomb calorimeter produces 26.38 kJ of heat. Suppose 1.000 g of benzoic acid is combusted in a calorimeter, leading to a temperature increase of  $4.857^\circ\text{C}$ . The heat capacity of the calorimeter is then  $C_{\text{cal}} = 26.38 \text{ kJ}/4.857^\circ\text{C} = 5.431 \text{ kJ}/^\circ\text{C}$ . Once we know  $C_{\text{cal}}$ , we can measure temperature changes produced by other reactions, and from these we can calculate the heat evolved in the reaction,  $q_{\text{rxn}}$ :

$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T \quad [5.23]$$

Because reactions in a bomb calorimeter are carried out at constant volume, the heat transferred corresponds to the change in internal energy,  $\Delta E$ , rather than the change in enthalpy,  $\Delta H$  (Equation 5.13). For most reactions, however, the difference between  $\Delta E$  and  $\Delta H$  is very small. For the reaction discussed in Sample Exercise 5.7, for example, the difference between  $\Delta E$  and  $\Delta H$  is about 1 kJ/mol—a difference of less than 0.1%. It is possible to calculate  $\Delta H$  from  $\Delta E$ , but we need not concern ourselves with how these small corrections are made.



### Sample Exercise 5.7

#### Measuring $q_{\text{rxn}}$ Using a Bomb Calorimeter



The combustion of methylhydrazine ( $\text{CH}_6\text{N}_2$ ), a liquid rocket fuel, produces  $\text{N}_2(g)$ ,  $\text{CO}_2(g)$ , and  $\text{H}_2\text{O}(l)$ :



When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 to  $39.50^\circ\text{C}$ . In a separate experiment the heat capacity of the calorimeter is measured to be  $7.794 \text{ kJ}/^\circ\text{C}$ . Calculate the heat of reaction for the combustion of a mole of  $\text{CH}_6\text{N}_2$ .

#### SOLUTION

**Analyze** We are given a temperature change and the total heat capacity of the calorimeter. We are also given the amount of reactant combusted. Our goal is to calculate the enthalpy change per mole for combustion of the reactant.

**Plan** We will first calculate the heat evolved for the combustion of the 4.00 g sample. We will then convert this heat to a molar quantity.

#### Solve

For combustion of the 4.00 g sample of methylhydrazine, the temperature change of the calorimeter is:

$$\Delta T = (39.50^\circ\text{C} - 25.00^\circ\text{C}) = 14.50^\circ\text{C}$$

We can use  $\Delta T$  and the value for  $C_{\text{cal}}$  to calculate the heat of reaction (Equation 5.23):

$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T = -(7.794 \text{ kJ}/^\circ\text{C})(14.50^\circ\text{C}) = -113.0 \text{ kJ}$$

We can readily convert this value to the heat of reaction for a mole of CH<sub>6</sub>N<sub>2</sub>:

$$\left( \frac{-113.0 \text{ kJ}}{4.00 \text{ g CH}_6\text{N}_2} \right) \times \left( \frac{46.1 \text{ g CH}_6\text{N}_2}{1 \text{ mol CH}_6\text{N}_2} \right) = -1.30 \times 10^3 \text{ kJ/mol CH}_6\text{N}_2$$

**Check** The units cancel properly, and the sign of the answer is negative as it should be for an exothermic reaction. The magnitude of the answer seems reasonable.

### ► Practice Exercise

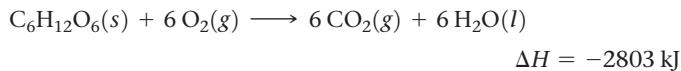
A 0.5865 g sample of lactic acid (HC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>) reacts with oxygen in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10 to 24.95 °C. Calculate the heat of combustion of lactic acid (**a**) per gram and (**b**) per mole.

## CHEMISTRY AND LIFE

### The Regulation of Body Temperature

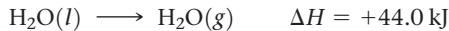
For most of us, being asked the question “Are you running a fever?” was one of our first introductions to medical diagnosis. Indeed, a deviation in body temperature of only a few degrees indicates something amiss. Maintaining a near-constant temperature is one of the primary physiological functions of the human body.

To understand how the body’s heating and cooling mechanisms operate, we can view the body as a thermodynamic system. The body increases its internal energy content by ingesting foods from the surroundings. The foods, such as glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), are metabolized—a process that is essentially controlled oxidation to CO<sub>2</sub> and H<sub>2</sub>O:



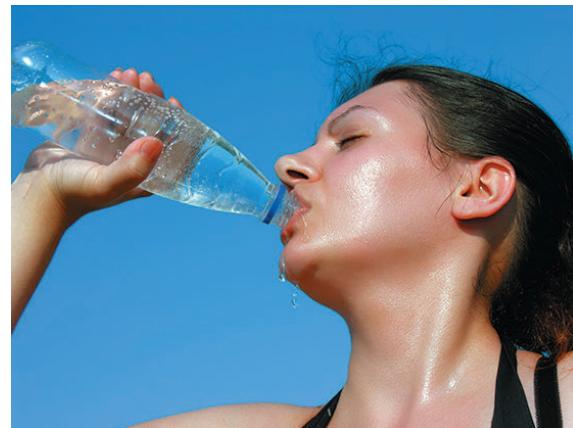
Roughly 40% of the energy produced is ultimately used to do work in the form of muscle contractions and nerve cell activities. The remainder is released as heat, part of which is used to maintain body temperature. When the body produces too much heat, as in times of heavy physical exertion, it dissipates the excess to the surroundings.

Heat is transferred from the body to its surroundings primarily by *radiation*, *convection*, and *evaporation*. Radiation is the direct loss of heat from the body to cooler surroundings, much as a hot stovetop radiates heat to its surroundings. Convection is heat loss by virtue of heating air that is in contact with the body. The heated air rises and is replaced with cooler air, and the process continues. Warm clothing decreases convective heat loss in cold weather. Evaporative cooling occurs when perspiration is generated at the skin surface by the sweat glands (Figure 5.20). Heat is removed from the body as the perspiration evaporates. Perspiration is predominantly water, so the process is the endothermic conversion of liquid water into water vapor:



The speed with which evaporative cooling occurs decreases as the atmospheric humidity increases, which is why we feel more sweaty and uncomfortable on hot, humid days.

When body temperature becomes too high, heat loss increases in two principal ways. First, blood flow near the skin surface increases,



▲ Figure 5.20 Perspiration.

which allows for increased radiational and convective cooling. The reddish, “flushed” appearance of a hot individual is due to this increased blood flow. Second, we sweat, which increases evaporative cooling. During extreme activity, the amount of perspiration can be as high as 2 to 4 liters per hour. As a result, the body’s water supply must be replenished during these periods. If the body loses too much liquid through perspiration, it will no longer be able to cool itself and blood volume decreases, which can lead to either *heat exhaustion* or the more serious *heat stroke*. However, replenishing water without replenishing the electrolytes lost during perspiration can also lead to serious problems. If the normal blood sodium level drops too low, dizziness and confusion set in, and the condition can become critical. Drinking a sport drink that contains some electrolytes helps to prevent this problem.

When body temperature drops too low, blood flow to the skin surface decreases, thereby decreasing heat loss. The lower temperature also triggers small involuntary contractions of the muscles (shivering); the biochemical reactions that generate the energy to do this work also generate heat for the body. If the body is unable to maintain a normal temperature, the very dangerous condition called *hypothermia* can result.

## Self-Assessment Exercise

- 5.21** How much energy (heat) does it take to heat an Al saucepan (0.20 kg) containing 1.0 L of water from room temperature (20 °C) to boiling? Assume thermal equilibrium between the pan and water at all times (specific heat capacity for Al is 0.90 J/g K and H<sub>2</sub>O is 4.18 J/g K. Assume the density of water is 1 g/mL).

(a)  $q = +15 \text{ kJ}$

(b)  $q = +87 \text{ kJ}$

(c)  $q = +330 \text{ kJ}$

(d)  $q = +330 \text{ kJ}$

## Exercises

- 5.22** (a) Derive an equation to convert the specific heat of a pure substance to its molar heat capacity. (b) The specific heat of aluminum is  $0.9\text{ J}/(\text{g K})$ . Calculate its molar heat capacity. (c) If you know the specific heat of aluminum, what additional information do you need to calculate the heat capacity of a particular piece of an aluminum component?
- 5.23** (a) What amount of heat (in joules) is required to raise the temperature of 1 g of water by 1 kelvin? (b) What is the heat capacity of 370 g of liquid water? (c) How many kJ of heat are needed to raise the temperature of 5.00 kg of liquid water from 24.6 to  $46.2^\circ\text{C}$ ?
- 5.24** The specific heat of octane,  $\text{C}_8\text{H}_{18}(l)$ , is  $2.22\text{ J/g K}$ . (a) How many J of heat are needed to raise the temperature of 80.0 g of octane from 10.0 to  $25.0^\circ\text{C}$ ? (b) Which will require more heat, increasing the temperature of 1 mol of  $\text{C}_8\text{H}_{18}(l)$  by a certain amount or increasing the temperature of 1 mol of  $\text{H}_2\text{O}(l)$  by the same amount?
- 5.25** When an 18.6 g sample of solid potassium hydroxide dissolves in 200.0 g of water in a coffee-cup calorimeter (Figure 5.18), the temperature rises from 23.7 to  $44.5^\circ\text{C}$ .

(a) Calculate the quantity of heat (in kJ) released in the reaction. (b) Using your result from part (a), calculate  $\Delta H$  (in  $\text{kJ/mol KOH}$ ) for the solution process. Assume that the specific heat of the solution is the same as that of pure water.

- 5.26** A 1.50 g sample of quinone ( $\text{C}_6\text{H}_4\text{O}_2$ ) is burned in a bomb calorimeter whose total heat capacity is  $8.500\text{ kJ}/^\circ\text{C}$ . The temperature of the calorimeter increases from 25.00 to  $29.49^\circ\text{C}$ . (a) Write a balanced chemical equation for the bomb calorimeter reaction. (b) What is the heat of combustion per gram of quinone and per mole of quinone?
- 5.27** Under constant-volume conditions, the heat of combustion of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) is  $16.49\text{ kJ/g}$ . A 3.00 g sample of sucrose is burned in a bomb calorimeter. The temperature of the calorimeter increases from 21.94 to  $24.62^\circ\text{C}$ . (a) What is the total heat capacity of the calorimeter? (b) If the size of the sucrose sample had been exactly twice as large, what would the temperature change of the calorimeter have been?

5.21 (d)

Answers to Self-Assessment Exercise



## 5.6 | Hess's Law



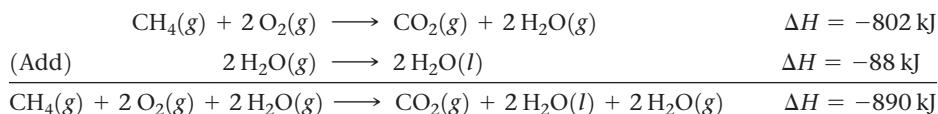
A fish ladder is a device that allows the movement of fish up a river when an obstruction such as a weir is built across their pathway. It provides an alternative route to get to the same end point. There are many reactions in chemistry where it may be difficult to determine the enthalpy change. Hess's Law allows us to calculate such a change from data that is easier to obtain.

By the end of this section, you should be able to

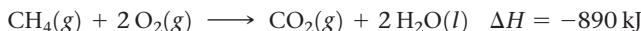
- Use Hess's law to determine enthalpy changes for reactions.

It is often possible to calculate the  $\Delta H$  for a reaction from the tabulated  $\Delta H$  values of other reactions. Thus, it is not necessary to make calorimetric measurements for all reactions.

Because enthalpy is a state function, the enthalpy change,  $\Delta H$ , associated with any chemical process depends only on the amount of matter that undergoes change and on the nature of the initial state of the reactants and the final state of the products. This means that whether a particular reaction is carried out in one step or in a series of steps, the sum of the enthalpy changes associated with the individual steps must be the same as the enthalpy change associated with the one-step process. As an example, combustion of methane gas,  $\text{CH}_4(g)$ , to form  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  can be thought of as occurring in one step, as represented on the left in **Figure 5.21**, or in two steps, as represented on the right in Figure 5.21: (1) combustion of  $\text{CH}_4(g)$  to form  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$  and (2) condensation of  $\text{H}_2\text{O}(g)$  to form  $\text{H}_2\text{O}(l)$ . The enthalpy change for the overall process is the sum of the enthalpy changes for these two steps:



The net equation is

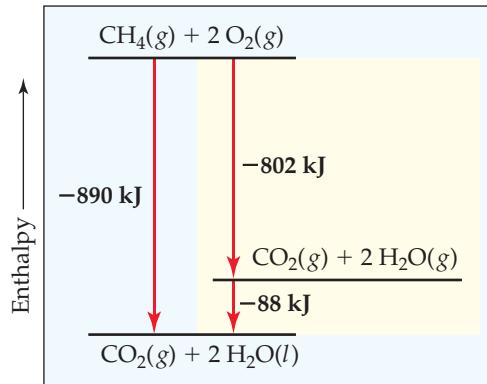


**Hess's law** states that *if a reaction is carried out in a series of steps,  $\Delta H$  for the overall reaction equals the sum of the enthalpy changes for the individual steps*. The overall enthalpy change for the process is independent of the number of steps and independent of the path by which the reaction is carried out. This law is a consequence of the fact that enthalpy is a state function. We can therefore calculate  $\Delta H$  for any process as long as we find a route for which  $\Delta H$  is known for each step. This means that a relatively small number of experimental measurements can be used to calculate  $\Delta H$  for a vast number of reactions.

Hess's law provides a useful means of calculating energy changes that are difficult to measure directly. For instance, it is impossible to measure directly the enthalpy for the combustion of carbon to form carbon monoxide. Combustion of 1 mol of carbon with 0.5 mol of  $\text{O}_2$  produces both CO and  $\text{CO}_2$ , leaving some carbon unreacted. However, solid carbon and carbon monoxide can both be completely burned in  $\text{O}_2$  to produce  $\text{CO}_2$ . We can therefore use the enthalpy changes of these reactions to calculate the heat of combustion of carbon as illustrated in Sample Exercise 5.8.

### Go Figure

What process corresponds to the  $-88 \text{ kJ}$  enthalpy change?



▲ **Figure 5.21** Enthalpy diagram for combustion of 1 mol of methane. The enthalpy change of the one-step reaction equals the sum of the enthalpy changes of the reaction run in two steps:  $-890 \text{ kJ} = -802 \text{ kJ} + (-88 \text{ kJ})$ .

### Sample Exercise 5.8

#### Using Hess's Law to Calculate $\Delta H$

The enthalpy of reaction for the combustion of C to  $\text{CO}_2$  is  $-393.5 \text{ kJ/mol C}$ , and the enthalpy for the combustion of CO to  $\text{CO}_2$  is  $-283.0 \text{ kJ/mol CO}$ :



Using these data, calculate the enthalpy for the combustion of C to CO:



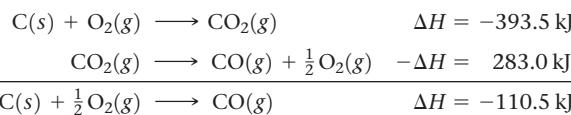
Continued

**SOLUTION**

**Analyze** We are given two thermochemical equations, and our goal is to combine them in such a way as to obtain the third equation and its enthalpy change.

**Plan** We will use Hess's law. In doing so, we first note the number of moles of substances among the reactants and products in the target equation (3). We then manipulate equations (1) and (2) to give the same number of moles of these substances, so that when the resulting equations are added, we obtain the target equation. At the same time, we keep track of the enthalpy changes, which we add.

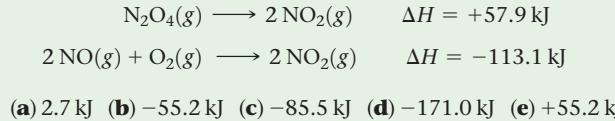
**Solve** To use equations (1) and (2), we arrange them so that C(s) is on the reactant side and CO(g) is on the product side of the arrow, as in the target reaction, equation (3). Because equation (1) has C(s) as a reactant, we can use that equation just as it is. We need to turn equation (2) around, however, so that CO(g) is a product. Remember that when reactions are turned around, the sign of  $\Delta H$  is reversed. We arrange the two equations so that they can be added to give the desired equation:



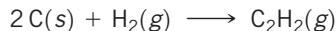
When we add the two equations, CO<sub>2</sub>(g) appears on both sides of the arrow and therefore cancels out. Likewise,  $\frac{1}{2}\text{O}_2(g)$  is eliminated from each side.

**► Practice Exercise**

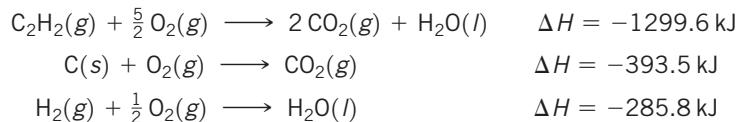
Calculate  $\Delta H$  for  $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$ , using the following information:

**Sample Exercise 5.9****Using Hess's Law with Three Equations to Calculate  $\Delta H$** 

Calculate  $\Delta H$  for the reaction



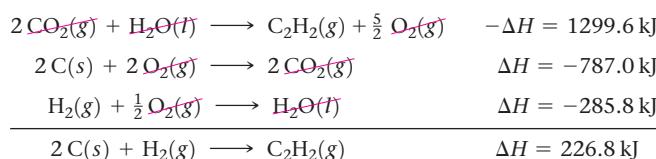
given the following chemical equations and their respective enthalpy changes:

**SOLUTION**

**Analyze** We are given a chemical equation and asked to calculate its  $\Delta H$  using three chemical equations and their associated enthalpy changes.

**Plan** We will use Hess's law, summing the three equations or their reverses and multiplying each by an appropriate coefficient so that they add to give the net equation for the reaction of interest. At the same time, we keep track of the  $\Delta H$  values, reversing their signs if the reactions are reversed and multiplying them by whatever coefficient is employed in the equation.

**Solve** Because the target equation has C<sub>2</sub>H<sub>2</sub> as a product, we turn the first equation around; the sign of  $\Delta H$  is therefore changed. The desired equation has 2 C(s) as a reactant, so we multiply the second equation and its  $\Delta H$  by 2. Because the target equation has H<sub>2</sub> as a reactant, we keep the third equation as it is. We then add the three equations and their enthalpy changes in accordance with Hess's law:

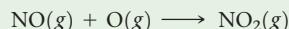


When the equations are added, there are 2 CO<sub>2</sub>,  $\frac{5}{2}$  O<sub>2</sub>, and H<sub>2</sub>O on both sides of the arrow. These are canceled in writing the net equation.

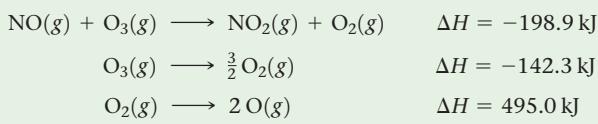
**Check** The procedure must be correct because we obtained the correct net equation. In cases like this, you should go back over the numerical manipulations of the  $\Delta H$  values to ensure that you did not make an inadvertent error with signs.

**► Practice Exercise**

Calculate  $\Delta H$  for the reaction

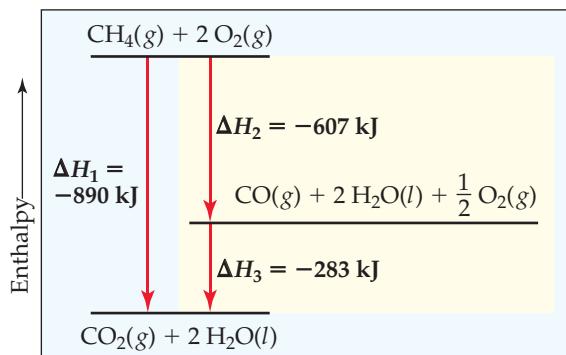


given the following information:



**Go Figure**

Suppose the overall reaction were modified to produce  $2 \text{ H}_2\text{O}(g)$  rather than  $2 \text{ H}_2\text{O}(l)$ . Would any of the values of  $\Delta H$  in the diagram stay the same?



**▲ Figure 5.22** Enthalpy diagram illustrating Hess's law. The net reaction is the same as in Figure 5.21, but here we imagine different reactions in our two-step version. As long as we can write a series of equations, each with a known value of  $\Delta H$ , that add up to the equation we need, we can calculate the overall  $\Delta H$ .

The key point of these examples is that  $H$  is a state function.

*Because  $H$  is a state function, for a particular set of reactants and products,  $\Delta H$  is the same whether the reaction takes place in one step or in a series of steps.*

We reinforce this point by giving one more example of an enthalpy diagram and Hess's law. Again we use combustion of methane to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , our reaction from Figure 5.21. This time we envision a different two-step path, with the initial formation of  $\text{CO}$ , which is then combusted to  $\text{CO}_2$  (Figure 5.22). Even though the two-step path is different from that in Figure 5.21, the overall reaction again has  $\Delta H_1 = -890 \text{ kJ}$ . Because  $H$  is a state function, both paths *must* produce the same value of  $\Delta H$ . In Figure 5.22, that means  $\Delta H_1 = \Delta H_2 + \Delta H_3$ . We will soon see that breaking up reactions in this way allows us to derive the enthalpy changes for reactions that are hard to carry out in the laboratory.

## Self-Assessment Exercise

**5.28** Calculate the enthalpy change for the reaction:  
 $\text{CO}(g) + \text{NO}(g) \longrightarrow \text{CO}_2(g) + \frac{1}{2}\text{N}_2(g)$

Given:  $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad \Delta H = -283 \text{ kJ/mol}$   
 $\text{NO}(g) \longrightarrow \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \quad \Delta H = -90.3 \text{ kJ/mol}$

- (a)  $\Delta H = +373 \text{ kJ/mol}$
- (b)  $\Delta H = +193 \text{ kJ/mol}$
- (c)  $\Delta H = -193 \text{ kJ/mol}$
- (d)  $\Delta H = -373 \text{ kJ/mol}$

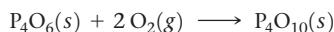
## Exercises

**5.29** Consider the following hypothetical reactions:

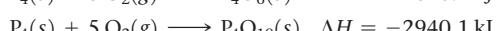


- (a) Use Hess's law to calculate the enthalpy change for the reaction  $\text{A} \longrightarrow \text{C}$ .
- (b) Construct an enthalpy diagram for substances A, B, and C, and show how Hess's law applies.

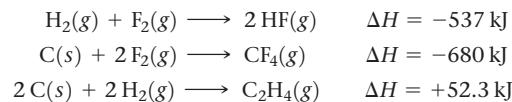
**5.30** Calculate the enthalpy change for the reaction



given the following enthalpies of reaction:



**5.31** From the enthalpies of reaction



calculate  $\Delta H$  for the reaction of ethylene with  $\text{F}_2$ :

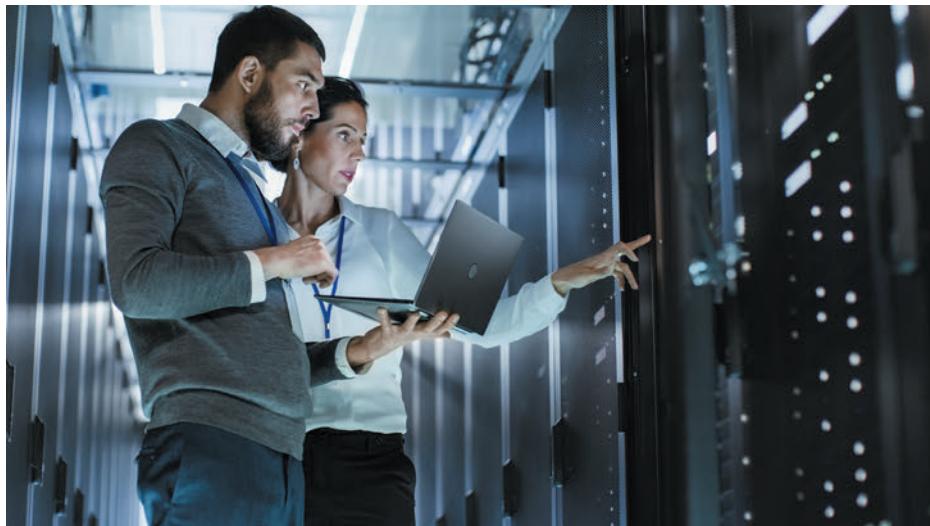


5.28 (d)

Answers to Self-Assessment Exercise



## 5.7 | Enthalpies of Formation



Data banks play an important part in modern society, empowering decisions that have been informed by ready access to relevant data. In the area of thermochemistry, the compilation of standard enthalpies of formation is the most important. We examine how to use this wealth of knowledge in this section, by the end of which you should be able to

- Use standard enthalpies of formation to calculate heats of reaction.

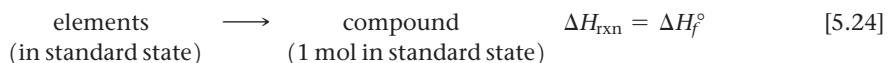
We can use the methods just discussed to calculate enthalpy changes for a great many reactions from tabulated  $\Delta H$  values. For example, extensive tables exist of *enthalpies of vaporization* ( $\Delta H$  for converting liquids to gases), *enthalpies of fusion* ( $\Delta H$  for melting solids), *enthalpies of combustion* ( $\Delta H$  for combusting a substance in oxygen), and so forth. A particularly important process used for tabulating thermochemical data is the formation of a compound from its constituent elements. The enthalpy change associated with this process is called the **enthalpy of formation** (or *heat of formation*),  $\Delta H_f$ , where the subscript *f* indicates that the substance has been *formed* from its constituent elements.

The magnitude of any enthalpy change depends on the temperature, pressure, and state (gas, liquid, or solid crystalline form) of the reactants and products. To compare enthalpies of different reactions, we must define a set of conditions, called a *standard state*, at which most enthalpies are tabulated. The standard state of a substance is its pure form at atmospheric pressure (100 kPa) and the temperature of interest, which we usually choose to be 298 K (25 °C). The **standard enthalpy change** of a reaction is defined as the enthalpy change when all reactants and products are in their standard states. We denote a standard enthalpy change as  $\Delta H^\circ$ , where the superscript  $^\circ$  indicates standard-state conditions.

**TABLE 5.3 Standard Enthalpies of Formation,  $\Delta H_f^\circ$ , at 298 K**

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)	Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	-92.30
Ammonia	$NH_3(g)$	-46.19	Hydrogen fluoride	$HF(g)$	-268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	-1207.1	Methane	$CH_4(g)$	-74.80
Calcium oxide	$CaO(s)$	-635.5	Methanol	$CH_3OH(l)$	-238.6
Carbon dioxide	$CO_2(g)$	-393.5	Propane	$C_3H_8(g)$	-103.85
Carbon monoxide	$CO(g)$	-110.5	Silver chloride	$AgCl(s)$	-127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	-947.7
Ethane	$C_2H_6(g)$	-84.68	Sodium carbonate	$Na_2CO_3(s)$	-1130.9
Ethanol	$C_2H_5OH(l)$	-277.7	Sodium chloride	$NaCl(s)$	-410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	-2221
Glucose	$C_6H_{12}O_6(s)$	-1273	Water	$H_2O(l)$	-285.8
Hydrogen bromide	$HBr(g)$	-36.23	Water vapor	$H_2O(g)$	-241.8

The **standard enthalpy of formation** of a compound,  $\Delta H_f^\circ$ , is the change in enthalpy for the reaction that forms one mole of the compound from its elements with all substances in their standard states:



We usually report  $\Delta H_f^\circ$  values at 298 K. If an element exists in more than one form under standard conditions, the most stable form of the element is usually used for the formation reaction. For example, the standard enthalpy of formation for ethanol,  $C_2H_5OH$ , is the enthalpy change for the reaction



The elemental source of oxygen is  $O_2$ , not  $O$  or  $O_3$ , because  $O_2$  is the stable form of oxygen at 298 K and atmospheric pressure. Similarly, the elemental source of carbon is graphite and not diamond because graphite is the more stable (lower-energy) form at 298 K and atmospheric pressure. Likewise, the most stable form of hydrogen under standard conditions is  $H_2(g)$ , so this is used as the source of hydrogen in Equation 5.25.

The stoichiometry of formation reactions always indicates that one mole of the desired substance is produced, as in Equation 5.25. As a result, standard enthalpies of formation are reported in kJ/mol of the substance being formed. Some values are given in **Table 5.3**, and a more extensive table is provided in Appendix C.

By definition, the *standard enthalpy of formation of the most stable form of any element is zero* because there is no formation reaction needed when the element is already in its standard state. Thus, the values of  $\Delta H_f^\circ$  for  $C(\text{graphite})$ ,  $H_2(g)$ ,  $O_2(g)$ , and the standard states of other elements are zero by definition.



### Sample Exercise 5.10

#### Equations Associated with Enthalpies of Formation



For which of these reactions at 25 °C does the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose  $\Delta H$  is an enthalpy of formation?

- (a)  $2 Na(s) + \frac{1}{2} O_2(g) \longrightarrow Na_2O(s)$
- (b)  $2 K(l) + Cl_2(g) \longrightarrow 2 KCl(s)$
- (c)  $C_6H_{12}O_6(s) \longrightarrow 6 C(\text{diamond}) + 6 H_2(g) + 3 O_2(g)$

*Continued*

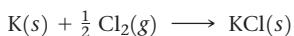
**SOLUTION**

**Analyze** The standard enthalpy of formation is represented by a reaction in which each reactant is an element in its standard state and the product is one mole of the compound.

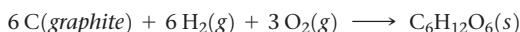
**Plan** We need to examine each equation to determine (1) whether the reaction is one in which one mole of substance is formed from the elements, and (2) whether the reactant elements are in their standard states.

**Solve** In (a) 1 mol Na<sub>2</sub>O is formed from the elements sodium and oxygen in their proper states, solid Na and O<sub>2</sub> gas, respectively. Therefore, the enthalpy change for reaction (a) corresponds to a standard enthalpy of formation.

In (b) potassium is given as a liquid. It must be changed to the solid form, its standard state at room temperature. Furthermore, 2 mol KCl are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of KCl(s). The equation for the formation reaction of 1 mol of KCl(s) is



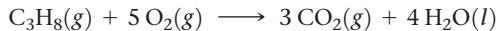
Reaction (c) does not form a substance from its elements. Instead, a substance decomposes to its elements, so this reaction must be reversed. Next, the element carbon is given as diamond, whereas graphite is the standard state of carbon at room temperature and 101.3 kPa pressure. The equation that correctly represents the enthalpy of formation of glucose from its elements is

**► Practice Exercise**

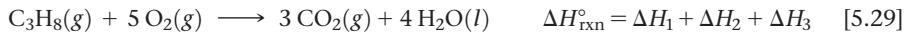
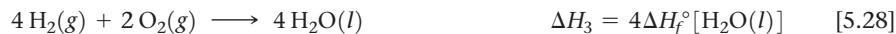
Write the equation corresponding to the standard enthalpy of formation of liquid carbon tetrachloride (CCl<sub>4</sub>) and look up  $\Delta H_f^\circ$  for this compound in Appendix C.

## Using Enthalpies of Formation to Calculate Enthalpies of Reaction

We can use Hess's law and tabulations of  $\Delta H_f^\circ$  values, such as those in Table 5.3 and Appendix C, to calculate the standard enthalpy change for any reaction for which we know the  $\Delta H_f^\circ$  values for all reactants and products. For example, consider the combustion of propane under standard conditions:



We can write this equation as the sum of three equations associated with standard enthalpies of formation:



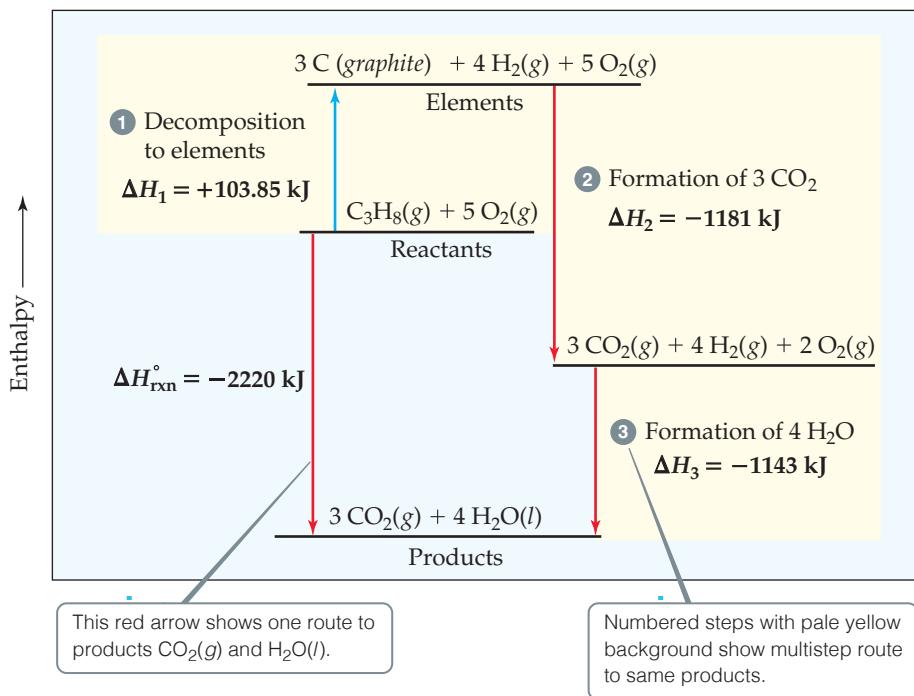
(Note that it is sometimes useful to add subscripts to the enthalpy changes, as we have done here, to keep track of the associations between reactions and their  $\Delta H$  values.)

Notice that we have used Hess's law to write the standard enthalpy change for Equation 5.29 as the sum of the enthalpy changes for Equations 5.26 through 5.28. We can use values from Table 5.3 to calculate  $\Delta H_{\text{rxn}}^\circ$ :

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= -\Delta H_f^\circ[\text{C}_3\text{H}_8(g)] + 3\Delta H_f^\circ[\text{CO}_2(g)] + 4\Delta H_f^\circ[\text{H}_2\text{O}(l)] \\ &= -(-103.85 \text{ kJ}) + 3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ}) = -2220 \text{ kJ} \end{aligned} \quad [5.30]$$

The enthalpy diagram in Figure 5.23 shows the components of this calculation. In Step ① the reactants are decomposed into their constituent elements in their standard states. In Steps ② and ③ the products are formed from the elements. Several aspects of how we use enthalpy changes in this process depend on the guidelines we discussed in Section 5.4.

**① Decomposition.** Equation 5.26 is the reverse of the formation reaction for C<sub>3</sub>H<sub>8</sub>(g), so the enthalpy change for this decomposition reaction is the negative of the  $\Delta H_f^\circ$  value for the propane formation reaction:  $-\Delta H_f^\circ[\text{C}_3\text{H}_8(g)]$ .



- 2 Formation of  $\text{CO}_2$ .** Equation 5.27 is the formation reaction for 3 mol of  $\text{CO}_2(\text{g})$ . Because enthalpy is an extensive property, the enthalpy change for this step is  $3\Delta H_f^\circ[\text{CO}_2(\text{g})]$ .
- 3 Formation of  $\text{H}_2\text{O}$ .** The enthalpy change for Equation 5.28, formation of 4 mol of  $\text{H}_2\text{O}$ , is  $4\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})]$ . The reaction specifies that  $\text{H}_2\text{O}(\text{l})$  is produced, so be careful to use the value of  $\Delta H_f^\circ$  for  $\text{H}_2\text{O}(\text{l})$  and not the value for  $\text{H}_2\text{O}(\text{g})$ .

Note that in this analysis we assume that the stoichiometric coefficients in the balanced equation represent the number of moles of each substance. For Equation 5.29, therefore,  $\Delta H_{rxn}^\circ = -2220 \text{ kJ}$  represents the enthalpy change for the reaction of 1 mol  $\text{C}_3\text{H}_8$  and 5 mol  $\text{O}_2$  to form 3 mol  $\text{CO}_2$  and 4 mol  $\text{H}_2\text{O}$ .

We can break down any reaction into formation reactions as we have done here. When we do, we obtain the general result that the standard enthalpy change of a reaction is the sum of the standard enthalpies of formation of the products minus the standard enthalpies of formation of the reactants:

$$\Delta H_{rxn}^\circ = \Sigma n \Delta H_f^\circ(\text{products}) - \Sigma m \Delta H_f^\circ(\text{reactants}) \quad [5.31]$$

The symbol  $\Sigma$  (sigma) means “the sum of,” and  $n$  and  $m$  are the stoichiometric coefficients of the relevant chemical equation. The first term on the right in Equation 5.31 represents the formation reactions of the products, which are written in the “forward” direction in the chemical equation, that is, elements reacting to form products. This term is analogous to Equations 5.27 and 5.28. The second term on the right in Equation 5.31 represents the reverse of the formation reactions of the reactants, analogous to Equation 5.26, which is why this term is preceded by a minus sign.



### Sample Exercise 5.11

#### Calculating an Enthalpy of Reaction from Enthalpies of Formation

- (a) Calculate the standard enthalpy change for the combustion of 1 mol of benzene,  $\text{C}_6\text{H}_6(\text{l})$ , to  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ .  
(b) Compare the quantity of heat produced by combustion of 1.00 g propane with that produced by 1.00 g benzene.



◀ Figure 5.23 Enthalpy diagram for propane combustion.

**SOLUTION**

**Analyze** (a) We are given a reaction (combustion of  $C_6H_6(l)$ ) to form  $CO_2(g)$  and  $H_2O(l)$ ) and asked to calculate its standard enthalpy change,  $\Delta H^\circ$ . (b) We then need to compare the quantity of heat produced by combustion of 1.00 g  $C_6H_6$  with that produced by 1.00 g  $C_3H_8$ , whose combustion was treated previously in the text. (See Equations 5.29 and 5.30.)

**Solve**

- (a) We know that a combustion reaction involves  $O_2(g)$  as a reactant. Thus, the balanced equation for the combustion reaction of 1 mol  $C_6H_6(l)$  is:

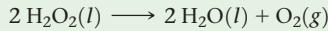
We can calculate  $\Delta H^\circ$  for this reaction by using Equation 5.31 and data in Table 5.3. Remember to multiply the  $\Delta H_f^\circ$  value for each substance in the reaction by that substance's stoichiometric coefficient. Recall also that  $\Delta H_f^\circ = 0$  for any element in its most stable form under standard conditions, so  $\Delta H_f^\circ[O_2(g)] = 0$ .

- (b) From the example worked in the text,  $\Delta H^\circ = -2220 \text{ kJ}$  for the combustion of 1 mol of propane. In part (a) of this exercise we determined that  $\Delta H^\circ = -3267 \text{ kJ}$  for the combustion of 1 mol benzene. To determine the heat of combustion per gram of each substance, we use the molar masses to convert moles to grams:

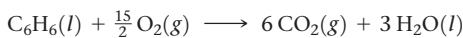
**Comment** Both propane and benzene are hydrocarbons. As a rule, the energy obtained from the combustion of a gram of hydrocarbon is between 40 and 50 kJ.

**► Practice Exercise**

Calculate the enthalpy change for the reaction



**Plan** (a) We first write the balanced equation for the combustion of  $C_6H_6$ . We then look up  $\Delta H_f^\circ$  values in Appendix C or in Table 5.3 and apply Equation 5.31 to calculate the enthalpy change for the reaction. (b) We use the molar mass of  $C_6H_6$  to change the enthalpy change per mole to that per gram. We similarly use the molar mass of  $C_3H_8$  and the enthalpy change per mole calculated in the text previously to calculate the enthalpy change per gram of that substance.



$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= [6\Delta H_f^\circ(CO_2) + 3\Delta H_f^\circ(H_2O)] - [\Delta H_f^\circ(C_6H_6) + \frac{15}{2}\Delta H_f^\circ(O_2)] \\ &= [6(-393.5 \text{ kJ}) + 3(-285.8 \text{ kJ})] - [(49.0 \text{ kJ}) + \frac{15}{2}(0 \text{ kJ})] \\ &= (-2361 - 857.4 - 49.0) \text{ kJ} \\ &= -3267 \text{ kJ}\end{aligned}$$

$$C_3H_8(g): (-2220 \text{ kJ/mol})(1 \text{ mol}/44.1 \text{ g}) = -50.3 \text{ kJ/g}$$

$$C_6H_6(l): (-3267 \text{ kJ/mol})(1 \text{ mol}/78.1 \text{ g}) = -41.8 \text{ kJ/g}$$

using enthalpies of formation:

$$\Delta H_f^\circ[H_2O_2(l)] = -187.8 \text{ kJ/mol} \quad \Delta H_f^\circ[H_2O(l)] = -285.8 \text{ kJ/mol}$$

- (a) -88.0 kJ
- (b) -196.0 kJ
- (c) +88.0 kJ
- (d) +196.0 kJ
- (e) more information needed

**Sample Exercise 5.12****Calculating an Enthalpy of Formation Using an Enthalpy of Reaction**

The standard enthalpy change for the reaction  $CaCO_3[s] \longrightarrow CaO[s] + CO_2[g]$  is 178.1 kJ. Use Table 5.3 to calculate the standard enthalpy of formation of  $CaCO_3[s]$ .

**SOLUTION**

**Analyze** Our goal is to obtain  $\Delta H_f^\circ[CaCO_3]$ .

**Plan** We begin by writing the expression for the standard enthalpy change for the reaction:

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ[CaO] + \Delta H_f^\circ[CO_2] - \Delta H_f^\circ[CaCO_3]$$

**Solve**

Inserting the given  $\Delta H_{\text{rxn}}^\circ$  and the known  $\Delta H_f^\circ$  values from Table 5.3 or Appendix C, we have:

$$178.1 \text{ kJ} = -635.5 \text{ kJ} - 393.5 \text{ kJ} - \Delta H_f^\circ[CaCO_3]$$

Solving for  $\Delta H_f^\circ[CaCO_3]$  gives:

$$\Delta H_f^\circ[CaCO_3] = -1207.1 \text{ kJ/mol}$$

**Check** We expect the enthalpy of formation of a stable solid such as calcium carbonate to be negative, as obtained.

### ► Practice Exercise

Given  $2 \text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{SO}_3(g)$ , which of the following equations is correct?

- (a)  $\Delta H_f^\circ[\text{SO}_3] = \Delta H_{\text{rxn}}^\circ - \Delta H_f^\circ[\text{SO}_2]$
- (b)  $\Delta H_f^\circ[\text{SO}_3] = \Delta H_{\text{rxn}}^\circ + \Delta H_f^\circ[\text{SO}_2]$

(c)  $2\Delta H_f^\circ[\text{SO}_3] = \Delta H_{\text{rxn}}^\circ + 2\Delta H_f^\circ[\text{SO}_2]$

(d)  $2\Delta H_f^\circ[\text{SO}_3] = \Delta H_{\text{rxn}}^\circ - 2\Delta H_f^\circ[\text{SO}_2]$

(e)  $2\Delta H_f^\circ[\text{SO}_3] = 2\Delta H_f^\circ[\text{SO}_2] - \Delta H_{\text{rxn}}^\circ$

## Self-Assessment Exercise

- 5.32** The equation for the combustion of urea is:  $(\text{NH}_2)_2\text{CO}(s) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{CO}_2(g) + \text{N}_2(g) + 2 \text{H}_2\text{O}(l)$

Use  $\Delta H_f^\circ$  (urea) =  $-333 \text{ kJ}$  and the values in Table 5.3 to calculate the enthalpy of combustion of urea.

(a)  $\Delta H = -346 \text{ kJ}$

(b)  $\Delta H = -632 \text{ kJ}$

(c)  $\Delta H = -1300 \text{ kJ}$

## Exercises

- 5.33** (a) What is meant by the term *standard conditions* with reference to enthalpy changes? (b) What is meant by the term *enthalpy of formation*? (c) What is meant by the term *standard enthalpy of formation*?

- 5.34** For each of the following compounds, write a balanced thermochemical equation depicting the formation of one mole of the compound from its elements in their standard states and then look up  $\Delta H_f^\circ$  for each substance in Appendix C. (a)  $\text{NO}_2(g)$ , (b)  $\text{SO}_3(g)$ , (c)  $\text{NaBr}(s)$ , (d)  $\text{Pb}(\text{NO}_3)_2(s)$ .

- 5.35** The following is known as the thermite reaction:

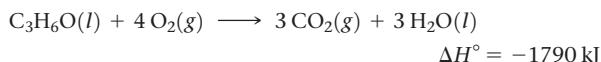


This highly exothermic reaction is used for welding massive units, such as propellers for large ships. Using standard enthalpies of formation in Appendix C, calculate  $\Delta H^\circ$  for this reaction.

- 5.36** Using values from Appendix C, calculate the standard enthalpy change for each of the following reactions:

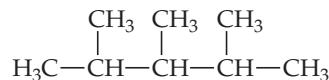
- (a)  $2 \text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{SO}_3(g)$
- (b)  $\text{Mg}(\text{OH})_2(s) \longrightarrow \text{MgO}(s) + \text{H}_2\text{O}(l)$
- (c)  $\text{N}_2\text{O}_4(g) + 4 \text{H}_2(g) \longrightarrow \text{N}_2(g) + 4 \text{H}_2\text{O}(g)$
- (d)  $\text{SiCl}_4(l) + 2 \text{H}_2\text{O}(l) \longrightarrow \text{SiO}_2(s) + 4 \text{HCl}(g)$

- 5.37** Complete combustion of 1 mol of acetone ( $\text{C}_3\text{H}_6\text{O}$ ) liberates 1790 kJ:



Using this information together with the standard enthalpies of formation of  $\text{O}_2(g)$ ,  $\text{CO}_2(g)$ , and  $\text{H}_2\text{O}(l)$  from Appendix C, calculate the standard enthalpy of formation of acetone.

- 5.38** Petrol is composed primarily of hydrocarbons, including many with eight carbon atoms, called *octanes*. One of the cleanest-burning octanes is a compound called 2,3,4-trimethylpentane, which has the following structural formula:



The complete combustion of one mole of this compound to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$  leads to  $\Delta H^\circ = -5064.9 \text{ kJ}$ .

- (a) Write a balanced equation for the combustion of 1 mol of  $\text{C}_8\text{H}_{18}(l)$ .
- (b) By using the information in this problem and data in Table 5.3, calculate  $\Delta H_f^\circ$  for 2,3,4-trimethylpentane.

- 5.39** Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is blended with petrol as a vehicle fuel.
- (a) Write a balanced equation for the combustion of liquid ethanol in air.
  - (b) Calculate the standard enthalpy change for the reaction, assuming  $\text{H}_2\text{O}(g)$  as a product.
  - (c) Calculate the heat produced per liter of ethanol by combustion of ethanol under constant pressure. Ethanol has a density of  $0.789 \text{ g/mL}$ .
  - (d) Calculate the mass of  $\text{CO}_2$  produced per kJ of heat emitted.

5.32 (b)

Answers to Self-Assessment Exercise



## 5.8 | Bond Enthalpies

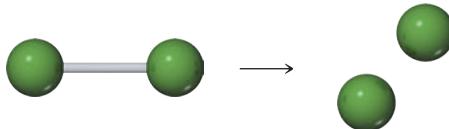


38.22	39.37	40.55	41.77	43.02	44
24.32	25.05	25.81	26.58	27.38	28
48.65	50.11	51.61	53.16	54.75	56
37.07	38.18	39.32	40.50	41.72	4
25.48	26.25	27.03	27.85	28.68	2
55.60	57.27	58.98	60.75	62.58	6
37.07	38.18	39.32	40.50	41.72	4
49.81	51.30	52.84	54.42	56.06	6
54.44	56.07	57.76	59.45	61.27	6
53.28	54.88	56.53	58.22	59.97	6
57.91	59.65	61.44	63.21	64.98	6
24.32	25.05	25.81	26.58	27.35	28
33.59	34.60	35.64	36.71	37.78	38
6.76	58.46	60.21	62.02	63.88	6
8.22	39.37	40.55	41.77	43.02	4

Knowing the limitations of the data that you are using is an important part of estimating errors. As we shall see with bond enthalpies, the data is compiled from reactions involving gases. While this is useful in estimating enthalpy changes for some reactions—principally gas phase ones—it may be less accurate for reactions in liquid or solid states. Nevertheless, it can still give us useful approximations of energy changes. By the end of this section, you should be able to

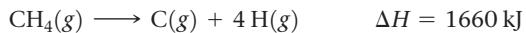
- Use average bond enthalpies to estimate the reaction enthalpies of reactions where all reactants and products are in the gas phase.

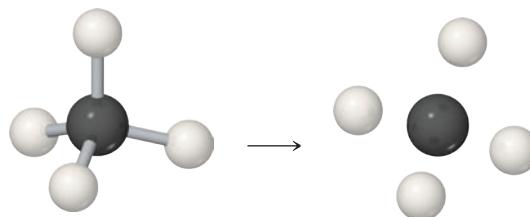
The energy changes that accompany chemical reactions are closely related to the changes associated with forming and breaking chemical bonds—breaking bonds requires energy and forming bonds releases energy. It follows that if we measure the enthalpy of a reaction and keep track of the bonds that are broken and formed, we can assign an enthalpy value to specific bonds. The **bond enthalpy** is the enthalpy change,  $\Delta H$ , for the breaking of a particular bond in one mole of a gaseous substance. It is easiest to determine bond enthalpies from simple reactions where only one bond is broken, such as the dissociation of  $\text{Cl}_2(g)$ . A  $\text{Cl}_2$  molecule is held together by a single covalent bond, which is represented as  $\text{Cl}—\text{Cl}$ . The dissociation of  $\text{Cl}_2(g)$  into chlorine atoms results when the  $\text{Cl}—\text{Cl}$  bond is broken:



The bond enthalpy for a  $\text{Cl}—\text{Cl}$  bond is equal to the enthalpy of this reaction, 242 kJ/mol. The bond enthalpy is a positive number because energy must be supplied from the surroundings to break the  $\text{Cl}—\text{Cl}$  bond. We use the letter  $D$  followed by the bond in question to represent bond enthalpies. For example,  $D(\text{Cl}—\text{Cl})$  is the bond enthalpy for the  $\text{Cl}_2$  bond, and  $D(\text{H}—\text{Br})$  is the bond enthalpy for the  $\text{HBr}$  bond.

It is straightforward to assign bond enthalpies for a reaction involving the breaking of a bond in a diatomic molecule: the bond enthalpy is simply equal to the enthalpy of the reaction. However, many important bonds, such as the C—H bond, exist only in polyatomic molecules. For these bonds, we usually use average bond enthalpies. For example, the enthalpy change for the following process in which a methane molecule is decomposed into its five constituent atoms can be used to define an average bond enthalpy for the C—H bond:



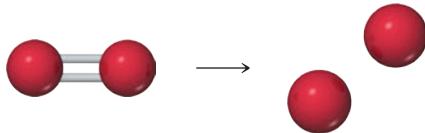


Because there are four equivalent C—H bonds in methane, the enthalpy of this reaction is four times the enthalpy needed to break a single C—H bond. Therefore, the average C—H bond enthalpy in CH<sub>4</sub> is  $D(\text{C—H}) = (1660/4) \text{ kJ/mol} = 415 \text{ kJ/mol}$ .

The exact bond enthalpy for a given pair of atoms, say C—H, depends on the rest of the molecule containing the atom pair. However, the variation from one molecule to another is generally small. If we consider C—H bond enthalpies in many different compounds, we find that the average bond enthalpy is 413 kJ/mol, close to the 415 kJ/mol value we just calculated from the dissociation of CH<sub>4</sub>.

*The bond enthalpy is always a positive quantity because energy is required to break chemical bonds. Conversely, energy is always released when a bond forms between two gaseous atoms or molecular fragments. The greater the bond enthalpy, the stronger the bond.*

**Table 5.4** lists average bond enthalpies for a number of atom pairs. Further, a molecule with strong chemical bonds is generally less likely to undergo chemical change than one with weak bonds. As we will learn in later chapters, atom pairs are sometimes held together by multiple bonds. For example, the oxygen atoms in an O<sub>2</sub> molecule are held together by a double bond, O=O, rather than a single bond, O—O.



Inspection of Table 5.4 shows that  $D(\text{O=O}) = 495 \text{ kJ/mol}$ , which is larger but not exactly twice the enthalpy of an oxygen–oxygen single bond,  $D(\text{O—O}) = 146 \text{ kJ/mol}$ . We will consider the variations in bond enthalpy for double and triple bonds in more detail in Chapter 8.

### Bond Enthalpies and the Enthalpies of Reactions

Because enthalpy is a state function, we can use average bond enthalpies to estimate the enthalpies of reactions in which bonds are broken and new bonds are formed. This procedure allows us to estimate quickly whether a given reaction will be endothermic

**TABLE 5.4 Average Bond Enthalpies (kJ/mol)**

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C=C	614	N—O	201	O=O	495	Cl—F	253
C—N	293	N—F	272	O—F	190	Cl—Cl	242
C—O	358	N—Cl	200	O—Cl	203		
C=O	799	N—Br	243	O—I	234	Br—F	237
C—F	485					Br—Cl	218
C—Cl	328	H—H	436			Br—Br	193
C—Br	276	H—F	567				
C—I	240	H—Cl	431			I—Cl	208
		H—Br	366			I—Br	175
		H—I	299			I—I	151

( $\Delta H > 0$ ) or exothermic ( $\Delta H < 0$ ), even if we do not know  $\Delta H_f^\circ$  for all of the species involved.

Our strategy for estimating reaction enthalpies is a straightforward application of Hess's law. We use the fact that breaking bonds is always endothermic and forming bonds is always exothermic. We therefore imagine that the reaction occurs in two steps:

1. We supply enough energy to break those bonds in the reactants that are not present in the products. The enthalpy of the system is increased by the sum of the bond enthalpies of the bonds that are broken.
2. We form the bonds in the products that were not present in the reactants. This step releases energy and therefore lowers the enthalpy of the system by the sum of the bond enthalpies of the bonds that are formed.

The enthalpy of the reaction,  $\Delta H_{\text{rxn}}$ , is estimated as the sum of the bond enthalpies of the bonds broken minus the sum of the bond enthalpies of the bonds formed:

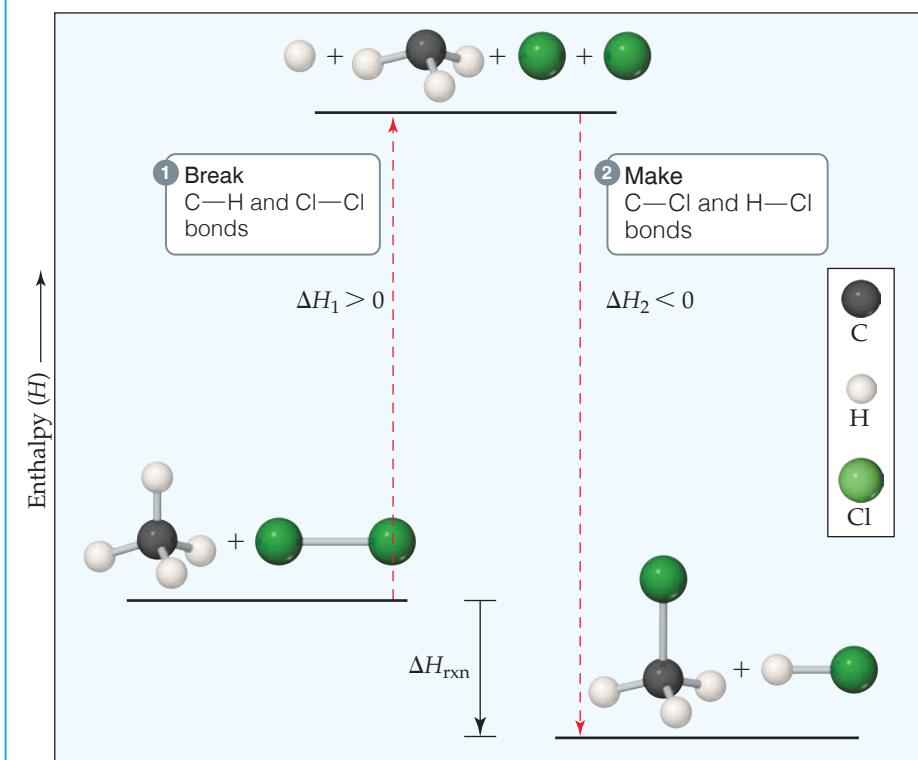
$$\Delta H_{\text{rxn}} = \sum (\text{bond enthalpies of bonds broken}) - \sum (\text{bond enthalpies of bonds formed}) \quad [5.32]$$

If the total enthalpy of the broken bonds is larger, the reaction is endothermic ( $\Delta H_{\text{rxn}} > 0$ ); if the total enthalpy of the newly formed bonds is larger, the reaction is exothermic ( $\Delta H_{\text{rxn}} < 0$ ).

Consider for example, the gas-phase reaction between methane,  $\text{CH}_4$ , and chlorine to produce chloromethane,  $\text{CH}_3\text{Cl}$ , and hydrogen chloride,  $\text{HCl}$ :



### Go Figure Is this reaction exothermic or endothermic?



**▲ Figure 5.24** Using bond enthalpies to estimate  $\Delta H_{\text{rxn}}$ . Average bond enthalpies are used to estimate  $\Delta H_{\text{rxn}}$  for the reaction of methane with chlorine to make methyl chloride and hydrogen chloride.

Our two-step procedure is outlined in **Figure 5.24**. We note that the following bonds are broken and formed:

*Bonds broken:* 1 mol C—H, 1 mol Cl—Cl

*Bonds formed:* 1 mole C—Cl, 1 mol H—Cl

We first supply enough energy to break the C—H and Cl—Cl bonds, which raises the enthalpy of the system (indicated as  $\Delta H_1 > 0$  in Figure 5.24). We then form the C—Cl and H—Cl bonds, which release energy and lower the enthalpy of the system ( $\Delta H_2 < 0$  in Figure 5.24). We then use Equation 5.32 to estimate the enthalpy of the reaction:

$$\Delta H_{\text{rxn}} = [D(\text{C—H}) + D(\text{Cl—Cl})] - [D(\text{C—Cl}) + D(\text{H—Cl})]$$

$$\Delta H_{\text{rxn}} = (413 \text{ kJ} + 242 \text{ kJ}) - (328 \text{ kJ} + 431 \text{ kJ}) = -104 \text{ kJ}$$

The reaction is exothermic because the bonds in the products are stronger than the bond in the reactants.

Typically, bond enthalpies are used to estimate  $\Delta H_{\text{rxn}}$  only if the needed  $\Delta H_f^\circ$  values are not readily available. For the preceding reaction, we cannot calculate  $\Delta H_{\text{rxn}}$  from  $\Delta H_f^\circ$  values and Hess's law because  $\Delta H_f^\circ$  for  $\text{CH}_3\text{Cl}(g)$  is not given in Appendix C. If we obtain the value of  $\Delta H_f^\circ$  for  $\text{CH}_3\text{Cl}(g)$  from another source and use Equation 5.31, we find that  $\Delta H_{\text{rxn}} = -99.8 \text{ kJ}$  for the reaction in Equation 5.33. The two values are slightly different because bond enthalpies are averaged over many compounds, but the use of average bond enthalpies provides a reasonably accurate estimate of the actual reaction enthalpy change.

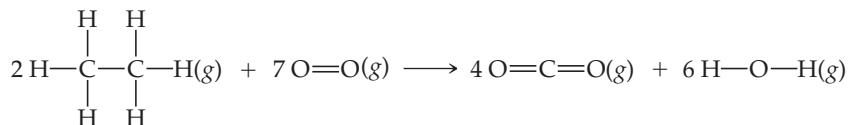
It is important to remember that bond enthalpies are derived for gaseous molecules. In solids, liquids, and solutions, intermolecular forces between different molecules must also be taken into account. We will examine the strengths of those forces in detail in Chapter 11, but for now it is sufficient to remember that bond enthalpies cannot be used to accurately estimate the enthalpies of reactions containing solids, liquids, or solutions.



### Sample Exercise 5.13

#### Estimating Reaction Enthalpies from Bond Enthalpies

Use Table 5.4 to estimate  $\Delta H$  for the following combustion reaction.



#### SOLUTION

**Analyze** We are asked to use average bond enthalpies to estimate the enthalpy change for a chemical reaction.

**Plan** Energy is required to break twelve C—H bonds and two C—C bonds in the two molecules of  $\text{C}_2\text{H}_6$ , and seven O=O bonds in the seven  $\text{O}_2$  molecules. Energy is released by forming eight C=O bonds, two per molecule of  $\text{CO}_2$ , and twelve O—H bonds, two per  $\text{H}_2\text{O}$  molecule.

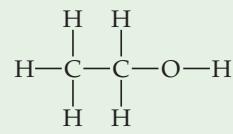
**Solve** Using Equation 5.32 and data from Table 5.4, we have

$$\begin{aligned}
 \Delta H &= [12D(\text{C—H}) + 2D(\text{C—C}) + 7D(\text{O=O})] \\
 &\quad - [8D(\text{C=O}) + 12D(\text{O—H})] \\
 &= [12(413 \text{ kJ}) + 2(348 \text{ kJ}) + 7(495 \text{ kJ})] \\
 &\quad - [8(799 \text{ kJ}) + 12(463 \text{ kJ})] \\
 &= 9117 \text{ kJ} - 11948 \text{ kJ} \\
 &= -2831 \text{ kJ}
 \end{aligned}$$

**Check** This estimate can be compared with the value of  $-2856 \text{ kJ}$  calculated from more accurate thermochemical data; the agreement is good.

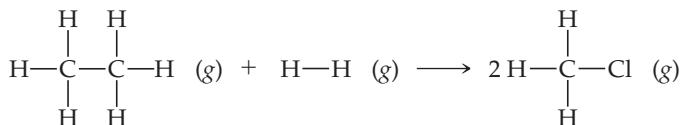
#### ► Practice Exercise

Use the average bond enthalpies in Table 5.4 to estimate  $\Delta H$  for the combustion of ethanol.



## Self-Assessment Exercise

- 5.40** Use average bond enthalpies from Table 5.4 to estimate the enthalpy change in the reaction:



- (a)  $\Delta H = -42 \text{ kJ}$   
 (b)  $\Delta H = +42 \text{ kJ}$   
 (c)  $\Delta H = +371 \text{ kJ}$

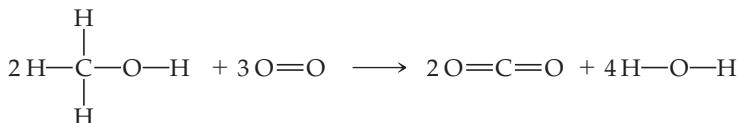
## Exercises

- 5.41** Without doing any calculations, predict the sign of  $\Delta H$  for each of the following reactions:

- (a)  $\text{NaCl}(s) \longrightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$   
 (b)  $2 \text{H}(\text{g}) \longrightarrow \text{H}_2(\text{g})$   
 (c)  $\text{Na}(\text{g}) \longrightarrow \text{Na}^+(\text{g}) + \text{e}^-$   
 (d)  $\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{l})$

- 5.42** Use bond enthalpies in Table 5.4 to estimate  $\Delta H$  for each of the following reactions:

- (a)  $\text{H}—\text{H}(\text{g}) + \text{Br}—\text{Br}(\text{g}) \longrightarrow 2 \text{H}—\text{Br}(\text{g})$   
 (b)



- 5.43** (a) Use enthalpies of formation given in Appendix C to calculate  $\Delta H$  for the reaction  $\text{Br}_2(\text{g}) \longrightarrow 2 \text{Br}(\text{g})$ , and use this value to estimate the bond enthalpy  $D(\text{Br}—\text{Br})$ . (b) How large is the difference between the value calculated in part (a) and the value given in Table 5.4?

- 5.44** Consider the reaction  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{H}_2\text{O}(\text{l})$ .  
 (a) Use the bond enthalpies in Table 5.4 to estimate  $\Delta H$  for this reaction, ignoring the fact that water is in the liquid state. (b) Without doing a calculation, predict whether your estimate in part (a) is more negative or less negative than the true reaction enthalpy. (c) Use the enthalpies of formation in Appendix C to determine the true reaction enthalpy.

5.40 (a)

Answers to Self-Assessment Exercise

## 5.9 | Foods and Fuels



Everything we do is connected in one way or another with energy. Without energy, modern society could not function and life itself would not exist. The issues surrounding energy—its sources, production, distribution, consumption, and environmental impact—pervade conversations in science, politics, economics, and public policy.

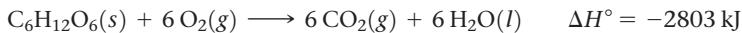
At the end of this section, you should have

- An insight into global energy issues

Most chemical reactions used for the production of heat are combustion reactions. The energy released when one gram of any substance is combusted is the **fuel value** of the substance. The fuel value of any food or fuel can be measured by calorimetry.

## Foods

Most of the energy our bodies need comes from carbohydrates and fats. The carbohydrates known as starches are decomposed in the intestines into glucose,  $C_6H_{12}O_6$ . Glucose is soluble in blood, and in the human body it is known as blood sugar. It is transported by the blood to cells where it reacts with  $O_2$  in a series of steps, eventually producing  $CO_2(g)$ ,  $H_2O(l)$ , and energy:



Because carbohydrates break down rapidly, their energy is quickly supplied to the body. However, the body stores only a very small amount of carbohydrates. The average fuel value of carbohydrates is 17 kJ/g. Although fuel values represent the heat released in a combustion reaction, by convention fuel values are reported as positive numbers.

Like carbohydrates, fats produce  $CO_2$  and  $H_2O$  when metabolized. The reaction of tristearin,  $C_{57}H_{110}O_6$ , a typical fat, is



The body uses the chemical energy from foods to maintain body temperature (see the “Chemistry and Life” box in Section 5.5), to contract muscles, and to construct and repair tissues. Any excess energy is stored as fats. Fats are well suited to serve as the body’s energy reserve for at least two reasons: (1) They are insoluble in water, which facilitates storage in the body, and (2) they produce more energy per gram than either proteins or carbohydrates, which makes them efficient energy sources on a mass basis. The average fuel value of fats is 38 kJ/g.

The combustion of carbohydrates and fats in a bomb calorimeter gives the same products as when they are metabolized in the body. The metabolism of proteins produces less energy than combustion in a calorimeter because the products are different. Proteins contain nitrogen, which is released in the bomb calorimeter as  $N_2$ . In the body this nitrogen ends up mainly as urea,  $(NH_2)_2CO$ . Proteins are used by the body mainly as building materials for organ walls, skin, hair, muscle, and so forth. On average, the metabolism of proteins produces 17 kJ/g, the same as for carbohydrates.

Fuel values for some common foods are shown in **Table 5.5**. Labels on packaged foods show the amounts of carbohydrate, fat, and protein contained in an average serving, as well as the amount of energy supplied by a serving (**Figure 5.25**).

The amount of energy our bodies require varies considerably, depending on such factors as weight, age, and muscular activity. About 100 kJ per kilogram of body mass per day is required to keep the body functioning at a minimal level. An average 70 kg person expends about 800 kJ/h when doing light work, and strenuous activity often requires 2000 kJ/h or more. When the fuel value, or caloric content, of the food we ingest exceeds the energy we expend, our body stores the surplus as fat.

## Go Figure

Which value would change most if this label were for skim milk instead of whole milk: grams of fat, grams of total carbohydrate, or grams of protein?

Vitamin D Milk	
Nutrition Facts	
Serving Size 1 cup (236mL)	
Amount Per Serving	Calories from Fat 70
Calories 150	% Daily Value*
Total Fat 8g	12%
Saturated Fat 5g	25%
Trans Fat 0g	
Cholesterol 35mg	11%
Sodium 125mg	6%
Total Carbohydrate 12g	4%
Dietary Fiber 0g	0%
Sugars 12g	
Protein 8g	
Vitamin A 6% • Vitamin C 4%	
Calcium 30% • Iron 0%	
Vitamin D 25%	
* Percent Daily Values are based on a 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs.	
Total Fat	Less than 65g 80g
Sat Fat	Less than 20g 25g
Cholesterol	Less than 300mg 350mg
Sodium	Less than 2,400mg 2,400mg
Total Carbohydrate	300g 375g
Dietary Fiber	25g 30g
Ingredients: Grade A Pasteurized Milk, Vitamin D3.	



▲ Figure 5.25 Nutrition label for whole milk.

**TABLE 5.5 Compositions and Fuel Values of Some Common Foods**

	Approximate Composition (% by Mass)			Fuel Value
	Carbohydrate	Fat	Protein	kJ/g
Carbohydrate	100	—	—	17
Fat	—	100	—	38
Protein	—	—	100	17
Apples	13	0.5	0.4	2.5
Beer <sup>a</sup>	1.2	—	0.3	1.8
Bread	52	3	9	12
Cheese	4	37	28	20
Eggs	0.7	10	13	6.0
Fudge	81	11	2	18
Green beans	7.0	—	1.9	1.5
Hamburger	—	30	22	15
Milk (whole)	5.0	4.0	3.3	3.0
Peanuts	22	39	26	23

<sup>a</sup> Beer typically contains 3.5% ethanol, which has fuel value.

## Sample Exercise 5.14

### Estimating the Fuel Value of a Food from Its Composition

(a) A 28 g serving of a popular breakfast cereal served with 120 mL of skim milk provides 8 g protein, 26 g carbohydrates, and 2 g fat. Using the average fuel values of these substances, estimate the fuel value of this serving. (b) A person of average weight uses about 420 kJ/km when running or jogging. How many servings of this cereal provide the fuel value requirements to run 3 km?

#### SOLUTION

**Analyze** (a) The fuel value of the serving will be the sum of the fuel values of the protein, carbohydrates, and fat. (b) Here we are faced with the reverse problem, calculating the quantity of food that provides a specific fuel value.

**Plan** (a) We are given the masses of the protein, carbohydrates, and fat contained in a serving. We can use the data in Table 5.4 to convert these masses to their fuel values, which we can sum to get the total fuel value. (b) The problem statement provides a conversion factor between Calories and kilometers. The answer to part (a) provides us with a conversion factor between servings and Calories.

#### Solve

(a)

$$(8 \text{ g protein})\left(\frac{17 \text{ kJ}}{1 \text{ g protein}}\right) + (26 \text{ g carbohydrate})\left(\frac{17 \text{ kJ}}{1 \text{ g carbohydrate}}\right) \\ + (2 \text{ g fat})\left(\frac{38 \text{ kJ}}{1 \text{ g fat}}\right) = 650 \text{ kJ} \text{ (to two significant figures)}$$

(b) We can use these factors in a straightforward dimensional analysis to determine the number of servings needed, rounded to the nearest whole number:

$$\text{Servings} = (3 \text{ km})\left(\frac{420 \text{ kJ}}{1 \text{ km}}\right)\left(\frac{1 \text{ serving}}{650 \text{ kJ}}\right) = 2 \text{ servings}$$

#### ► Practice Exercise

(a) Dry red beans contain 62% carbohydrate, 22% protein, and 1.5% fat. Estimate the fuel value of these beans.

(b) During a very light activity, such as reading or watching television, the average adult expends about 7 kJ/min. How many minutes of such activity can be sustained by the energy provided by a serving of chicken noodle soup containing 13 g protein, 15 g carbohydrate, and 5 g fat?

**TABLE 5.6 Fuel Values and Compositions of Some Common Fuels**

	Approximate Elemental Composition (Mass %)			Fuel Value (kJ/g)
	C	H	O	
Wood (pine)	50	6	44	18
Anthracite coal (Pennsylvania)	82	1	2	31
Bituminous coal (Pennsylvania)	77	5	7	32
Charcoal	100	0	0	34
Crude oil (Texas)	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49
Hydrogen	0	100	0	142

## Fuels

During the complete combustion of fuels, carbon is converted to  $\text{CO}_2$  and hydrogen is converted to  $\text{H}_2\text{O}$ , both of which have large negative enthalpies of formation. Consequently, the greater the percentage of carbon and hydrogen in a fuel, the higher its fuel value. In **Table 5.6**, for example, compare the compositions and fuel values of bituminous coal and wood. The coal has a higher fuel value because of its greater carbon content.

Coal, petroleum, and natural gas, which are the world's major sources of energy, are known as **fossil fuels**. All have formed over millions of years from the decomposition of plants and animals and are being depleted far more rapidly than they are being formed.

**Natural gas** consists of gaseous hydrocarbons, compounds of hydrogen and carbon. It contains primarily methane ( $\text{CH}_4$ ), with small amounts of ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), and butane ( $\text{C}_4\text{H}_{10}$ ). We determined the fuel value of propane in Sample Exercise 5.10. Natural gas burns with far fewer by-products and produces less  $\text{CO}_2$  than either petroleum or coal. **Petroleum** is a liquid composed of hundreds of compounds, most of which are hydrocarbons, with the remainder being chiefly organic compounds containing sulfur, nitrogen, or oxygen. **Coal**, which is solid, contains hydrocarbons of high molecular weight as well as compounds containing sulfur, oxygen, or nitrogen. Coal is the most abundant fossil fuel; current reserves are projected to last for well over 100 years at current consumption rates. However, the use of coal presents a number of problems.

Coal is a complex mixture of substances, and it contains components that cause air pollution. When coal is combusted, the sulfur it contains is converted mainly to sulfur dioxide,  $\text{SO}_2$ , a troublesome air pollutant. Because coal is a solid, recovery from its underground deposits is expensive and often dangerous. Furthermore, coal deposits are not always close to locations of high-energy use, so there are often substantial shipping costs.

Fossil fuels release energy in combustion reactions, which ideally produce only  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The production of  $\text{CO}_2$  has become a major issue that involves science and public policy because of concerns that increasing concentrations of atmospheric  $\text{CO}_2$  are causing global climate changes. We will discuss the environmental aspects of atmospheric  $\text{CO}_2$  in Chapter 18.

## Other Energy Sources

**Nuclear energy** is the energy released in either the fission (splitting) or the fusion (combining) of atomic nuclei. Nuclear energy is, in principle, free of the polluting emissions that are a major problem with fossil fuels. However, nuclear power plants produce radioactive waste products, and their use has therefore been controversial. We will discuss issues related to the production of nuclear energy in Chapter 21.

Fossil fuels and nuclear energy are *nonrenewable* sources of energy—they are limited resources that we are consuming at a much greater rate than they can be regenerated. Eventually these fuels will be expended, although estimates vary greatly as to when this will occur. Because nonrenewable energy sources will eventually be used up, a great deal of research is being conducted on **renewable energy sources**, sources that are essentially

inexhaustible. Renewable energy sources include *solar energy* from the Sun, *wind energy* harnessed by windmills, *geothermal energy* from the heat stored inside Earth, *hydroelectric energy* from flowing rivers, and *biomass energy* from crops and biological waste matter.

Fulfilling our future energy needs will depend on developing technology to harness solar energy with greater efficiency. Solar energy is the world's largest energy source. On a clear day about 1 kJ of solar energy reaches each square meter of Earth's surface every second. Harnessing this energy is difficult because it is dilute (that is, distributed over a wide area) and varies with time of day and weather conditions. The effective use of solar energy will depend on the development of some means of storing and distributing it. One practical way to do this is to use the Sun's energy to drive an endothermic chemical process that can be later reversed to release heat. One such reaction is



This reaction proceeds in the forward direction at high temperatures, which can be obtained in a solar furnace. The CO and H<sub>2</sub> formed in the reaction could then be stored and allowed to react later, with the heat released being put to useful work.

## CHEMISTRY PUT TO WORK

### The Scientific and Political Challenges of Biofuels\*

One of the biggest challenges facing us in the twenty-first century is production of abundant sources of energy, both food and fuels. At the end of 2020, the global population was estimated to be 7.8 billion people, and growing at a rate of about 750 million per decade. A growing world population puts greater demands on the global food supply, especially in Asia and Africa, which together make up more than 75% of the world population.

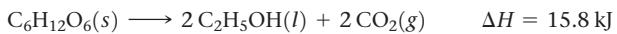
A growing population also increases demands on the production of fuels for transportation, industry, electricity, heating, and cooling. As populous countries such as China and India have modernized, their per capita consumption of energy has increased significantly. In China, for instance, per capita energy consumption roughly doubled between 1990 and 2010.

Global fuel energy consumption in 2012 was more than  $5 \times 10^{17}$  kJ, a staggeringly large number. More than 80% of current energy requirements comes from combustion of nonrenewable fossil fuels, especially coal and petroleum. The exploration of new fossil fuel sources often involves environmentally sensitive regions, making the search for new supplies of fossil fuels a major political and economic issue.

The global importance of petroleum is in large part because it provides liquid fuels, such as gasoline, that are critical to supplying transportation needs. One of the most promising—but controversial—alternatives to petroleum-based fuels is *biofuels*, liquid fuels derived from biological matter. The most common approach to producing biofuels is to transform plant sugars and other carbohydrates into combustible liquids.

The most commonly produced biofuel is *bioethanol*, which is ethanol (C<sub>2</sub>H<sub>5</sub>OH) made from fermentation of plant carbohydrates. The fuel value of ethanol is about two-thirds that of gasoline and is therefore comparable to that of coal (Table 5.6). The United States and Brazil dominate bioethanol production, together supplying 85% of the world's total.

In the United States, nearly all the bioethanol currently produced is made from yellow feed corn. Glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) in the corn is converted to ethanol and CO<sub>2</sub>:



Notice that this reaction is *anaerobic*—it does not involve O<sub>2</sub>(g)—and that the enthalpy change is positive and much smaller in magnitude than for most combustion reactions. Other carbohydrates can be converted to ethanol in similar fashion.

Producing bioethanol from corn is controversial for two main reasons. First, growing and transporting corn are both energy-intensive

processes, and growing it requires the use of fertilizers. It is estimated that the *energy return* on corn-based bioethanol is only 34%—that is, for each 1.00 J of energy expended to produce the corn, 1.34 J of energy is produced in the form of bioethanol. Second, the use of corn as a starting material for making bioethanol competes with its use as an important component of the food chain (the so-called food versus fuel debate).

Much current research focuses on the formation of bioethanol from *cellulosic* plants, plants that contain the complex carbohydrate cellulose. Cellulose is not readily metabolized and so does not compete with the food supply. However, the chemistry for converting cellulose to ethanol is much more complex than that for converting corn. Cellulosic bioethanol could be produced from very fast-growing nonfood plants, such as prairie grasses and switchgrass, which readily renew themselves without the use of fertilizers.

The Brazilian bioethanol industry uses sugarcane as its feedstock (Figure 5.26). Sugarcane grows much faster than corn and without the need for fertilizers or tending. Because of these differences, the energy



**▲ Figure 5.26** Sugarcane can be converted to a sustainable bioethanol product.

\* Data from the *Annual Energy Outlook 2012*, U.S. Energy Information Administration.

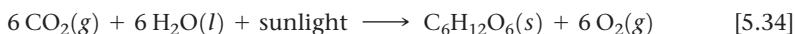
return for sugarcane is much higher than the energy return for corn. It is estimated that for each 1.0 J of energy expended in growing and processing sugarcane, 8.0 J of energy is produced as bioethanol.

Other biofuels that are also becoming a major part of the world economy include *biodiesel*, a substitute for petroleum-derived diesel

fuel. Biodiesel is typically produced from crops that have a high oil content, such as soybeans and canola. It can also be produced from animal fats and waste vegetable oil from the food and restaurant industry.

**Related Exercise: 5.122**

Plants utilize solar energy in *photosynthesis*, the reaction in which the energy of sunlight is used to convert CO<sub>2</sub> and H<sub>2</sub>O into carbohydrates and O<sub>2</sub>:



Photosynthesis is an important part of Earth's ecosystem because it replenishes atmospheric O<sub>2</sub>, produces an energy-rich molecule that can be used as fuel, and consumes some atmospheric CO<sub>2</sub>.

Perhaps the most direct way to use the Sun's energy is to convert it directly into electricity in photovoltaic devices, or *solar cells*, which we mentioned at the beginning of this chapter. The efficiencies of such devices have increased dramatically during the past few years. Technological advances have led to solar panels that last longer and produce electricity with greater efficiency at steadily decreasing unit cost. Indeed, the future of solar energy is, like the Sun itself, very bright.

## SAMPLE INTEGRATIVE EXERCISE

### Putting Concepts Together

Trinitroglycerin, C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>O<sub>9</sub> (usually referred to simply as nitroglycerin), has been widely used as an explosive. Alfred Nobel used it to make dynamite in 1866. Rather surprisingly, it also is used as a medication, to relieve angina (chest pains resulting from partially blocked arteries to the heart) by dilating the blood vessels. At 100 kPa pressure and 25 °C, the enthalpy of decomposition of trinitroglycerin to form nitrogen gas, carbon dioxide gas, liquid water, and oxygen gas is −1541.4 kJ/mol.

- (a) Write a balanced chemical equation for the decomposition of trinitroglycerin.
- (b) Calculate the standard heat of formation of trinitroglycerin.
- (c) A standard dose of trinitroglycerin for relief of angina is 0.60 mg. If the sample is eventually oxidized in the body (not explosively, though!) to nitrogen gas, carbon dioxide gas, and liquid water, what energy is released?
- (d) One common form of trinitroglycerin melts at about 3 °C. From this information and the formula for the substance, would you expect it to be a molecular or ionic compound? Explain.
- (e) Describe the various conversions of forms of energy when trinitroglycerin is used as an explosive to break rockfaces in highway construction.

### SOLUTION

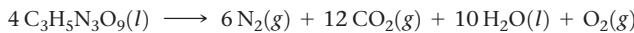
- (a) The general form of the equation we must balance is



We go about balancing in the usual way. To obtain an even number of nitrogen atoms on the left, we multiply the formula for C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>O<sub>9</sub> by 2, which gives us 3 mol of N<sub>2</sub>, 6 mol of CO<sub>2</sub> and 5 mol of H<sub>2</sub>O. Everything is then balanced except for oxygen. We have an odd number of oxygen atoms on the right. We can balance the oxygen by using the coefficient  $\frac{1}{2}$  for O<sub>2</sub> on the right:

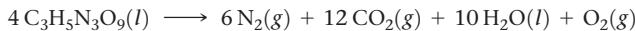


We multiply through by 2 to convert all coefficients to whole numbers:



(At the temperature of the explosion, water is a gas rather than a liquid. The rapid expansion of the gaseous products creates the force of an explosion.)

- (b) We can obtain the standard enthalpy of formation of nitroglycerin by using the heat of decomposition of trinitroglycerin together with the standard enthalpies of formation of the other substances in the decomposition equation:



The enthalpy change for this decomposition is  $4(-1541.4 \text{ kJ}) = -6165.6 \text{ kJ}$ . [We need to multiply by 4 because there are 4 mol of C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>O<sub>9</sub>(l) in the balanced equation.]

This enthalpy change equals the sum of the heats of formation of the products minus the heats of formation of the reactants, each multiplied by its coefficient in the balanced equation:

$$-6165.6 \text{ kJ} = 6\Delta H_f^\circ[\text{N}_2(g)] + 12\Delta H_f^\circ[\text{CO}_2(g)] + 10\Delta H_f^\circ[\text{H}_2\text{O}(l)] + \Delta H_f^\circ[\text{O}_2(g)] - 4\Delta H_f^\circ[\text{C}_3\text{H}_5\text{N}_3\text{O}_9(l)]$$

The  $\Delta H_f^\circ$  values for N<sub>2</sub>(g) and O<sub>2</sub>(g) are zero, by definition. Using the values for H<sub>2</sub>O(l) and CO<sub>2</sub>(g) from Table 5.3 or Appendix C, we have

$$-6165.6 \text{ kJ} = 12(-393.5 \text{ kJ}) + 10(-285.8 \text{ kJ}) - 4\Delta H_f^\circ[\text{C}_3\text{H}_5\text{N}_3\text{O}_9(l)] \quad \Delta H_f^\circ[\text{C}_3\text{H}_5\text{N}_3\text{O}_9(l)] = -353.6 \text{ kJ/mol}$$

- (c) Converting 0.60 mg C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>O<sub>9</sub>(l) to moles and using the fact that the decomposition of 1 mol of C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>O<sub>9</sub>(l) yields 1541.4 kJ we have:

$$(0.60 \times 10^{-3} \text{ g C}_3\text{H}_5\text{N}_3\text{O}_9) \left( \frac{1 \text{ mol C}_3\text{H}_5\text{N}_3\text{O}_9}{227 \text{ g C}_3\text{H}_5\text{N}_3\text{O}_9} \right) \left( \frac{1541.4 \text{ kJ}}{1 \text{ mol C}_3\text{H}_5\text{N}_3\text{O}_9} \right) = 4.1 \times 10^{-3} \text{ kJ} = 4.1 \text{ J}$$

(d) Because trinitroglycerin melts below room temperature, we expect that it is a molecular compound. With few exceptions, ionic substances are generally hard, crystalline materials that melt at high temperatures. Also, the molecular formula suggests that it is a molecular substance because all of its constituent elements are nonmetals.

(e) The energy stored in trinitroglycerin is chemical potential energy. When the substance reacts explosively, it forms carbon dioxide, water, and nitrogen gas, which are of lower potential energy. In the course of the chemical transformation, energy is

released in the form of heat; the gaseous reaction products are very hot. This high heat energy is transferred to the surroundings. Work is done as the gases expand against the surroundings, moving the solid materials and imparting kinetic energy to them. For example, a chunk of rock might be impelled upward. It has been given kinetic energy by transfer of energy from the hot, expanding gases. As the rock rises, its kinetic energy is transformed into potential energy. Eventually, it again acquires kinetic energy as it falls to Earth. When it strikes Earth, its kinetic energy is converted largely to thermal energy, though some work may be done on the surroundings as well.

## Exercises

**5.45** (a) What is meant by the term *fuel value*? (b) Which is a greater source of energy as food, 5 g of fat or 9 g of carbohydrate? (c) The metabolism of glucose produces  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$ . How does the human body expel these reaction products?

**5.46** (a) A serving of a particular ready-to-serve brown & wild rice meal contains 4.5 g fat, 42 g carbohydrate, and 4.0 g protein. Estimate the number of calories in a serving. (b) According to its nutrition label, the same meal also contains 140 mg of potassium ions. Do you think the potassium contributes to the caloric content of the food?

**5.47** The heat of combustion of fructose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is  $-2812 \text{ kJ/mol}$ . If a fresh golden delicious apple weighing 120 g contains 16.0 g of fructose, what caloric content does the fructose contribute to the apple?

**5.48** The standard enthalpies of formation of gaseous propane ( $\text{C}_3\text{H}_8$ ), propene ( $\text{C}_3\text{H}_6$ ), and propane ( $\text{C}_3\text{H}_8$ ) are  $+185.4$ ,  $+20.4$ , and  $-103.8 \text{ kJ/mol}$ , respectively. (a) Calculate the heat evolved per mole on combustion of each substance to yield  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$ . (b) Calculate the heat evolved on combustion of 1 kg of each substance. (c) Which is the most efficient fuel in terms of heat evolved per unit mass?

## Chapter Summary and Key Terms

**CHEMICAL ENERGY (INTRODUCTION AND SECTION 5.1)** Thermodynamics is the study of energy and its transformations. In this chapter we have focused on **thermochemistry**, the transformations of energy—especially heat—during chemical reactions.

An object can possess energy in two forms: (1) **kinetic energy**, which is the energy due to the motion of the object, and (2) **potential energy**, which is the energy that an object possesses by virtue of its position relative to other objects. An electron in motion near a proton has kinetic energy because of its motion and potential energy because of its electrostatic attraction to the proton.

Chemical energy originates largely from electrostatic interactions at the atomic level. Energy must be supplied to break chemical bonds leading to an increase in potential energy. Conversely, energy is released when chemical bonds form as the potential energy decreases.

**THE FIRST LAW OF THERMODYNAMICS (SECTION 5.2)** When we study thermodynamic properties, we define a specific amount of matter as the **system**. Everything outside the system is the **surroundings**. When we study a chemical reaction, the system is generally the reactants and products. A closed system can exchange energy, but not matter, with the surroundings. The **internal energy** of a system is the sum of all the kinetic and potential energies of its component parts. The internal energy of a system can change because of energy transferred between the system and the surroundings.

According to the **first law of thermodynamics**, the change in the internal energy of a system,  $\Delta E$ , is the sum of the heat,  $q$ , transferred into or out of the system and the work,  $w$ , done on or by the system:  $\Delta E = q + w$ . Both  $q$  and  $w$  have a sign that indicates the direction of energy transfer. When heat is transferred from the surroundings to the system,  $q > 0$ . Likewise, when the surroundings do work on the system,  $w > 0$ . In an **endothermic** process the system absorbs heat from the surroundings; in an **exothermic** process the system releases heat to the surroundings.

The internal energy,  $E$ , is a **state function**. The value of any state function depends only on the state or condition of the system and not on the details of how it came to be in that state. Heat,  $q$ , and work,  $w$ , are not state functions; their values depend on the particular way by which a system changes its state.

**ENTHALPY (SECTIONS 5.3 AND 5.4)** When a gas is produced or consumed in a chemical reaction occurring at constant pressure, the system may perform **pressure-volume (P-V) work** against the prevailing pressure of the surroundings. For this reason, we define a new state function called **enthalpy**,  $H$ , which is related to energy:  $H = E + PV$ . In systems where only pressure-volume work is involved, the change in the enthalpy of a system,  $\Delta H$ , equals the heat gained or lost by the system at constant pressure:  $\Delta H = q_p$  (the subscript  $P$  denotes constant pressure). For an endothermic process,  $\Delta H > 0$ ; for an exothermic process,  $\Delta H < 0$ .

In a chemical process, the **enthalpy of reaction** is the enthalpy of the products minus the enthalpy of the reactants:  $\Delta H_{rxn} = H(\text{products}) - H(\text{reactants})$ . Enthalpies of reaction follow some simple rules: (1) The enthalpy of reaction is proportional to the amount of reactant that reacts. (2) Reversing a reaction changes the sign of  $\Delta H$ . (3) The enthalpy of reaction depends on the physical states of the reactants and products.

**CALORIMETRY (SECTION 5.5)** The amount of heat transferred between the system and the surroundings is measured experimentally by **calorimetry**. A **calorimeter** measures the temperature change accompanying a process. The temperature change of a calorimeter depends on its **heat capacity**, the amount of heat required to raise its temperature by 1 K. The heat capacity for one mole of a pure substance is called its **molar heat capacity**; for one gram of the substance, we use the term **specific heat**. Water has a very high specific heat,  $4.18 \text{ J/g K}$ . The amount of heat,  $q$ , absorbed by a substance is the product of its specific heat ( $c$ ), its mass, and its temperature change:  $q = c \times m \times \Delta T$ .

If a calorimetry experiment is carried out under a constant pressure, the heat transferred provides a direct measure of the enthalpy change of the reaction. Constant-volume calorimetry is carried out in a vessel of fixed volume called a **bomb calorimeter**. The heat transferred under constant-volume conditions is equal to  $\Delta E$ . Corrections can be applied to  $\Delta E$  values to yield  $\Delta H$ .

**HESS'S LAW (SECTION 5.6)** Because enthalpy is a state function,  $\Delta H$  depends only on the initial and final states of the system. Thus, the enthalpy change of a process is the same whether the process is carried out in one step or in a series of steps. **Hess's law** states that if a reaction is carried out in a series of steps,  $\Delta H$  for the reaction will be equal to the sum of the enthalpy changes for the steps. We can therefore calculate  $\Delta H$  for any process, as long as we can write the process as a series of steps for which  $\Delta H$  is known.

**ENTHALPIES OF FORMATION (SECTION 5.7)** The **enthalpy of formation**,  $\Delta H_f^\circ$ , of a substance is the enthalpy change for the reaction in which the substance is formed from its constituent elements. Usually, enthalpies are tabulated for reactions where reactants and products are in their *standard states*. The standard state of a substance is its pure, most stable form at 100 kPa and the temperature of interest (usually 298 K). Thus, the **standard enthalpy change** of a reaction,  $\Delta H^\circ$ , is the enthalpy change when all reactants and products are in their standard states. The **standard enthalpy of formation**,  $\Delta H_f^\circ$ , of a substance is the change in enthalpy for the reaction that forms one mole of the substance from its elements in their standard states. For any element in its standard state,  $\Delta H_f^\circ = 0$ .

The standard enthalpy change for any reaction can be readily calculated from the standard enthalpies of formation of the reactants and products in the reaction:

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

**BOND ENTHALPIES (SECTION 5.8)** The strength of a covalent bond is measured by its bond enthalpy, which is the molar enthalpy change required to break a particular bond. Average bond enthalpies can be determined for a wide variety of covalent bonds. We can estimate the enthalpy changes during chemical reactions involving gaseous substances by adding the average bond enthalpies of the bonds that are broken and subtracting the average bond enthalpies of the bonds that are formed. When the energy needed to break bonds is larger than the energy released by forming bonds the reaction enthalpy is positive; when the opposite situation holds the reaction enthalpy is negative.

**FOODS AND FUELS (SECTION 5.9)** The **fuel value** of a substance is the heat released when one gram of the substance is combusted. Different types of foods have different fuel values and differing abilities to be stored in the body. The most common fuels are hydrocarbons that are found as **fossil fuels**, such as **natural gas**, **petroleum**, and **coal**. **Renewable energy sources** include solar energy, wind energy, biomass, and hydroelectric energy. Nuclear power does not utilize fossil fuels but does create controversial waste-disposal problems.

## Learning Outcomes After studying this chapter, you should be able to:

- Describe the changes in potential energy that accompany the formation and breaking of chemical bonds. (Section 5.1) *Related Exercises: 5.3, 5.64*
- Distinguish between the system and the surroundings in thermodynamics. (Section 5.2) *Related Exercises: 5.6, 5.66*
- Calculate internal energy from heat and work and state the sign conventions of these quantities. (Section 5.2) *Related Exercises: 5.8, 5.9, 5.68, 5.69*
- Explain the concept of a state function and give examples. (Section 5.2) *Related Exercises: 5.10, 5.70*
- Calculate  $\Delta H$  from  $\Delta E$  and  $P\Delta V$  (Section 5.3) *Related Exercises: 5.15, 5.74, 5.75*
- Relate  $q_p$  to  $\Delta H$  and indicate how the signs of  $q$  and  $\Delta H$  relate to whether a process is exothermic or endothermic. (Sections 5.2 and 5.3) *Related Exercises: 5.18, 5.78*
- Use thermochemical equations to relate the amount of heat energy transferred in reactions at constant pressure ( $\Delta H$ ) to the amount of substance involved in the reaction. (Section 5.4) *Related Exercises: 5.19, 5.20, 5.79, 5.80*
- Calculate the heat transferred in a process from temperature measurements together with heat capacities or specific heats (calorimetry). (Section 5.5) *Related Exercises: 5.24, 5.81–5.83*
- Use Hess's law to determine enthalpy changes for reactions. (Section 5.6) *Related Exercises: 5.30, 5.31, 5.88, 5.89*
- Use standard enthalpies of formation to calculate  $\Delta H^\circ$  for reactions. (Section 5.7) *Related Exercises: 5.34–5.37*
- Use average bond enthalpies to estimate the reaction enthalpies of reactions where all reactants and products are in the gas phase. (Section 5.8) *Related Exercises: 5.41–5.44*

## Key Equations

• $w = F \times d$	[5.1]	Relates work to force and distance
• $E_{\text{el}} = \kappa Q_1 Q_2 / d$	[5.2]	Electrostatic potential energy.
• $\Delta E = E_{\text{final}} - E_{\text{initial}}$	[5.3]	The change in internal energy
• $\Delta E = q + w$	[5.4]	Relates the change in internal energy to heat and work (the first law of thermodynamics)
• $H = E + PV$	[5.5]	Defines enthalpy
• $w = -P \Delta V$	[5.7]	The work done by an expanding gas at constant pressure
• $\Delta H = \Delta E + P \Delta V = q_p$	[5.9]	Enthalpy change at constant pressure
• $q = C_s \times m \times \Delta T$	[5.21]	Heat gained or lost based on specific heat, mass, and temperature change

•  $q_{rxn} = -C_{cal} \times \Delta T$  [5.23] Heat exchanged between a reaction and calorimeter

•  $\Delta H_{rxn}^\circ = \Sigma n \Delta H_f^\circ(\text{products}) - \Sigma m \Delta H_f^\circ(\text{reactants})$  [5.31] Standard enthalpy change of a reaction

•  $\Delta H_{rxn} = (\text{bond enthalpies of bonds broken}) - (\text{bond enthalpies of bonds formed})$  [5.32] The reaction enthalpy as a function of average bond enthalpies for reactions involving gas-phase molecules.

## Exercises

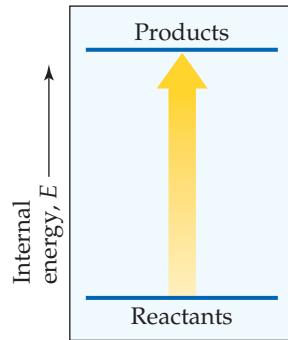
### Visualizing Concepts

- 5.49** Two positively charged spheres, each with a charge of  $2.0 \times 10^{-5}$  C, a mass of 1.0 kg, and separated by a distance of 1.0 cm, are held in place on a frictionless track. (a) What is the electrostatic potential energy of this system? (b) If the spheres are released, will they move toward or away from each other? (c) What speed will each sphere attain as the distance between the spheres approaches infinity? [Section 5.1]

- 5.50** The accompanying photo shows a pipevine swallowtail caterpillar climbing up a twig. (a) As the caterpillar climbs, its potential energy is increasing. What source of energy has been used to effect this change in potential energy? (b) If the caterpillar is the system, can you predict the sign of  $q$  as the caterpillar climbs? (c) Does the caterpillar do work in climbing the twig? Explain. (d) Does the amount of work done in climbing a 30-cm section of the twig depend on the speed of the caterpillar's climb? (e) Does the change in potential energy depend on the caterpillar's speed of climb? [Section 5.1]

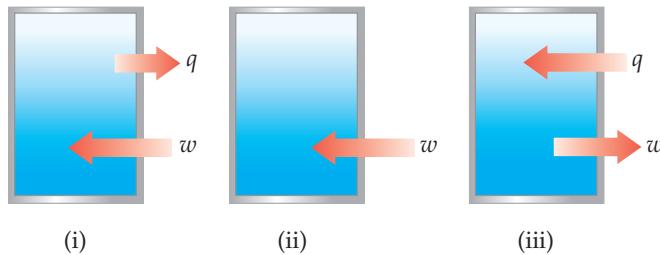


- 5.51** Consider the accompanying energy diagram. (a) Does this diagram represent an increase or decrease in the internal energy of the system? (b) What sign is given to  $\Delta E$  for this process? (c) If there is no work associated with the process, is it exothermic or endothermic? [Section 5.2]



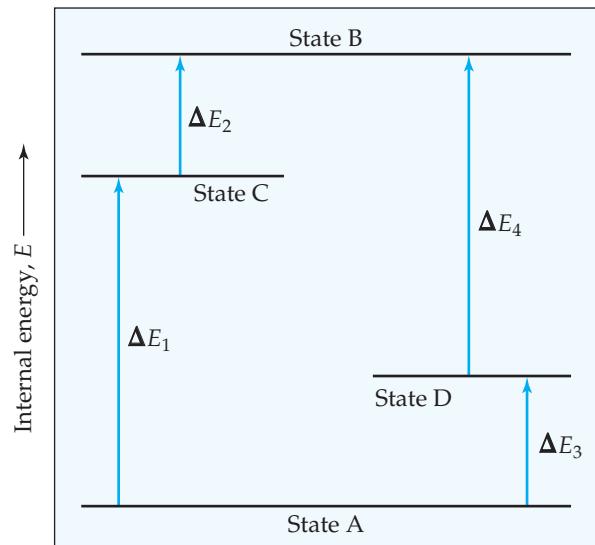
- 5.52** The contents of the closed box in each of the following illustrations represent a system, and the arrows show the changes to the system during some process. The lengths of the arrows represent the relative magnitudes of  $q$  and  $w$ .

- (a) Which of these processes is endothermic? (b) For which of these processes, if any, is  $\Delta E < 0$ ? (c) For which process, if any, does the system experience a net gain in internal energy? [Section 5.2]



- 5.53** Imagine that you are climbing a mountain. (a) Is the distance you travel to the top a state function? (b) Is the change in elevation between your base camp and the peak a state function? [Section 5.2]

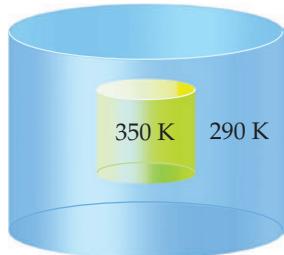
- 5.54** The diagram shows four states of a system, each with different internal energy,  $E$ . (a) Which of the states of the system has the greatest internal energy? (b) In terms of the  $\Delta E$  values, write two expressions for the difference in internal energy between State A and State B. (c) Write an expression for the difference in energy between State C and State D. (d) Suppose there is another state of the system, State E, and its energy relative to State A is  $\Delta E = \Delta E_1 + \Delta E_4$ . Where would State E be on the diagram? [Section 5.2]



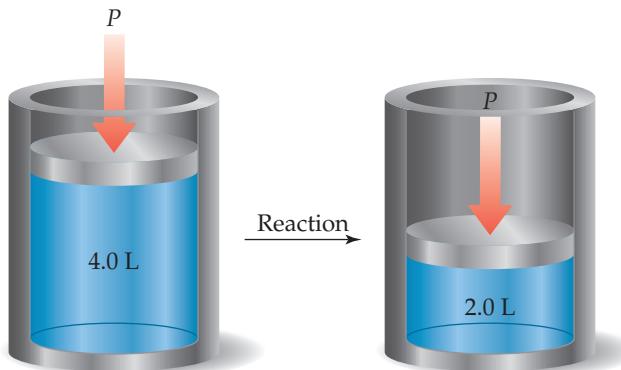
- 5.55** You may have noticed that when you compress the air in a bicycle pump, the body of the pump gets warmer. (a) Assuming the pump and the air in it comprise the system, what is the sign of  $w$  when you compress the air? (b) What is the sign

of  $q$  for this process? (c) Based on your answers to parts (a) and (b), can you determine the sign of  $\Delta E$  for compressing the air in the pump? If not, what would you expect for the sign of  $\Delta E$ ? What is your reasoning? [Section 5.2]

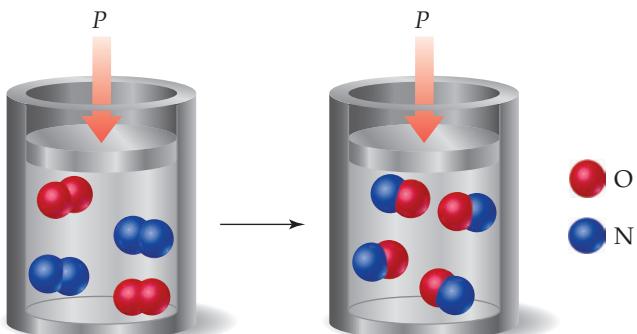
- 5.56** Imagine a container placed in a tub of water, as depicted in the accompanying diagram. (a) If the contents of the container are the system and heat is able to flow through the container walls, what qualitative changes will occur in the temperatures of the system and in its surroundings? From the system's perspective, is the process exothermic or endothermic? (b) If neither the volume nor the pressure of the system changes during the process, how is the change in internal energy related to the change in enthalpy? [Sections 5.2 and 5.3]



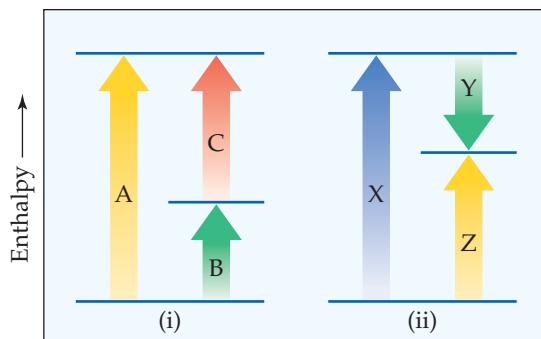
- 5.57** In the accompanying cylinder diagram, a chemical process occurs at constant temperature and pressure. (a) Is the sign of  $w$  indicated by this change positive or negative? (b) If the process is endothermic, does the internal energy of the system within the cylinder increase or decrease during the change and is  $\Delta E$  positive or negative? [Sections 5.2 and 5.3]



- 5.58** The gas-phase reaction shown, between  $N_2$  and  $O_2$ , was run in an apparatus designed to maintain a constant pressure. (a) Write a balanced chemical equation for the reaction depicted and predict whether  $w$  is positive, negative, or zero. (b) Using data from Appendix C, determine  $\Delta H$  for the formation of one mole of the product. [Sections 5.3 and 5.7]



- 5.59** Consider the two diagrams that follow. (a) Based on (i), write an equation showing how  $\Delta H_A$  is related to  $\Delta H_B$  and  $\Delta H_C$ . (b) Based on (ii), write an equation relating  $\Delta H_Z$  to the other enthalpy changes in the diagram. (c) The equations you obtained in parts (a) and (b) are based on what law? (d) Would similar relationships hold for the work involved in each process? [Section 5.6]



- 5.60** Consider the conversion of compound A into compound B:  $A \longrightarrow B$ . For both compounds A and B,  $\Delta H_f^\circ > 0$ . (a) Sketch an enthalpy diagram for the reaction that is analogous to Figure 5.23. (b) Suppose the overall reaction is exothermic. What can you conclude? [Section 5.7]

### The Nature of Chemical Energy (Section 5.1)

- 5.61** (a) What is the electrostatic potential energy (in joules) between two electrons that are separated by 460 pm? (b) What is the change in potential energy if the distance separating the two electrons is increased to 1.0 nm? (c) Does the potential energy of the two particles increase or decrease when the distance is increased to 1.0 nm?

- 5.62** (a) The electrostatic force (not energy) of attraction between two oppositely charged objects is given by the equation  $F = \kappa(Q_1Q_2/d^2)$  where  $\kappa = 8.99 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2$ ,  $Q_1$  and  $Q_2$  are the charges of the two objects in Coulombs, and  $d$  is the distance separating the two objects in meters. What is the electrostatic force of attraction (in Newtons) between an electron and a proton that are separated by 0.23 nm? (b) The force of gravity acting between two objects is given by the equation  $F = G(m_1m_2/d^2)$  where  $G$  is the gravitational constant,  $G = 6.674 \times 10^{-11} \text{ N}\cdot\text{m}^2/\text{kg}^2$ ,  $m_1$  and  $m_2$  are the masses of the two objects, and  $d$  is the distance separating them. What is the gravitational force of attraction (in Newtons) between the electron and proton? (c) How many times larger is the electrostatic force of attraction?

- 5.63** Use the equations given in Exercise 5.62 to calculate: (a) The electrostatic force of repulsion for two electrons separated by 75 pm. (b) The gravitational force of attraction for two electrons separated by 75 pm. (c) If allowed to move, will the electrons be repelled or attracted to one another?

- 5.64** A magnesium ion,  $Mg^{2+}$ , with a charge of  $3.2 \times 10^{-19} \text{ C}$  and an oxide ion,  $O^{2-}$ , with a charge of  $-3.2 \times 10^{-19} \text{ C}$ , are separated by a distance of 0.35 nm. How much work would be required to increase the separation of the two ions to an infinite distance?

- 5.65** Identify the force present and explain whether work is done when (a) an electron moves in a circle at a fixed distance from a proton, (b) an iron nail is attracted by and pulled onto a magnet.

## The First Law of Thermodynamics (Section 5.2)

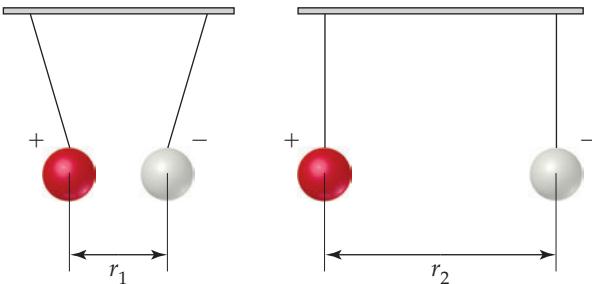
- 5.66** In a thermodynamic study, a scientist focuses on the properties of a solution in an apparatus as illustrated. A solution is continuously flowing into the apparatus at the top and out at the bottom, such that the amount of solution in the apparatus is constant with time. **(a)** Is the solution in the apparatus a closed system, open system, or isolated system? **(b)** If the inlet and outlet were closed, what type of system would it be?



- 5.67** **(a)** Write an equation that expresses the first law of thermodynamics in terms of heat and work. **(b)** Under what conditions will the quantities  $q$  and  $w$  be negative numbers?

- 5.68** For the following processes, calculate the change in internal energy of the system and determine whether the process is endothermic or exothermic: **(a)** A balloon is cooled by removing 0.655 kJ of heat. It shrinks on cooling, and the atmosphere does 382 J of work on the balloon. **(b)** A 100.0 g bar of gold is heated from 25 °C to 50 °C during which it absorbs 322 J of heat. Assume the volume of the gold bar remains constant.

- 5.69** Consider a system consisting of two oppositely charged spheres hanging by strings and separated by a distance  $r_1$ , as shown in the accompanying illustration. Suppose they are separated to a larger distance  $r_2$ , by moving them apart. **(a)** What change, if any, has occurred in the potential energy of the system? **(b)** What effect, if any, does this process have on the value of  $\Delta E$ ? **(c)** What can you say about  $q$  and  $w$  for this process?



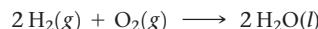
- 5.70** Indicate which of the following is independent of the path by which a change occurs: **(a)** the change in potential energy when a book is transferred from table to shelf, **(b)** the heat evolved when a cube of sugar is oxidized to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$ , **(c)** the work accomplished in burning a gallon of gasoline.

## Enthalpy (Section 5.3 and 5.4)

- 5.71** How much work (in J) is involved in a chemical reaction if the volume decreases from 33.6 L to 11.2 L against a constant pressure of 90.5 kPa?
- 5.72** **(a)** Under what condition will the enthalpy change of a process equal the amount of heat transferred into or out of the system? **(b)** During a constant-pressure process, the system

releases heat to the surroundings. Does the enthalpy of the system increase or decrease during the process? **(c)** In a constant-pressure process,  $\Delta H = 0$ . What can you conclude about  $\Delta E$ ,  $q$ , and  $w$ ?

- 5.73** Assume that 2 moles of water are formed according to the following reaction at constant pressure (100 kPa) and constant temperature (298 K):



**(a)** Calculate the pressure-volume work for this reaction.

**(b)** Calculate  $\Delta E$  for the reaction using your answer to (a).

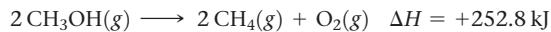
- 5.74** Suppose that the gas-phase reaction  $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}_2(g)$  were carried out in a constant-volume container at constant temperature. **(a)** Would the measured heat change represent  $\Delta H$  or  $\Delta E$ ? **(b)** If there is a difference, which quantity is larger for this reaction? **(c)** Explain your answer to part (b).

- 5.75** A gas is confined to a cylinder under constant atmospheric pressure, as illustrated in Figure 5.4. When 0.49 kJ of heat is added to the gas, it expands and does 214 J of work on the surroundings. What are the values of  $\Delta H$  and  $\Delta E$  for this process?

- 5.76** The decomposition of sodium hydrogen carbonate (baking soda),  $\text{NaHCO}_3(s)$ , into  $\text{Na}_2\text{CO}_3(s)$ ,  $\text{H}_2\text{O}(l)$ , and  $\text{CO}_2(g)$  at constant pressure requires the addition of 85 kJ of heat per two moles of  $\text{NaHCO}_3$ . **(a)** Write a balanced thermochemical equation for the reaction. **(b)** Draw an enthalpy diagram for the reaction.

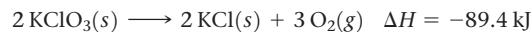
- 5.77** Without referring to tables, predict which of the following has the higher enthalpy in each case: **(a)** 1 mol  $\text{I}_2(s)$  or 1 mol  $\text{I}_2(g)$  at the same temperature, **(b)** 2 mol of iodine atoms or 1 mol of  $\text{I}_2$ , **(c)** 1 mol  $\text{I}_2(g)$  and 1 mol  $\text{H}_2(g)$  at 25 °C or 2 mol  $\text{HI}(g)$  at 25 °C, **(d)** 1 mol  $\text{H}_2(g)$  at 100 °C or 1 mol  $\text{H}_2(g)$  at 300 °C.

- 5.78** Consider the following reaction:



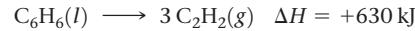
**(a)** Is this reaction exothermic or endothermic? **(b)** Calculate the amount of heat transferred when 24.0 g of  $\text{CH}_3\text{OH}(g)$  is decomposed by this reaction at constant pressure. **(c)** For a given sample of  $\text{CH}_3\text{OH}$ , the enthalpy change during the reaction is 82.1 kJ. How many grams of methane gas are produced? **(d)** How many kilojoules of heat are released when 38.5 g of  $\text{CH}_4(g)$  reacts completely with  $\text{O}_2(g)$  to form  $\text{CH}_3\text{OH}(g)$  at constant pressure?

- 5.79** At one time, a common means of forming small quantities of oxygen gas in the laboratory was to heat  $\text{KClO}_3$ :



For this reaction, calculate  $\Delta H$  for the formation of **(a)** 1.36 mol of  $\text{O}_2$  and **(b)** 10.4 g of  $\text{KCl}$ . **(c)** The decomposition of  $\text{KClO}_3$  proceeds spontaneously when it is heated. Do you think that the reverse reaction, the formation of  $\text{KClO}_3$  from  $\text{KCl}$  and  $\text{O}_2$ , is likely to be feasible under ordinary conditions? Explain your answer.

- 5.80** Consider the decomposition of liquid benzene,  $\text{C}_6\text{H}_6(l)$ , to gaseous acetylene,  $\text{C}_2\text{H}_2(g)$ :



**(a)** What is the enthalpy change for the reverse reaction?

**(b)** What is  $\Delta H$  for the formation of 1 mol of acetylene?

**(c)** Which is more likely to be thermodynamically favored, the forward reaction or the reverse reaction?

**(d)** If  $\text{C}_6\text{H}_6(g)$  were consumed instead of  $\text{C}_6\text{H}_6(l)$ , would you expect the magnitude of  $\Delta H$  to increase, decrease, or stay the same? Explain.

## Calorimetry (Section 5.5)

- 5.81** Two solid objects, A and B, are placed in boiling water and allowed to come to the temperature of the water. Each is then lifted out and placed in separate beakers containing 1000 g of water at 10.0 °C. Object A increases the water temperature by 3.50 °C; B increases the water temperature by 2.60 °C.  
**(a)** Which object has the larger heat capacity? **(b)** What can you say about the specific heats of A and B?
- 5.82** **(a)** Which substance in Table 5.2 requires the smallest amount of energy to increase the temperature of 50.0 g of that substance by 10 K? **(b)** Calculate the energy needed for this temperature change.
- 5.83** Consider the data about gold metal in Exercise 5.68(b).  
**(a)** Based on the data, calculate the specific heat of Au(s).  
**(b)** Suppose that the same amount of heat is added to two 10.0 g blocks of metal, both initially at the same temperature. One block is gold metal, and one is iron metal. Which block will have the greater rise in temperature after the addition of the heat? **(c)** What is the molar heat capacity of Au(s)?
- 5.84** **(a)** When an 8.50 g sample of solid ammonium nitrate ( $\text{NH}_4\text{NO}_3(s)$ ) dissolves in 120.0 g of water in a coffee-cup calorimeter (Figure 5.18), the temperature drops from 24.0 to 18.9 °C. Calculate  $\Delta H$  (in kJ/mol  $\text{NH}_4\text{NO}_3$ ) for the solution process:



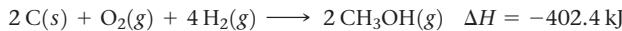
Assume that the specific heat of the solution is the same as that of pure water. **(b)** Is this process endothermic or exothermic?

- 5.85** A 2.20 g sample of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) was burned in a bomb calorimeter whose total heat capacity is 11.90 kJ/°C. The temperature of the calorimeter plus contents increased from 21.50 to 27.50 °C. **(a)** Write a balanced chemical equation for the bomb calorimeter reaction. **(b)** What is the heat of combustion per gram of phenol and per mole of phenol?
- 5.86** Under constant-volume conditions, the heat of combustion of naphthalene ( $\text{C}_{10}\text{H}_8$ ) is 40.18 kJ/g. A 2.50 g sample of naphthalene is burned in a bomb calorimeter. The temperature of the calorimeter increases from 21.50 to 28.83 °C. **(a)** What is the total heat capacity of the calorimeter? **(b)** A 1.50 g sample of a new organic substance is combusted in the same calorimeter. The temperature of the calorimeter increases from 21.14 to 25.08 °C. What is the heat of combustion per gram of the new substance? **(c)** Suppose that in changing samples, a portion of the water in the calorimeter were lost. In what way, if any, would this change the heat capacity of the calorimeter?

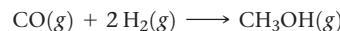
## Hess's Law (Section 5.6)

- 5.87** Can you use an approach similar to Hess's law to calculate the change in internal energy,  $\Delta E$ , for an overall reaction by summing the  $\Delta E$  values of individual reactions that add up to give the desired overall reaction?

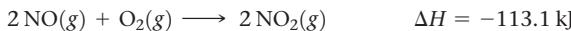
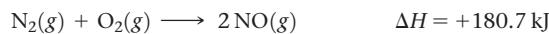
- 5.88** From the enthalpies of reaction



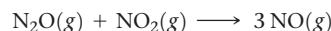
calculate  $\Delta H$  for the reaction



- 5.89** Given the data

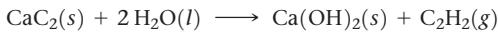


use Hess's law to calculate  $\Delta H$  for the reaction



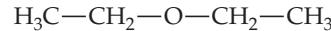
## Enthalpies of Formation (Section 5.7)

- 5.90** **(a)** Why does the standard enthalpy of formation of both the very reactive fluorine ( $\text{F}_2$ ) and the almost inert gas nitrogen ( $\text{N}_2$ ) both read zero? **(b)** Write the chemical equation for the reaction whose enthalpy change is the standard enthalpy of formation of naphthalene ( $\text{C}_{10}\text{H}_8$ ).
- 5.91** Write balanced equations that describe the formation of the following compounds from elements in their standard states, and then look up the standard enthalpy of formation for each substance in Appendix C: **(a)**  $\text{CH}_3\text{OH}(l)$ , **(b)**  $\text{CaSO}_4(s)$ , **(c)**  $\text{NO}(g)$ , **(d)**  $\text{P}_4\text{O}_6(s)$ .
- 5.92** Acetylene ( $\text{C}_2\text{H}_2(g)$ ) is used for welding because oxyacetylene is the hottest burning common fuel gas. Using standard enthalpies of formation, calculate the quantity of heat produced when 10 g of acetylene is completely combusted in air under standard conditions.
- 5.93** Using values from Appendix C, calculate the value of  $\Delta H$  for each of the following reactions:
- (a)**  $\text{CaO}(s) + 2\text{HF}(g) \longrightarrow \text{CaF}_2(s) + \text{H}_2\text{O}(g)$
- (b)**  $\text{Fe}_2\text{O}_3(s) + 3\text{C}(s) \longrightarrow 2\text{Fe}(s) + 3\text{CO}(g)$
- (c)**  $2 \text{CO}(g) + 2 \text{NO}(g) \longrightarrow \text{N}_2(s) + 2 \text{CO}_2(g)$
- (d)**  $4 \text{NH}_3(g) + 5 \text{O}_2(g) \longrightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$
- 5.94** Calcium carbide ( $\text{CaC}_2$ ) reacts with water to form acetylene ( $\text{C}_2\text{H}_2$ ) and  $\text{Ca}(\text{OH})_2$ . From the following enthalpy of reaction data and data in Appendix C, calculate  $\Delta H_f^\circ$  for  $\text{CaC}_2(s)$ :



$$\Delta H^\circ = -127.2 \text{ kJ}$$

- 5.95** Diethyl ether,  $\text{C}_4\text{H}_{10}\text{O}(l)$ , a flammable compound that was once used as a surgical anesthetic, has the structure



The complete combustion of 1 mol of  $\text{C}_4\text{H}_{10}\text{O}(l)$  to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  yields  $\Delta H^\circ = -2723.7 \text{ kJ}$ . **(a)** Write a balanced equation for the combustion of 1 mol of  $\text{C}_4\text{H}_{10}\text{O}(l)$ . **(b)** By using the information in this problem and data in Table 5.3, calculate  $\Delta H_f^\circ$  for diethyl ether.

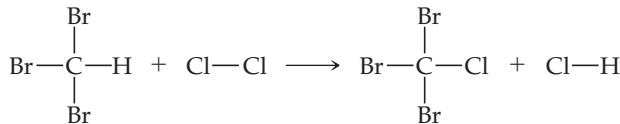
- 5.96** Methanol ( $\text{CH}_3\text{OH}$ ) is used as a fuel in race cars. **(a)** Write a balanced equation for the combustion of liquid methanol in air. **(b)** Calculate the standard enthalpy change for the reaction, assuming  $\text{H}_2\text{O}(g)$  as a product. **(c)** Calculate the heat produced by combustion per liter of methanol. Methanol has a density of 0.791 g/mL. **(d)** Calculate the mass of  $\text{CO}_2$  produced per kJ of heat emitted.

## Bond Enthalpies (Section 5.8)

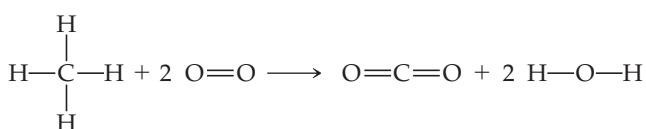
- 5.97** Without doing any calculations, predict the sign of  $\Delta H$  for each of the following reactions:
- (a)**  $2 \text{NO}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$
- (b)**  $2 \text{F}(g) \longrightarrow \text{F}_2(g)$
- (c)**  $\text{Mg}^{2+}(g) + 2 \text{Cl}^-(g) \longrightarrow \text{MgCl}_2(s)$
- (d)**  $\text{HBr}(g) \longrightarrow \text{H}(g) + \text{Br}(g)$

- 5.98** Use bond enthalpies in Table 5.4 to estimate  $\Delta H$  for each of the following reactions:

**(a)**



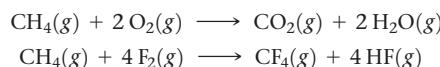
(b)



- 5.99** (a) The nitrogen atoms in an  $\text{N}_2$  molecule are held together by a triple bond; use enthalpies of formation in Appendix C to estimate the enthalpy of this bond,  $D(\text{N}\equiv\text{N})$ . (b) Consider the reaction between hydrazine and hydrogen to produce ammonia,  $\text{N}_2\text{H}_4(g) + \text{H}_2(g) \longrightarrow 2 \text{NH}_3(g)$ . Use enthalpies of formation and bond enthalpies to estimate the enthalpy of the nitrogen–nitrogen bond in  $\text{N}_2\text{H}_4$ . (c) Based on your answers to parts (a) and (b), would you predict that the nitrogen–nitrogen bond in hydrazine is weaker than, similar to, or stronger than the bond in  $\text{N}_2$ ?
- 5.100** Consider the reaction  $\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2 \text{HBr}(g)$ . (a) Use the bond enthalpies in Table 5.4 to estimate  $\Delta H$  for this reaction, ignoring the fact that bromine is in the liquid state. (b) Without doing a calculation, predict whether your estimate in part (a) is more negative or less negative than the true reaction enthalpy. (c) Use the enthalpies of formation in Appendix C to determine the true reaction enthalpy.

## Foods and Fuels (Section 5.9)

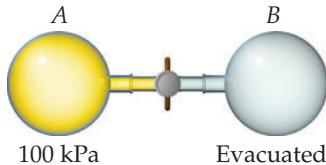
- 5.101** (a) Which releases the most energy when metabolized, 1 g of carbohydrates or 1 g of fat? (b) A particular chip snack food is composed of 12% protein, 14% fat, and the rest carbohydrate. What percentage of the calorie content of this food is fat? (c) How many grams of protein provide the same fuel value as 25 g of fat?
- 5.102** A hamburger contains 28 g fat, 46 g carbohydrate, and 25 g protein. What is the fuel value in kJ in one hamburger? How many calories does it provide?
- 5.103** The heat of combustion of ethanol,  $\text{C}_2\text{H}_5\text{OH}(l)$ , is  $-1367 \text{ kJ/mol}$ . A bottle of stout (dark beer) contains up to 6.0% ethanol by mass. Assuming the density of the beer to be 1.0 g/mL, what is the caloric content due to the alcohol (ethanol) in a bottle of beer (500 mL)?
- 5.104** It is interesting to compare the “fuel value” of a hydrocarbon in a hypothetical world where oxygen is not the combustion agent. The enthalpy of formation of  $\text{CF}_4(g)$  is  $-679.9 \text{ kJ/mol}$ . Which of the following two reactions is the more exothermic?



## Additional Exercises

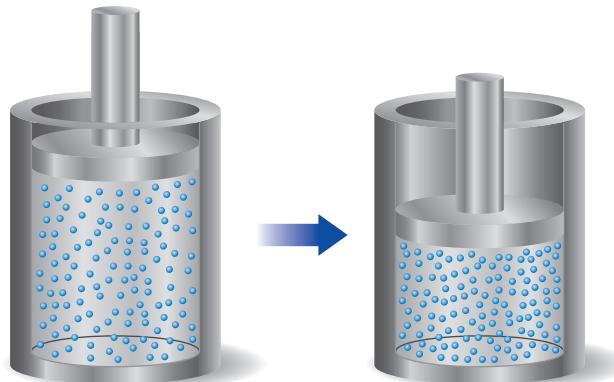
- 5.105** The air bags that provide protection in automobiles in the event of an accident expand because of a rapid chemical reaction. From the viewpoint of the chemical reactants as the system, what do you expect for the signs of  $q$  and  $w$  in this process?

- 5.106** Consider a system consisting of the following apparatus, in which gas is confined in one flask and there is a vacuum in the other flask. The flasks are separated by a valve. Assume that the flasks are perfectly insulated and will not allow the flow of heat into or out of the flasks to the surroundings. When the valve is opened, gas flows from the filled flask to the evacuated one. (a) Is work performed during the expansion of the gas? (b) Why or why not? (c) Can you determine the value of  $\Delta E$  for the process?

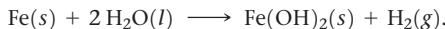


- 5.107** A sample of gas is contained in a cylinder-and-piston arrangement. There is an external pressure of 100 kPa. The gas undergoes the change in state shown in the drawing. (a) Assume first that the cylinder and piston are perfect thermal insulators that do not allow heat to be transferred. What is the value of  $q$  for the state change? What is the sign of  $w$  for the state change? What can be said about  $\Delta E$  for the state change? (b) Now assume that the cylinder and piston are made up of a thermal conductor such as a metal. During the state change, the cylinder gets colder to the touch. What is the sign of  $q$  for the state change in this case? Describe the difference in the state of the system at the end of the process

in the two cases. What can you say about the relative values of  $\Delta E$ ?

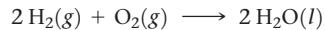


- 5.108** The corrosion (rusting) of iron in oxygen-free water includes the formation of iron(II) hydroxide from iron by the following reaction:



If 1 mol of iron reacts at 298 K under 101.3 kPa pressure, the reaction performs 2.48 kJ of  $P\text{-}V$  work, pushing back the atmosphere as the gaseous  $\text{H}_2$  forms. At the same time, 11.73 kJ of heat is released to the environment. What are the values of  $\Delta H$  and of  $\Delta E$  for this reaction?

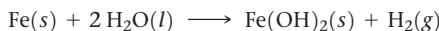
- 5.109** Both oxyhydrogen torches and fuel cells use the following reaction to produce energy:



Both processes occur at constant pressure. In both cases the change in state of the system is the same: the reactant is

oxyhydrogen and the product is water. Yet, with an oxyhydrogen torch, the heat evolved is large and with a fuel cell it is small. If heat at constant pressure is considered to be a state function, why does it depend on path?

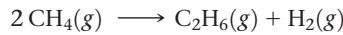
- 5.110** A house is designed to have passive solar energy features. Brickwork incorporated into the interior of the house acts as a heat absorber. Each brick weighs approximately 1.8 kg. The specific heat of the brick is 0.85 J/g K. How many bricks must be incorporated into the interior of the house to provide the same total heat capacity as  $1.7 \times 10^3$  gal of water?
- 5.111** A coffee-cup calorimeter of the type shown in Figure 5.18 contains 150.0 g of water at 25.2 °C. A 200 g block of silver metal is heated to 100.5 °C by putting it in a beaker of boiling water. The specific heat of Ag(s) is 0.233 J/(g K). The Ag is added to the calorimeter, and after some time the contents of the cup reach a constant temperature of 30.2 °C. (a) Determine the amount of heat, in J, lost by the silver block. (b) Determine the amount of heat gained by the water. The specific heat of water is 4.184 J/(g K). (c) The difference between your answers for (a) and (b) is due to heat loss through the Styrofoam® cups and the heat necessary to raise the temperature of the inner wall of the apparatus. The heat capacity of the calorimeter is the amount of heat necessary to raise the temperature of the apparatus (the cups and the stopper) by 1 K. Calculate the heat capacity of the calorimeter in J/K. (d) What would be the final temperature of the system if all the heat lost by the silver block were absorbed by the water in the calorimeter?
- 5.112** (a) When a 0.47 g sample of benzoic acid is combusted in a bomb calorimeter (Figure 5.19), the temperature rises by 3.284 °C. When a 0.53 g sample of caffeine, C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>, is burned, the temperature rises by 3.05 °C. Using the value of 26.38 kJ/g for the heat of combustion of benzoic acid, calculate the heat of combustion per mole of caffeine at constant volume. (b) Assuming that there is an uncertainty of 0.002 °C in each temperature reading and that the masses of samples are measured to 0.001 g, what is the estimated uncertainty in the value calculated for the heat of combustion per mole of caffeine?
- 5.113** The corrosion (rusting) of iron in oxygen-free water includes the formation of iron(II) hydrosulfide from iron by the following reaction:



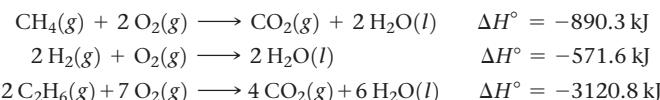
- (a) Calculate the standard enthalpy change for this reaction (the molar enthalpy of formation of Fe(OH)<sub>2</sub> is −583.39 kJ/mol).  
(b) Calculate the number of grams of Fe needed to release enough energy to increase the temperature of 250 mL of water from 22 to 30 °C.

- 5.114** Burning acetylene in oxygen can produce three different carbon-containing products: soot (very fine particles of graphite), CO(g), and CO<sub>2</sub>(g). (a) Write three balanced equations for the reaction of acetylene gas with oxygen to produce these three products. In each case assume that H<sub>2</sub>O(l) is the only other product. (b) Determine the standard enthalpies for the reactions in part (a). (c) Why, when the oxygen supply is adequate, is CO<sub>2</sub>(g) the predominant carbon-containing product of the combustion of acetylene?

- 5.115** We can use Hess's law to calculate enthalpy changes that cannot be measured. One such reaction is the conversion of methane to ethane:



Calculate the ΔH° for this reaction using the following thermochemical data:



- 5.116** From the following data for three prospective fuels, calculate which could provide the most energy per unit mass and per unit volume:

Fuel	Density at 101.3 kPa (g/cm <sup>3</sup> )	Molar Enthalpy of Combustion (MJ/mol)
Octane, C <sub>8</sub> H <sub>18</sub> (l)	0.70 at 20 °C	−5.53
Liquid Butane, C <sub>4</sub> H <sub>10</sub> (l)	0.60 at −1 °C	−2.88
Liquid hydrogen, H <sub>2</sub> (l)	0.07 at −253 °C	−0.29

- 5.117** The hydrocarbons cyclohexane (C<sub>6</sub>H<sub>12</sub>(l), ΔH° = −156 kJ/mol) and 1-hexene (C<sub>6</sub>H<sub>12</sub>(l), ΔH° = −74 kJ/mol) have the same empirical formula. (a) Calculate the standard enthalpy change for the transformation of cyclohexane to 1-hexene. (b) Which has greater enthalpy, cyclohexane or 1-hexene? (c) Without doing a further calculation and knowing the answer to (b), do you expect cyclohexane or 1-hexene to have the larger combustion enthalpy?

- 5.118** Butane C<sub>4</sub>H<sub>10</sub>(l) boils at −0.5 °C; at this temperature it has a density of 0.60 g/cm<sup>3</sup>. The enthalpy of formation of C<sub>4</sub>H<sub>10</sub>(g) is −124.7 kJ/mol, and the enthalpy of vaporization of C<sub>4</sub>H<sub>10</sub>(l) is 22.44 kJ/mol. Calculate the enthalpy change when 1 L of liquid C<sub>4</sub>H<sub>10</sub>(l) is burned in air to give CO<sub>2</sub>(g) and H<sub>2</sub>O(g). How does this compare with ΔH for the complete combustion of 1 L of liquid methanol, CH<sub>3</sub>OH(l)? For CH<sub>3</sub>OH(l), the density at 25 °C is 0.792 g/cm<sup>3</sup>, and ΔH° = −239 kJ/mol.

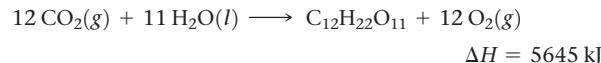
- 5.119** Three hydrocarbons that contain four carbons are listed here, along with their standard enthalpies of formation:

Hydrocarbon	Formula	ΔH° (kJ/mol)
Butane	C <sub>4</sub> H <sub>10</sub> (g)	−125
1-Butene	C <sub>4</sub> H <sub>8</sub> (g)	−1
1-Butyne	C <sub>4</sub> H <sub>6</sub> (g)	165

- (a) For each of these substances, calculate the molar enthalpy of combustion to CO<sub>2</sub>(g) and H<sub>2</sub>O(l). (b) Calculate the fuel value, in kJ/g, for each of these compounds. (c) For each hydrocarbon, determine the percentage of hydrogen by mass. (d) By comparing your answers for parts (b) and (c), propose a relationship between hydrogen content and fuel value in hydrocarbons.

- 5.120** A 100-kg man decides to add to his exercise routine by walking up six flights of stairs (30 m) 10 times per day. He figures that the work required to increase his potential energy in this way will permit him to eat an extra order of French fries, at 245 Cal, without adding to his weight. Is he correct in this assumption?

- 5.121** Sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) is produced by plants as follows:



About 4.8 g of sucrose is produced per day per square meter of the earth's surface. The energy for this endothermic reaction is supplied by the sunlight. About 0.1% of the sunlight that reaches the earth is used to produce sucrose. Calculate the

total energy the sun supplies for each square meter of surface area. Give your answer in kilowatts per square meter ( $\text{kW}/\text{m}^2$  where  $1\text{W} = 1\text{J/s}$ ).

- 5.122** It is estimated that the net amount of carbon dioxide fixed by photosynthesis on the landmass of Earth is  $5.5 \times 10^{16}\text{ g/yr}$  of  $\text{CO}_2$ . Assume that all this carbon is converted into glucose.

(a) Calculate the energy stored by photosynthesis on land per year, in kJ. (b) Calculate the average rate of conversion of solar energy into plant energy in megawatts, MW ( $1\text{W} = 1\text{J/s}$ ). A large nuclear power plant produces about  $10^3\text{ MW}$ . The energy of how many such nuclear power plants is equivalent to the solar energy conversion?

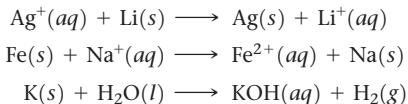
## Integrative Exercises

- 5.123** At  $25^\circ\text{C}$  (approximately room temperature) the rms velocity of an Ar atom in air is 1553 km/h. (a) What is the rms speed in m/s? (b) What is the kinetic energy (in J) of an Ar atom moving at this speed? (c) What is the total kinetic energy of 1 mol of Ar atoms moving at this speed?

- 5.124** Suppose an Olympic diver who weighs 52.0 kg executes a straight dive from a 10-m platform. At the apex of the dive, the diver is 10.8 m above the surface of the water. (a) What is the potential energy of the diver at the apex of the dive, relative to the surface of the water? (b) Assuming that all the potential energy of the diver is converted into kinetic energy at the surface of the water, at what speed, in m/s, will the diver enter the water? (c) Does the diver do work on entering the water? Explain.

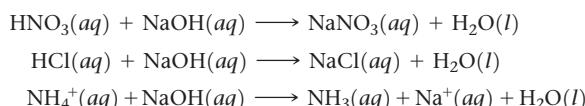
- 5.125** Consider the combustion of a single molecule of  $\text{CH}_4(g)$ , forming  $\text{H}_2\text{O}(l)$  as a product. (a) How much energy, in J, is produced during this reaction? (b) A typical X-ray light source has an energy of 8 keV (see inside back cover for conversion between eV and J). Is the energy released by the combustion of a  $\text{CH}_4$  molecule larger or smaller than the energy of an X-ray from this source?

- 5.126** Consider the following unbalanced oxidation-reduction reactions in aqueous solution:



(a) Balance each of the reactions. (b) By using data in Appendix C, calculate  $\Delta H^\circ$  for each of the reactions. (c) Based on the values you obtain for  $\Delta H^\circ$ , which of the reactions would you expect to be thermodynamically favored? (d) Use the activity series to predict which of these reactions should occur. Are these results in accord with your conclusion in part (c) of this problem?

- 5.127** Consider the following acid-neutralization reactions involving the strong base  $\text{NaOH}(aq)$ :



(a) By using data in Appendix C, calculate  $\Delta H^\circ$  for each of the reactions. (b) As we saw in Section 4.3, nitric acid and hydrochloric acid are strong acids. Write net ionic equations for the neutralization of these acids. (c) Compare the values of  $\Delta H^\circ$  for the first two reactions. What can you conclude? (d) In the third equation  $\text{NH}_4^+(aq)$  is acting as an acid. Based on the value of  $\Delta H^\circ$  for this reaction, do you think it is a strong or a weak acid? Explain.

- 5.128** Consider two solutions, the first being 50.0 mL of  $1.00\text{ M CuSO}_4$  and the second 50.0 mL of  $2.00\text{ M KOH}$ . When the two solutions are mixed in a constant-pressure calorimeter, a precipitate forms and the temperature of the mixture rises from  $21.5$  to  $27.7^\circ\text{C}$ . (a) Before mixing, how many grams of Cu are present in the solution of  $\text{CuSO}_4$ ? (b) Predict the identity of the precipitate in the reaction. (c) Write complete and net ionic equations for the reaction that occurs when the two solutions are mixed. (d) From the calorimetric data, calculate  $\Delta H$  for the reaction that occurs on mixing. Assume that the calorimeter absorbs only a negligible quantity of heat, that the total volume of the solution is 100.0 mL, and that the specific heat and density of the solution after mixing are the same as those of pure water.

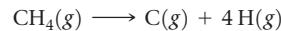
- 5.129** The precipitation reaction between  $\text{AgNO}_3(aq)$  and  $\text{NaCl}(aq)$  proceeds as follows:



(a) By using data in Appendix C, calculate  $\Delta H^\circ$  for the net ionic equation of this reaction. (b) What would you expect for the value of  $\Delta H^\circ$  of the overall molecular equation compared to that for the net ionic equation? Explain. (c) Use the results from (a) and (b) along with data in Appendix C to determine the value of  $\Delta H_f^\circ$  for  $\text{AgNO}_3(aq)$ .

- 5.130** A sample of a hydrocarbon is combusted completely in  $\text{O}_2(g)$  to produce 21.83 g  $\text{CO}_2(g)$ , 4.47 g  $\text{H}_2\text{O}(g)$ , and 311 kJ of heat. (a) What is the mass of the hydrocarbon sample that was combusted? (b) What is the empirical formula of the hydrocarbon? (c) Calculate the value of  $\Delta H_f^\circ$  per empirical-formula unit of the hydrocarbon. (d) Do you think that the hydrocarbon is one of those listed in Appendix C? Explain your answer.

- 5.131** The methane molecule,  $\text{CH}_4$ , has the geometry shown in Figure 2.15. Imagine a hypothetical process in which the methane molecule is “expanded,” by simultaneously extending all four C—H bonds to infinity. We then have the process



(a) Compare this process with the reverse of the reaction that represents the standard enthalpy of formation of  $\text{CH}_4(g)$ . (b) Calculate the enthalpy change in each case. Which is the more endothermic process? What accounts for the difference in  $\Delta H^\circ$  values? (c) Suppose that 3.45 g  $\text{CH}_4(g)$  reacts with 1.22 g  $\text{F}_2(g)$ , forming  $\text{CF}_4(g)$  and  $\text{HF}(g)$  as sole products. What is the limiting reagent in this reaction? If the reaction occurs at constant pressure, what amount of heat is evolved?

## Design an Experiment

One of the important ideas of thermodynamics is that energy can be transferred in the form of heat or work. Imagine that you lived 180 years ago when the relationships between heat and work were not well understood. You have formulated a hypothesis that work can be converted to heat with the same amount of work always generating the same amount of heat. To test this idea, you have designed an experiment using a device in which a falling weight is connected through pulleys to a shaft with an attached paddle wheel that is immersed in water. This is actually a classic experiment performed by James Joule in the 1840s. You can see various images of Joule's apparatus by searching the internet for "Joule experiment images."

- (a) Using this device, what measurements would you need to make to test your hypothesis? (b) What equations would you use in analyzing your experiment? (c) Do you think you could obtain a reasonable result from a single experiment? Why or why not? (d) In what way could the precision of your instruments affect the conclusions that you make? (e) List ways that you could modify the equipment to improve the data you obtain if you were performing this experiment today instead of 180 years ago. (f) Give an example of how you could demonstrate the relationship between heat and a form of energy other than mechanical work.