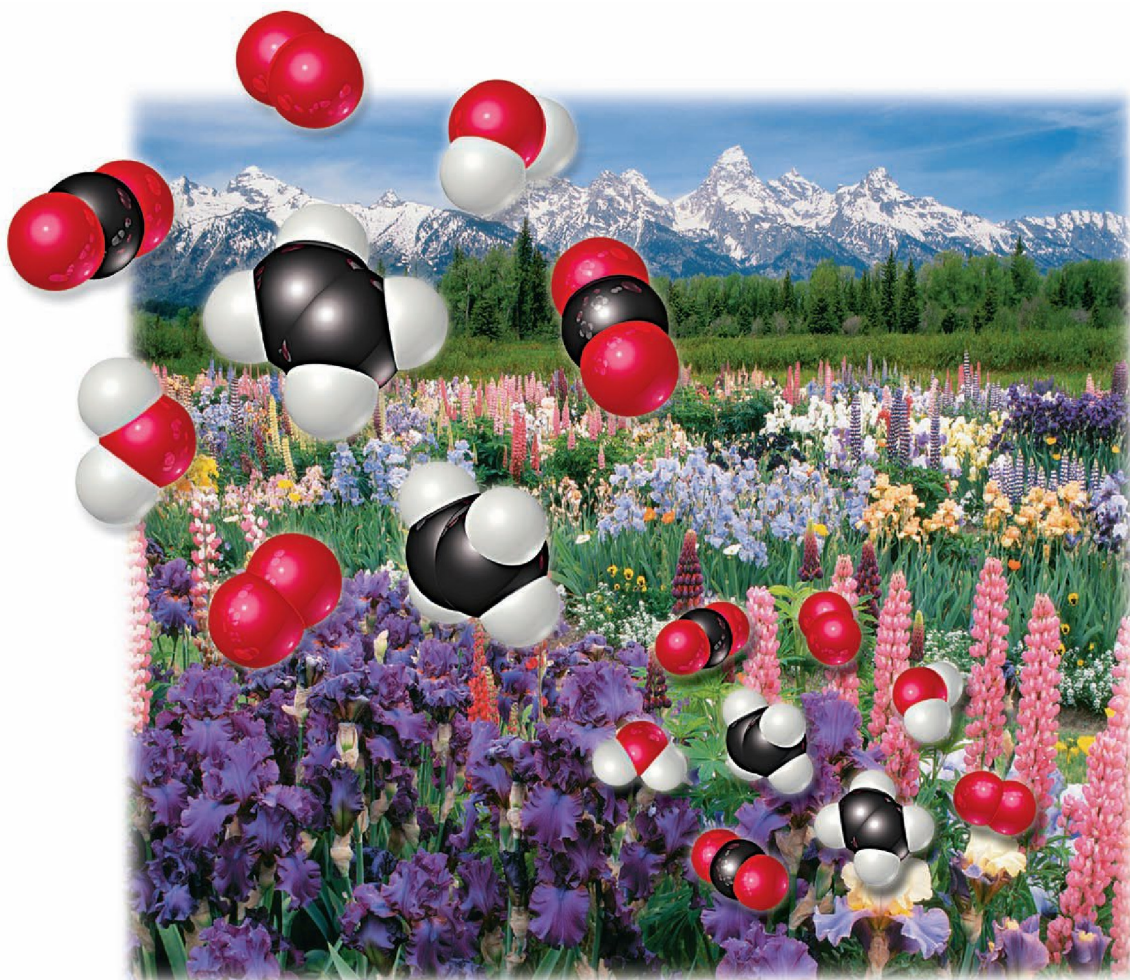


CHAPTER
5

THERMOCHEMISTRY



WILDFLOWERS. Plants use solar energy to carry out photosynthesis of carbohydrates, which provide the energy needed for plant growth. Among the molecules produced by plants are O₂ and ethylene, C₂H₄.

5.1 The Nature of Energy

We begin by considering the nature of *energy* and the forms it takes, notably *kinetic energy* and *potential energy*. We will also discuss the units used in measuring energy and the fact that energy can be used to accomplish *work* or to transfer *heat*. To study energy changes, we focus on a particular part of the universe, which we call the *system*. Everything else is called the *surroundings*.

5.2 The First Law of Thermodynamics

We will then explore the *first law of thermodynamics*: Energy cannot be created or destroyed, but it can be transformed from one form to another or transferred between systems and surroundings. The energy possessed by a system is called its *internal energy*. Internal energy, E , is a *state function*, a quantity whose value depends only on the state, or condition, of a system now, not on how the system came to be in that state.

5.3 Enthalpy

Next, we will encounter a state function called *enthalpy*, H , that relates to energy. This function is useful because the change in enthalpy, ΔH , measures the quantity of heat energy gained or lost by a system in a process occurring under a constant pressure.

5.4 Enthalpies of Reaction

We will see that the enthalpy change associated with a chemical reaction (ΔH_{rxn}) is given by the enthalpies of the products minus the enthalpies of the reactants. This quantity is directly proportional to the amount of reactant consumed in the process.

5.5 Calorimetry

We will next examine *calorimetry*, which is an experimental technique that we use to measure heat changes in chemical processes.

5.6 Hess's Law

We will observe that the enthalpy change for a reaction can be calculated using appropriate enthalpy changes for other reactions. To do so, we apply *Hess's law*, which uses the fact that enthalpy, like energy, is a state function.

5.7 Enthalpies of Formation

Then we will discuss how to establish standard values for enthalpy changes in chemical reactions and how to use them to calculate enthalpy changes for reactions (ΔH_{rxn}).

5.8 Foods and Fuels

Finally, we will examine foods and fuels as sources of energy and discuss some related health and social issues.

MODERN SOCIETY DEPENDS ON ENERGY for its existence.

Energy is used to drive our machinery and appliances, to power our transportation vehicles, and to keep us warm in the winter and cool in the summer. It is not just modern society, however, that depends on energy. Energy is

necessary for all life. Plants, such as those in the chapter-opening photograph, use solar energy to carry out photosynthesis, allowing the plants to grow. The plants, in turn, provide food, from which we humans derive the energy we need to move, to maintain body temperature, and to carry out bodily functions. What exactly is energy, though, and what principles are involved in its many transactions and transformations, such as those from the sun to plants to animals?

In this chapter we begin to explore energy and its changes. We are motivated partly by the fact that energy changes invariably accompany chemical reactions. Indeed, sometimes we use a chemical reaction specifically to obtain energy, as when we burn fuels. Thus, energy is very much a chemical topic. Nearly all of the energy on which we depend is derived from chemical reactions, whether those reactions are associated with the combustion of fuels, the discharge of a battery, or the metabolism of our foods. If we are to properly

understand chemistry, we must also understand the energy changes that accompany chemical reactions.

The study of energy and its transformations is known as **thermodynamics** (Greek: *thérme-*, “heat”; *dy’namis*, “power”). In this chapter we will examine an aspect of thermodynamics that involves the relationships between chemical reactions and energy changes involving heat. This portion of thermodynamics is called **thermochemistry**. We will discuss additional aspects of thermodynamics in Chapter 19.

5.1 THE NATURE OF ENERGY

Although the idea of energy is a familiar one, it is a bit challenging to deal with the concept in a precise way. **Energy** is commonly defined as *the capacity to do work or to transfer heat*. This definition requires us to understand the concepts of work and heat. We can think of **work** as *the energy used to cause an object with mass to move against a force* and **heat** as *the energy used to cause the temperature of an object to increase* (Figure 5.1 ◀). We will consider each of these concepts more closely to give them fuller meaning. Let’s begin by examining the ways in which matter can possess energy and how that energy can be transferred from one piece of matter to another.

Kinetic Energy and Potential Energy

Objects, whether they are tennis balls or molecules, can possess **kinetic energy**, the energy of *motion*. The magnitude of the kinetic energy, E_k , of an object depends on its mass, m , and speed, v :

$$E_k = \frac{1}{2}mv^2 \quad [5.1]$$

Equation 5.1 shows that the kinetic energy increases as the speed of an object increases. For example, a car moving at 55 miles per hour (mph) has greater kinetic energy than it does at 40 mph. For a given speed the kinetic energy increases with increasing mass. Thus, a large sport-utility vehicle traveling at 55 mph has greater kinetic energy than a small sedan traveling at the same speed because the SUV has greater mass than the sedan. Atoms and molecules have mass and are in motion. They therefore possess kinetic energy.

All other kinds of energy—the energy stored in chemical bonds, the energy of attraction of north and south poles of magnets, for example—are potential energy. An object can possess **potential energy** by virtue of its *position* relative to other objects. Potential energy arises when a force operates on an object. A **force** is any kind of push or pull exerted on an object. The most familiar force is the pull of gravity. Think of a cyclist poised at the top of a hill, as illustrated in Figure 5.2 ▼. Gravity acts upon her and her bicycle, exerting a force directed toward the center of Earth. At the top of the hill the cyclist and her bicycle possess a certain potential energy by virtue of their elevation. The potential energy, E_p ,

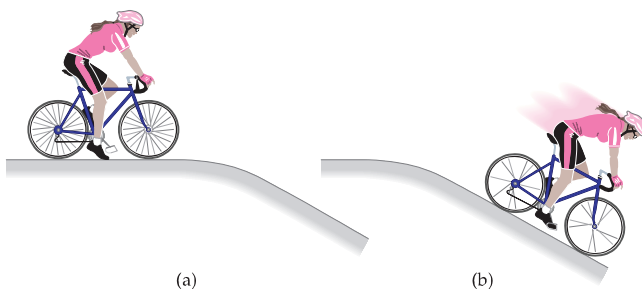


(a)



(b)

▲ **Figure 5.1 Work and heat.** Energy can be used to achieve two basic types of tasks: (a) Work is energy used to cause an object with mass to move. (b) Heat is energy used to cause the temperature of an object to increase.



(a)

(b)

► **Figure 5.2 Potential energy and kinetic energy.** (a) A bicycle at the top of a hill has a high potential energy relative to the bottom of the hill. (b) As the bicycle proceeds down the hill, the potential energy is converted into kinetic energy.

is given by the equation $E_p = mgh$, where m is the mass of the object in question (in this case the cyclist and her bicycle), h is the height of the object relative to some reference height, and g is the gravitational constant, 9.8 m/s^2 . Once in motion, without any further effort on her part, the cyclist gains speed as the bicycle rolls down the hill. Her potential energy decreases as she moves downward, but the energy does not simply disappear. It is converted to other forms of energy, principally kinetic energy, the energy of motion. This example illustrates that forms of energy are interconvertible.

Gravity is an important force for large objects, such as the cyclist and Earth. Chemistry, however, deals mostly with extremely small objects—atoms and molecules. Gravitational forces play a negligible role in the ways these submicroscopic objects interact with one another. Forces that arise from electrical charges are more important when dealing with atoms and molecules.

One of the most important forms of potential energy in chemistry is *electrostatic potential energy*, which arises from the interactions between charged particles. The electrostatic potential energy, E_{el} , is proportional to the electrical charges on the two interacting objects, Q_1 and Q_2 , and is inversely proportional to the distance separating them:

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

Here κ is simply a constant of proportionality, $8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$. (C is the coulomb, a unit of electrical charge ∞ (Section 2.2), and J is the joule, a unit of energy that we will soon discuss.) When dealing with molecular-level objects, the electrical charges Q_1 and Q_2 are typically on the order of magnitude of the charge of the electron ($1.60 \times 10^{-19} \text{ C}$). When Q_1 and Q_2 have the same sign (for example, both are positive), the two charges repel one another, pushing them apart; E_{el} is positive. When they have opposite signs, they attract one another, pulling them toward each other; E_{el} is negative. The lower the energy of a system, the more stable it is. Thus, the more strongly opposite charges interact, the more stable the system.

One of our goals in chemistry is to relate the energy changes that we see in our macroscopic world to the kinetic or potential energy of substances at the atomic or molecular level. Many substances—fuels, for example—release energy when they react. The *chemical energy* of these substances is due to the potential energy stored in the arrangements of their atoms. Likewise, we will see that the energy a substance possesses because of its temperature (its *thermal energy*) is associated with the kinetic energy of the molecules in the substance.

GIVE IT SOME THOUGHT

What are the terms for the energy an object possesses (a) because of its motion, (b) because of its position? What terms are used to describe changes of energy associated with (c) temperature changes, (d) moving an object against a force?

Units of Energy

The SI unit for energy is the **joule** (pronounced “jool”), J, in honor of James Joule (1818–1889), a British scientist who investigated work and heat: $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$. A mass of 2 kg moving at a speed of 1 m/s possesses a kinetic energy of 1 J:

$$E_k = \frac{1}{2} mv^2 = \frac{1}{2}(2 \text{ kg})(1 \text{ m/s})^2 = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 1 \text{ J}$$

A joule is not a large amount of energy, and we will often use *kilojoules* (kJ) in discussing the energies associated with chemical reactions.

Traditionally, energy changes accompanying chemical reactions have been expressed in calories, a non-SI unit still widely used in chemistry, biology, and biochemistry. A **calorie** (cal) was originally defined as the amount of energy

required to raise the temperature of 1 g of water from 14.5 °C to 15.5 °C. A calorie is now defined in terms of the joule:

$$1 \text{ cal} = 4.184 \text{ J (exactly)}$$

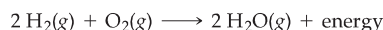
A related energy unit used in nutrition is the nutritional *Calorie* (note that this unit is capitalized): 1 Cal = 1000 cal = 1 kcal.

System and Surroundings

When we analyze energy changes, we need to focus our attention 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 the 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. A boiling pot of water on a stove, without its lid, 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*. A closed system can exchange energy but not matter with its surroundings. For example, consider a mixture of hydrogen gas, H₂, and oxygen gas, O₂, in a cylinder, as illustrated in Figure 5.3 ◀. The system in this case is just the hydrogen and oxygen; the cylinder, piston, and everything beyond them (including us) are the surroundings. If the hydrogen and oxygen 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; it undergoes no exchange of 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.



▲ **Figure 5.3 A closed system and its surroundings.** Hydrogen and oxygen gases are confined in a cylinder with a movable piston. If we are interested only in the properties of these gases, the gases are the system and the cylinder and piston are part of the surroundings. Because the system can exchange energy (in the form of heat and work) but not matter with its surroundings, it is a closed system.

GIVE IT SOME THOUGHT

Is a human being an isolated, closed, or open system? Explain your choice.

Transferring Energy: Work and Heat

Figure 5.1 illustrates the two ways that we experience energy changes in our everyday lives—in the form of work or heat. In Figure 5.1(a) energy is transferred from the tennis racquet to the ball, changing the direction and speed of the ball's movement. In Figure 5.1(b) energy is transferred in the form of heat. Indeed, energy is transferred between systems and surroundings in two general ways, as work or heat.

Energy used to cause an object to move against a force is called *work*. Thus, we can define work, *w*, as the energy transferred when a force moves an object. The magnitude of this work equals the product of the force, *F*, and the distance, *d*, that the object is moved:

$$w = F \times d \quad [5.3]$$

We perform work, for example, when we lift an object against the force of gravity or when we bring two like charges closer together. If we define the object as the system, then we—as part of the surroundings—are performing work on that system, transferring energy to it.

The other way in which energy is transferred is as heat. *Heat* is the energy transferred from a hotter object to a colder one. Or stating this idea in a slightly more abstract but nevertheless useful way, heat is the energy transferred between a system and its surroundings because of their difference in temperature. A combustion reaction, such as the burning of natural gas illustrated in Figure 5.1(b), releases the chemical energy stored in the molecules of the fuel. ∞ (Section 3.2) If we define the substances involved in the reaction as the system and everything else as the surroundings, we find that the released energy causes the temperature of the system to increase. Energy in the form of heat is then transferred from the hotter system to the cooler surroundings.

SAMPLE EXERCISE 5.1 | Describing and Calculating Energy Changes

A bowler lifts a 5.4-kg (12-lb) bowling ball from ground level to a height of 1.6 m (5.2 feet) and then drops the ball back to the ground. (a) What happens to the potential energy of the bowling ball as it is raised from the ground? (b) What quantity of work, in J, is used to raise the ball? (c) After the ball is dropped, it gains kinetic energy. If we assume that all of the work done in part (b) has been converted to kinetic energy by the time the ball strikes the ground, what is the speed of the ball at the instant just before it hits the ground? (Note: The force due to gravity is $F = m \times g$, where m is the mass of the object and g is the gravitational constant; $g = 9.8 \text{ m/s}^2$.)

SOLUTION

Analyze: We need to relate the potential energy of the bowling ball to its position relative to the ground. We then need to establish the relationship between work and the change in potential energy of the ball. Finally, we need to connect the change in potential energy when the ball is dropped with the kinetic energy attained by the ball.

Plan: We can calculate the work done in lifting the ball by using Equation 5.3: $w = F \times d$. The kinetic energy of the ball at the moment of impact equals its initial potential energy. We can use the kinetic energy and Equation 5.1 to calculate the speed, v , at impact.

Solve:

(a) Because the bowling ball is raised to a greater height above the ground, its potential energy increases.

(b) The ball has a mass of 5.4 kg, and it is lifted a distance of 1.6 m. To calculate the work performed to raise the ball, we use both Equation 5.3 and $F = m \times g$ for the force that is due to gravity:

$$w = F \times d = m \times g \times d = (5.4 \text{ kg})(9.8 \text{ m/s}^2)(1.6 \text{ m}) = 85 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 85 \text{ J}$$

Thus, the bowler has done 85 J of work to lift the ball to a height of 1.6 m.

(c) When the ball is dropped, its potential energy is converted to kinetic energy. At the instant just before the ball hits the ground, we assume that the kinetic energy is equal to the work done in part (b), 85 J:

$$E_k = \frac{1}{2}mv^2 = 85 \text{ J} = 85 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

We can now solve this equation for v :

$$v^2 = \left(\frac{2E_k}{m}\right) = \left(\frac{2(85 \text{ kg}\cdot\text{m}^2/\text{s}^2)}{5.4 \text{ kg}}\right) = 31.5 \text{ m}^2/\text{s}^2$$

$$v = \sqrt{31.5 \text{ m}^2/\text{s}^2} = 5.6 \text{ m/s}$$

Check: Work must be done in part (b) to increase the potential energy of the ball, which is in accord with our experience. The units are appropriate in both parts (b) and (c). The work is in units of J and the speed in units of m/s. In part (c) we have carried an additional digit in the intermediate calculation involving the square root, but we report the final value to only two significant figures, as appropriate.

Comment: A speed of 1 m/s is roughly 2 mph, so the bowling ball has a speed greater than 10 mph upon impact.

PRACTICE EXERCISE

What is the kinetic energy, in J, of (a) an Ar atom moving with a speed of 650 m/s, (b) a mole of Ar atoms moving with a speed of 650 m/s (Hint: 1 amu = 1.66×10^{-27} kg)

Answers: (a) 1.4×10^{-20} J, (b) 8.4×10^3 J

5.2 THE FIRST LAW OF THERMODYNAMICS

We have seen that the potential energy of a system can be converted into kinetic energy, and vice versa. We have also seen that energy can be transferred back and forth between a system and its surroundings in the forms of work and heat. In general, energy can be converted from one form to another, and it can be transferred from one place to another. All of these transactions proceed in accord with one of the most important observations in science—that energy can be neither created nor destroyed. A simple statement known as the **first law of thermodynamics** summarizes this simple truth: *Energy is conserved*. Any energy that is lost by the system must be gained by the surroundings, and vice versa. To apply the first law of thermodynamics quantitatively, we must first define the energy of a system more precisely.

Internal Energy

The **internal energy** of a system is the sum of *all* the kinetic and potential energies of all its components. For the system in Figure 5.3, for example, the internal energy includes the motions of the H₂ and O₂ molecules through space, their rotations, and their internal vibrations. It also includes the energies of the nuclei of each atom and of the component electrons. We represent the internal energy with the symbol E . (Some texts, particularly more advanced ones, use the symbol U .) We generally do not know the actual numerical value of E . What we can hope to know, however, is ΔE (read “delta E”),* the change in E that accompanies a change in the system.

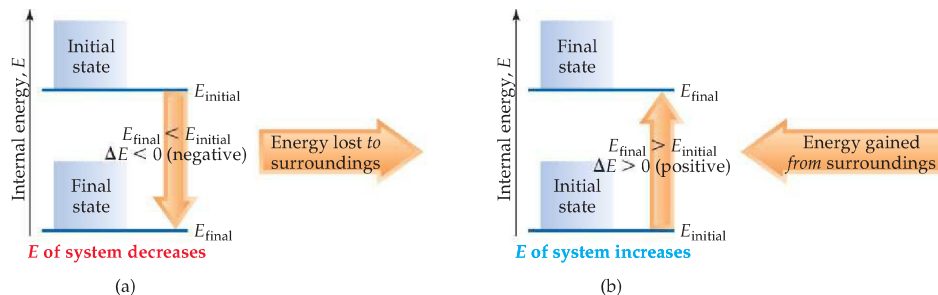
Imagine that we start with a system with an initial internal energy, E_{initial} . The system then undergoes a change, which might involve work being done or heat being transferred. After the change, the final internal energy of the system is E_{final} . We define the *change* in internal energy, ΔE , as the difference between E_{final} and E_{initial} :

$$\Delta E = E_{\text{final}} - E_{\text{initial}} \quad [5.4]$$

To apply the first law of thermodynamics, we need only the value of ΔE . We do not really need to know the actual values of E_{final} or E_{initial} for the system.

Thermodynamic quantities such as ΔE have three parts: (1) a number and (2) a unit, that together give the magnitude of the change, and (3) a sign that gives the direction. A *positive* value of ΔE results when $E_{\text{final}} > E_{\text{initial}}$, indicating the system has gained energy from its surroundings. A *negative* value of ΔE is obtained when $E_{\text{final}} < E_{\text{initial}}$, indicating 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 change in the energy of the system is accompanied by an opposite change in the energy of the surroundings. These features of energy changes are summarized in Figure 5.4 ▼.

▼ **Figure 5.4 Changes in internal energy.** (a) When a system loses energy, that energy is released to the surroundings. The loss of energy is represented by an arrow that points downward between the initial and final states of the system. In this case, the energy change of the system, $\Delta E = E_{\text{final}} - E_{\text{initial}}$, is negative. (b) When a system gains energy, that energy is gained from the surroundings. In this case, the gain of energy is represented by an arrow that points upward between the initial and final states of the system, and the energy change of the system is positive. Notice in both (a) and (b) that the vertical arrow originates at the initial state and has its head at the final state.



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

In a chemical reaction, the initial state of the system refers to the reactants, and the final state refers to the products. 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 ΔE for the process is negative. Thus, the *energy diagram* in Figure 5.5 shows that the internal energy of the mixture of H_2 and O_2 is greater than that of H_2O .

GIVE IT SOME THOUGHT

The internal energy for $\text{Mg}(s)$ and $\text{Cl}_2(g)$ is greater than that of $\text{MgCl}_2(s)$. Sketch an energy diagram that represents the reaction $\text{MgCl}_2(s) \longrightarrow \text{Mg}(s) + \text{Cl}_2(g)$.

Relating ΔE to Heat and Work

As we noted in Section 5.1, a system may exchange energy with its surroundings 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 it or by it. If we think of internal energy as the system's bank account of energy, we see that deposits or withdrawals can be made either in terms of heat or in terms of work. Deposits increase the energy of the system (positive ΔE), whereas withdrawals decrease the energy of the system (negative ΔE).

We can use these ideas to write a very useful algebraic expression of the first law of thermodynamics. When a system undergoes any chemical or physical change, the magnitude and sign of the accompanying change in internal energy, ΔE , is given by the heat added to or liberated from the system, q , plus the work done on or by the system, w :

$$\Delta E = q + w \quad [5.5]$$

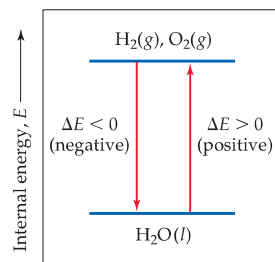
When heat is added to a system or work is done on a system, its internal energy increases. Therefore, when heat is transferred to the system from the surroundings, q has a positive value. Adding heat to the system is like making a deposit to the energy account—the total amount of energy goes up. Likewise, when work is done on the system by the surroundings, w has a positive value (Figure 5.6). Work also is a deposit, increasing the internal energy of the system. 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 as a result, lower the total amount of energy in the energy account. The sign conventions for q , w , and ΔE are summarized in Table 5.1. Notice that any energy entering the system as either heat or work carries a positive sign.

TABLE 5.1 Sign Conventions for q , w , and ΔE

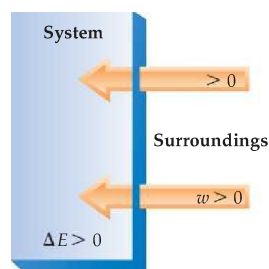
For q	+ means system <i>gains</i> heat	– means system <i>loses</i> heat
For w	+ means work done <i>on</i> system	– means work done <i>by</i> system
For ΔE	+ means <i>net gain</i> of energy by system	– means <i>net loss</i> of energy by system

SAMPLE EXERCISE 5.2 Relating Heat and Work to Changes of Internal Energy

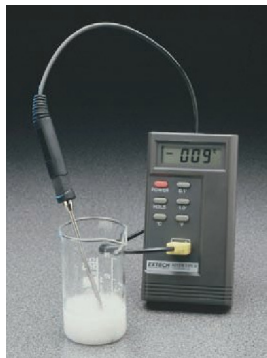
Two gases, $\text{A}(g)$ and $\text{B}(g)$, are confined in a cylinder-and-piston arrangement like that in Figure 5.3. Substances A and B react to form a solid product: $\text{A}(g) + \text{B}(g) \rightarrow \text{C}(s)$. As the reaction occurs, the system loses 1150 J of heat to the surroundings. The 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?



▲ Figure 5.5 Energy diagram for the interconversion of $\text{H}_2(g)$, $\text{O}_2(g)$, and $\text{H}_2\text{O}(l)$. A system composed of $\text{H}_2(g)$ and $\text{O}_2(g)$ has a greater internal energy than one composed of $\text{H}_2\text{O}(l)$. The system loses energy ($\Delta E < 0$) when H_2 and O_2 are converted to H_2O . It gains energy ($\Delta E > 0$) when H_2O is decomposed into H_2 and O_2 .



▲ Figure 5.6 Sign conventions for heat and work. Heat, q , gained by a system and work, w , done on a system are both positive quantities. Both increase the internal energy, E , of the system, causing ΔE to be a positive quantity.



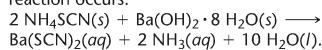
(a)



(b)

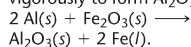
▲ Figure 5.7 Examples of endothermic and exothermic reactions.

(a) When ammonium thiocyanate and barium hydroxide octahydrate are mixed at room temperature, an endothermic reaction occurs:



As a result, the temperature of the system drops from about 20 °C to -9 °C.

(b) The reaction of powdered aluminum with Fe_2O_3 (the thermite reaction) is highly exothermic. The reaction proceeds vigorously to form Al_2O_3 and molten iron:



SOLUTION

Analyze: The question asks us to determine ΔE , given information about q and w .

Plan: We first determine the signs of q and w (Table 5.1) and then use Equation 5.5, $\Delta E = q + w$, to calculate ΔE .

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 $w = 480 \text{ kJ}$. Thus,

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

The negative value of ΔE 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

Calculate the change in the internal energy of the system for a process in which the system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings.

Answer: +55 J

Endothermic and Exothermic Processes

When a process occurs in which the system absorbs heat, the process is called **endothermic**. (*Endo-* is a prefix meaning “into.”) During an endothermic process, such as the melting of ice, heat flows *into* the system from its surroundings. If we, as part of the surroundings, touch a container in which ice is melting, it feels cold to us because heat has passed from our hands to the container.

A process in which the system loses heat is called **exothermic**. (*Exo-* is a prefix meaning “out of.”) During an exothermic process, such as the combustion of gasoline, heat *exits* or flows *out* of the system and into the surroundings. Figure 5.7 ◀ shows two examples of chemical reactions: one endothermic and the other highly exothermic. In the endothermic process shown in Figure 5.7(a), the temperature in the beaker decreases. In this example the system consists of the chemical reactants and products. The solvent in which they are dissolved is part of the surroundings. Heat flows from the solvent, as part of the surroundings, into the system as reactants are converted to products. Thus, the temperature of the solution drops.

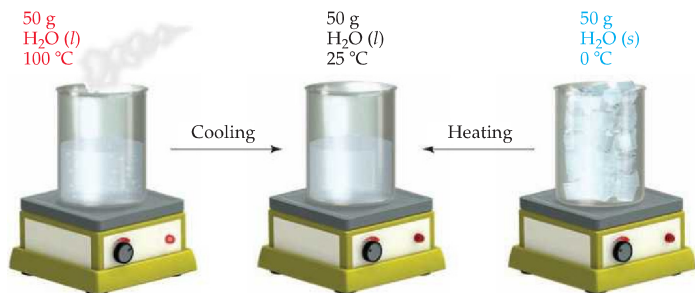
GIVE IT SOME THOUGHT

Using Figure 5.5 as a reference, indicate whether the reaction $2 \text{H}_2\text{O}(l) \longrightarrow 2 \text{H}_2(g) + \text{O}_2(g)$ is exothermic or endothermic. What feature(s) of the figure indicate whether the reaction is exothermic or endothermic?

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 total internal energy of a system is proportional to the total quantity of matter in the system because energy is an extensive property. ∞ (Section 1.3)

Suppose we define our system as 50 g of water at 25 °C, as in Figure 5.8 ▶. The system could have arrived at this state by cooling 50 g of water from 100 °C or by melting 50 g of ice and subsequently warming the water to 25 °C.



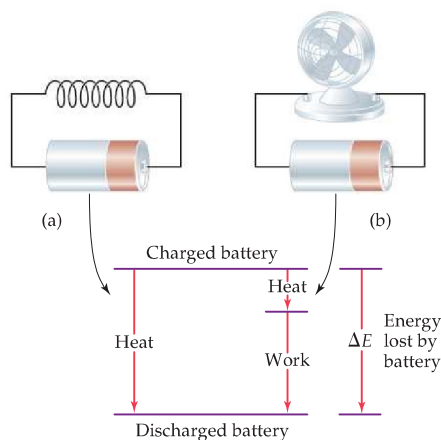
◀ **Figure 5.8 Internal energy, E , a state function.** E depends only on the present state of the system and not on the path by which it arrived at that state. The internal energy of 50 g of water at 25 °C is the same whether the water is cooled from a higher temperature to 25 °C or warmed from a lower temperature 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, ΔE depends only on the initial and final states of the system, not on how the change occurs.

An analogy may help to explain the difference between quantities that are state functions and those that are not. Suppose you are traveling between Chicago and Denver. Chicago is 596 ft above sea level; Denver is 5280 ft above sea level. No matter what route you take, the altitude change will be 4684 ft. The distance you travel, however, will depend 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. Although $\Delta E = q + w$ does not depend on how the change occurs, the specific amounts of heat and work produced depend on the way in which the change is carried out, analogous to the choice of travel route between Chicago and Denver. Nevertheless, 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 the value for ΔE for the two paths will be the same.

We can illustrate this principle with the example of a flashlight battery as our system. In Figure 5.9▶, we consider two possible ways of discharging the battery at constant temperature. If a coil of wire shorts out the battery, no work is accomplished because nothing is moved against a force. All the energy is lost from the battery in the form of heat. (The wire coil will get warmer and release heat to the surrounding air.) On the other hand, if the battery is used to make a small motor turn, the discharge of the battery produces work. Some heat will be released as well, although not as much as when the battery is shorted out. The magnitudes of q and w are different for these two cases. If the initial and final states of the battery are identical in both cases, however, then $\Delta E = q + w$ must be the same in both cases because ΔE is a state function. Thus, ΔE depends only on the initial and final states of the system, regardless of how the transfers of energy occur in terms of heat and work.



▶ **Figure 5.9 Internal energy is a state function, but heat and work are not.** The amounts of heat and work transferred between the system and the surroundings depend on the way in which the system goes from one state to another. (a) A battery shorted out by a wire loses energy to the surroundings only as heat; no work is performed by the system. (b) A battery discharged through a motor loses energy as work (to make the fan turn) and also loses energy as heat. Now, however, the amount of heat lost is much less than in (a). The value of ΔE is the same for both processes even though the values of q and w in (a) are different from the values of q and w in (b).

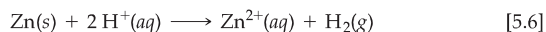
GIVE IT SOME THOUGHT

In what ways is the balance in your checkbook a state function?

5.3 ENTHALPY

The chemical and physical changes that occur around us, such as photosynthesis in the leaves of a plant, the evaporation of water from a lake, or a reaction in an open beaker in a laboratory, occur at essentially constant atmospheric pressure. The changes can result in the release or absorption of heat or can be accompanied by work that is done by or on the system. The heat flow is the easiest change to measure, so we will begin to focus on that aspect of reactions. Nevertheless, we still need to account for any work that accompanies the process.

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 the volume of the system. Consider, for example, the reaction of zinc metal with hydrochloric acid solution:



If we carry out this reaction in the laboratory hood in an open beaker, we can see the evolution of hydrogen gas, but it may not be so obvious that work is being done. Still, the hydrogen gas that is being produced must expand against the existing atmosphere, which requires the system to do work. We can see this better by conducting the reaction in a closed vessel at constant pressure, as illustrated in Figure 5.10. In this apparatus the piston moves up or down to maintain a constant pressure in the reaction vessel. If we assume for simplicity that the piston has no mass, the pressure in the apparatus is the same as the atmospheric pressure outside the apparatus. As the reaction proceeds, 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 that presses down on it.

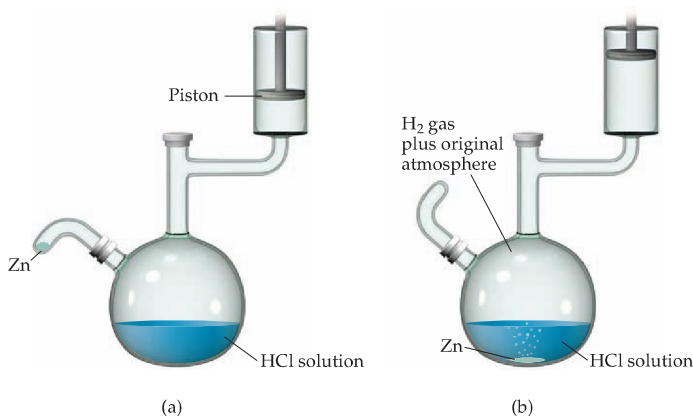
The work involved in the expansion or compression of gases is called **pressure-volume work** (or P - V work). When the pressure is constant, as in our example, the sign and magnitude of the pressure-volume work is given by

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

where P is pressure and ΔV is the change in volume of the system ($\Delta V = V_{\text{final}} - V_{\text{initial}}$). The negative sign in Equation 5.7 is necessary to conform to the sign conventions given in Table 5.1. Thus, when the volume expands, ΔV is a positive quantity and w is a negative quantity. That is, energy leaves the system as work, indicating that work is done *by* the system *on* the surroundings. On the other hand, when a gas is compressed, ΔV is a negative quantity

► **Figure 5.10 A system that does work on its surroundings.**

(a) An apparatus for studying the reaction of zinc metal with hydrochloric acid at constant pressure. The piston is free to move up and down in its cylinder to maintain a constant pressure equal to atmospheric pressure inside the apparatus. Notice the pellets of zinc in the L-shaped arm on the left. When this arm is rotated, the pellets will fall into the main container and the reaction will begin. (b) When zinc is added to the acid solution, hydrogen gas is evolved. The hydrogen gas does work on the surroundings, raising the piston against atmospheric pressure to maintain constant pressure inside the reaction vessel.



(the volume decreases), which makes w a positive quantity. That is, energy enters the system as work, indicating that work is done on the system by the surroundings. The “A Closer Look” box discusses pressure-volume work in more detail, but all you really need to keep in mind for now is Equation 5.7, which applies to processes occurring at constant pressure. We will take up the properties of gases in more detail in Chapter 10.

GIVE IT SOME THOUGHT

If a system does not change its volume during the course of a process, does it do pressure-volume work?

A thermodynamic function called **enthalpy** (from the Greek word *enthalpein*, meaning “to warm”) accounts for heat flow in processes occurring at constant pressure when no forms of work are performed other than P - V work. Enthalpy, which we denote by the symbol H , equals the internal energy plus the product of the pressure and volume of the system:

$$H = E + PV \quad [5.8]$$

Enthalpy is a state function because internal energy, pressure, and volume are all state functions.

When a change occurs at constant pressure, the change in enthalpy, ΔH , is given by the following relationship:

$$\begin{aligned} \Delta H &= \Delta(E + PV) \\ &= \Delta E + P \Delta V \end{aligned} \quad [5.9]$$

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

We can gain further insight into enthalpy change by recalling that $\Delta E = q + w$ (Equation 5.5) and that the work involved in the expansion or compression of gases is $w = -P \Delta V$. If we substitute $-w$ for $P \Delta V$ and $q + w$ for ΔE into Equation 5.9, we have

$$\Delta H = \Delta E + P \Delta V = (q_p + w) - w = q_p \quad [5.10]$$

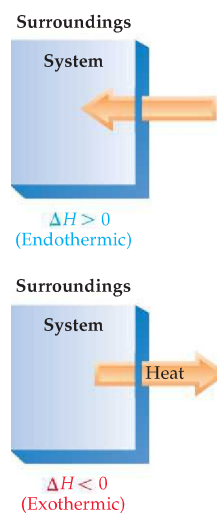
where the subscript P on the heat, q , emphasizes changes at constant pressure. Thus, *the change in enthalpy equals the heat gained or lost at constant pressure*. Because q_p is something we can either measure or readily calculate and because so many physical and chemical changes of interest to us occur at constant pressure, enthalpy is a more useful function than internal energy. For most reactions the difference in ΔH and ΔE is small because $P \Delta V$ is small.

When ΔH is positive (that is, when q_p is positive), the system has gained heat from the surroundings (Table 5.1), which is an endothermic process. When ΔH is negative, the system has released heat to the surroundings, which is an exothermic process. These cases are diagrammed in Figure 5.11 ▶.

Because H is a state function, ΔH (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 earlier 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 ΔH and heat (q_p) has the special limitations that only P - V work is involved and the pressure is constant.

GIVE IT SOME THOUGHT

What is the advantage of using enthalpy rather than internal energy to describe energy changes in reactions?



▲ **Figure 5.11 Endothermic and exothermic processes.** (a) If the system absorbs heat (endothermic process), ΔH will be positive ($\Delta H > 0$). (b) If the system loses heat (exothermic process), ΔH will be negative ($\Delta H < 0$).

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 will focus here only 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 the energy changes of a system.

Consider a gas confined to a cylinder with a movable piston of cross-sectional area A (Figure 5.12). A downward force, F , acts on the piston. The pressure, P , on the gas is the force per area: $P = F/A$. We will assume that the piston is weightless and that the only pressure acting on it is the atmospheric pressure that is due to the weight of Earth's atmosphere, which we will assume to be constant.

Suppose the gas in the cylinder expands and the piston moves a distance, Δh . From Equation 5.3, the magnitude of the

work done by the system equals the distance moved times the force acting on the piston:

$$\text{Magnitude of work} = \text{force} \times \text{distance} = F \times \Delta h \quad [5.11]$$

We can rearrange the definition of pressure, $P = F/A$, to $F = P \times A$. In addition, the volume change, ΔV , 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 5.11,

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

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

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

Now, if P - V work is the only work that can be done, we can substitute Equation 5.12 into Equation 5.5 to give

$$\Delta E = q + w = q - P \Delta V \quad [5.13]$$

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

$$\Delta E = q_V \quad (\text{constant volume}) \quad [5.14]$$

The subscript V indicates that the volume is constant.

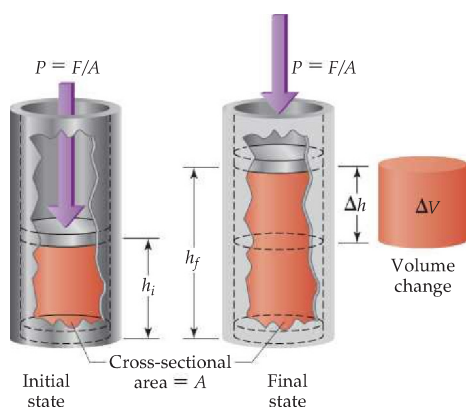
Most reactions are run under constant-pressure conditions. In this case Equation 5.13 becomes

$$\begin{aligned} \Delta E &= q_p - P \Delta V \text{ or} \\ q_p &= \Delta E + P \Delta V \quad (\text{constant pressure}) \quad [5.15] \end{aligned}$$

But we see from Equation 5.9 that the right-hand side of Equation 5.15 is just the enthalpy change under constant-pressure conditions. Thus, $\Delta H = q_p$, as we saw earlier in Equation 5.10.

In summary, the change in internal energy is equal to the heat gained or lost at constant volume; the change in enthalpy is equal to the heat gained or lost at constant pressure. The difference between ΔE and ΔH 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 ΔE and ΔH , small. It is generally satisfactory to use ΔH as the measure of energy changes during most chemical processes.

Related Exercises: 5.33, 5.34, 5.35, 5.36



▲ Figure 5.12 Pressure-volume work. A piston moving upward, expanding the volume of the system against an external pressure, P , does work on the surroundings. The amount of work done by the system on the surroundings is $w = -P \Delta V$.

SAMPLE EXERCISE 5.3 | Determining the Sign of ΔH

Indicate the sign of the enthalpy change, ΔH , in each of the following processes carried out under atmospheric pressure, and indicate whether the 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 ΔH is positive or negative for each process. Because each process appears to occur at constant pressure, the enthalpy change of each one equals the amount of heat absorbed or released, $\Delta H = q_p$.

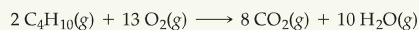
Plan: We must predict whether heat is absorbed or released by the system in each process. Processes in which heat is absorbed are endothermic and have a positive sign for ΔH ; those in which heat is released are exothermic and have a negative sign for ΔH .

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 ΔH 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 ΔH is negative and the process is exothermic.

PRACTICE EXERCISE

Suppose we confine 1 g of butane and sufficient oxygen to completely combust it in a cylinder like that in Figure 5.12. The cylinder is perfectly insulating, so no heat can escape to the surroundings. A spark initiates combustion of the butane, which forms carbon dioxide and water vapor. If we used this apparatus to measure the enthalpy change in the reaction, would the piston rise, fall, or stay the same?

Answer: The piston must move to maintain a constant pressure in the cylinder. The products contain more molecules of gas than the reactants, as shown by the balanced equation



As a result, the piston would rise to make room for the additional molecules of gas. Heat is given off, so the piston would also rise an additional amount to accommodate the expansion of the gases because of the temperature increase.

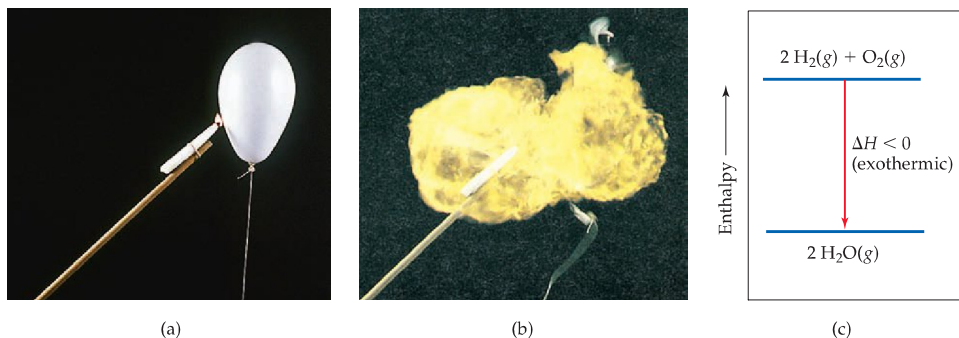
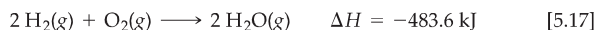
5.4 ENTHALPIES OF REACTION

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

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad [5.16]$$

The enthalpy change that accompanies a reaction is called the **enthalpy of reaction**, or merely the *heat of reaction*, and is sometimes written ΔH_{rxn} , where “rxn” is a commonly used abbreviation for “reaction.”

The combustion of hydrogen is shown in Figure 5.13. When the reaction is controlled so that 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

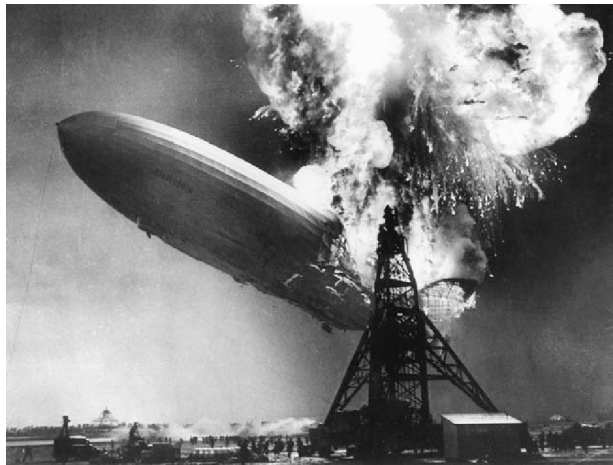


▲ Figure 5.13 Exothermic reaction of hydrogen with oxygen. (a) A candle is held near a balloon filled with hydrogen gas and oxygen gas. (b) The $\text{H}_2(\text{g})$ ignites, reacting with $\text{O}_2(\text{g})$ to form $\text{H}_2\text{O}(\text{g})$. The resultant explosion produces a ball of flame. The system gives off heat to its surroundings. (c) The enthalpy diagram for this reaction, showing its exothermic character.

ΔH is negative, so this reaction is exothermic. Notice that ΔH is reported at the end of the balanced equation, without explicitly mentioning 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*.

GIVE IT SOME THOUGHT

What information is summarized by the coefficients in a *thermochemical equation*?



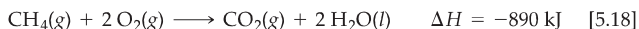
▲ **Figure 5.14** The burning of the hydrogen-filled airship *Hindenburg*. This photograph was taken only 22 seconds after the first explosion occurred. This tragedy, which occurred in Lakehurst, New Jersey, on May 6, 1937, led to the discontinuation of hydrogen as a buoyant gas in such craft. Modern-day blimps are filled with helium, which is not as buoyant as hydrogen but is not flammable.

The enthalpy change accompanying a reaction may also be represented in an *enthalpy diagram* such as that shown in Figure 5.13(c). Because the combustion of $\text{H}_2(\text{g})$ is exothermic, the enthalpy of the products in the reaction is lower than the enthalpy of the reactants. The enthalpy of the system is lower after the reaction because energy has been lost in the form of heat released to the surroundings.

The reaction of hydrogen with oxygen is highly exothermic (ΔH is negative and has a large magnitude), and it occurs rapidly once it starts. It can occur with explosive violence, too, as demonstrated by the disastrous explosions of the German airship *Hindenburg* in 1937 (Figure 5.14 ◀) and the space shuttle *Challenger* in 1986.

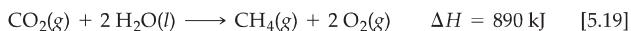
The following guidelines are helpful when using thermochemical equations and enthalpy diagrams:

1. *Enthalpy is an extensive property.* The magnitude of ΔH , therefore, is directly proportional to the amount of reactant consumed in the process. For the combustion of methane to form carbon dioxide and liquid water, for example, 890 kJ of heat is produced when 1 mol of CH_4 is burned in a constant-pressure system:



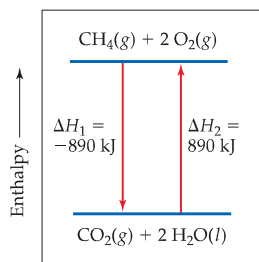
Because the combustion of 1 mol of CH_4 with 2 mol of O_2 releases 890 kJ of heat, the combustion of 2 mol of CH_4 with 4 mol of O_2 releases twice as much heat, 1780 kJ.

2. *The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.* For example, if we could reverse Equation 5.18 so that $\text{CH}_4(\text{g})$ and $\text{O}_2(\text{g})$ formed from $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, ΔH for the process would be +890 kJ:



When we reverse a reaction, we reverse the roles of the products and the reactants. As a result, the reactants in a reaction become the products of the reverse reaction, and so forth. From Equation 5.16, we can see that reversing the products and reactants leads to the same magnitude, but a change in sign for ΔH_{rxn} . This relationship is diagrammed for Equations 5.18 and 5.19 in Figure 5.15 ◀.

3. *The enthalpy change for a reaction depends on the state of the reactants and products.* If the product in the combustion of methane (Equation 5.18) were gaseous H_2O instead of liquid H_2O , ΔH_{rxn} would be -802 kJ instead of



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

−890 kJ. Less heat would be available for transfer to the surroundings because the enthalpy of $\text{H}_2\text{O}(\text{g})$ is greater than that of $\text{H}_2\text{O}(\text{l})$. 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 $\text{H}_2\text{O}(\text{l})$ to 2 mol $\text{H}_2\text{O}(\text{g})$ 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 ΔH 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 5.18.)

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 5.18, 890 kJ is released by the system when 1 mol CH_4 is burned at constant pressure ($\Delta H = -890 \text{ kJ}$).

Plan: Equation 5.18 provides us with a stoichiometric conversion factor: 1 mol $\text{CH}_4 \approx -890 \text{ kJ}$. Thus, we can convert moles of CH_4 to kJ of energy. First, however, we must convert grams of CH_4 to moles of CH_4 . Thus, the conversion sequence is grams CH_4 (given) \rightarrow moles $\text{CH}_4 \rightarrow$ kJ (unknown to be found).

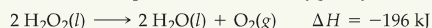
Solve: By adding the atomic weights of C and 4 H, we have 1 mol $\text{CH}_4 = 16.0 \text{ g CH}_4$. We can use the appropriate conversion factors to convert grams of CH_4 to moles of CH_4 to kilojoules:

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

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 following reaction:



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

Answer: −14.4 kJ

In many situations it is valuable to know the enthalpy change associated with a given chemical process. As we will see in the following sections, ΔH can be determined directly by experiment or calculated from the known enthalpy changes of other reactions by invoking the first law of thermodynamics.

5.5 CALORIMETRY

The value of ΔH 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.

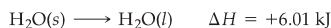
If you hold a brick in the air and let it go, it will fall as the force of gravity pulls it toward Earth. A process that is thermodynamically favored to happen, such as a falling brick, is called a *spontaneous* process. A spontaneous process can be either fast or slow. Speed is not the issue in thermodynamics.

Many chemical processes are thermodynamically favored, or spontaneous, too. By “spontaneous,” 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. The enthalpy change in a reaction gives one indication as to whether the reaction is likely to be spontaneous. The combustion of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$, for example, is a highly exothermic process:



Hydrogen gas and oxygen gas can exist together in a volume indefinitely without noticeable reaction occurring, as in Figure 5.13(a). Once initiated, however, energy is rapidly transferred from the system (the reactants) to the surroundings. As the reaction proceeds, large amounts of heat are released, which greatly increases the temperature of the reactants and the products. The system then loses enthalpy by transferring the heat to the surroundings. (Recall that the first law of thermodynamics indicates that the total energy of the system plus the surroundings will not change; energy is conserved.)

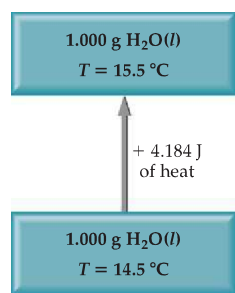
Enthalpy change is not the only consideration in the spontaneity of reactions, however, nor is it a foolproof guide. For example, the melting of ice is an endothermic process:



Even though this process is endothermic, it is spontaneous at temperatures above the freezing point of water (0°C). The reverse process, the freezing of water to ice, is spontaneous at temperatures below 0°C . Thus, we know that ice at room temperature will melt and that water put into a freezer at -20°C will turn into ice. Both of these 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, however, 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 ΔH is *large* and *negative* tend to be spontaneous. Reactions for which ΔH is *large* and *positive* tend to be spontaneous only in the reverse direction. The enthalpy of a reaction can be estimated in a number of ways. From these estimates, the likelihood of the reaction being thermodynamically favorable can be predicted.

Related Exercises: 5.45, 5.46



▲ **Figure 5.16 Specific heat of water.**

Specific heat indicates the amount of heat that must be added to one gram of a substance to raise its temperature by 1 K (or 1°C). Specific heats can vary slightly with temperature, so for precise measurements the temperature is specified. The specific heat of $\text{H}_2\text{O}(\text{l})$ at 14.5°C is $4.184\text{ J/g}\cdot\text{K}$; the addition of 4.184 J of heat to 1 g of liquid water at this temperature raises the temperature to 15.5°C . This amount of energy defines the calorie: $1\text{ cal} = 4.184\text{ J}$.

The temperature change experienced by an object when it absorbs a certain amount of heat is determined by its **heat capacity**, 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** (Figure 5.16 ◀). The specific heat, C_s , of a substance can be determined experimentally by measuring the temperature change, ΔT , that a known mass, m , of the substance undergoes when it gains or loses a specific quantity of heat, q :

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

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

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

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

A temperature change in kelvins is equal in magnitude to the temperature change in degrees Celsius: ΔT in $\text{K} = \Delta T$ in $^\circ\text{C}$. ∞ (Section 1.4) When the

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 ₂ (g)	1.04	H ₂ O(l)	4.18
Al(s)	0.90	CH ₄ (g)	2.20
Fe(s)	0.45	CO ₂ (g)	0.84
Hg(l)	0.14	CaCO ₃ (s)	0.82

sample gains heat (positive q), the temperature of the sample increases (positive ΔT). Rearranging Equation 5.21, we get

$$q = C_s \times m \times \Delta T \quad [5.22]$$

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

The specific heats of several substances are listed in Table 5.2▲. Notice that the specific heat of liquid water is higher than those of the other substances listed. For example, it is about five times as great as that of aluminum metal. The high specific heat of water affects Earth's climate because it makes the temperatures of the oceans relatively resistant to change. It also is very important in maintaining a constant temperature in our bodies, as we will discuss in the "Chemistry and Life" box later in this chapter.

GIVE IT SOME THOUGHT

Which substance in Table 5.2 will undergo the greatest temperature change when the same mass of each substance absorbs the same quantity of heat?

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 near its boiling point, 98 °C? The specific heat of water is 4.18 J/g·K. (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 (ΔT), and its specific heat (C_s). 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).

Plan: (a) Given C_s , m , and ΔT , we can calculate the quantity of heat, q , using Equation 5.22. (b) We can use the molar mass of water and dimensional analysis to convert from heat capacity per gram to heat capacity per mole.

Solve:

(a) The water undergoes a temperature change of

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

Using Equation 5.22, we have

$$\begin{aligned} q &= C_s \times m \times \Delta T \\ &= (4.18\text{ J/g}\cdot\text{K})(250\text{ g})(76\text{ K}) = 7.9 \times 10^4\text{ J} \end{aligned}$$

(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 given in part (a), we have

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

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?

Answers: (a) $4.9 \times 10^5\text{ J}$, (b) 11 K decrease = 11 °C decrease



▲ **Figure 5.17 Coffee-cup calorimeter.** This simple apparatus is used to measure heat-accompanying 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 ΔH is measured directly. (Recall that $\Delta H = q_p$.) Although the calorimeters used for highly accurate work are precision instruments, a very simple “coffee-cup” calorimeter, as shown in Figure 5.17, is often used in general chemistry labs to illustrate the principles of calorimetry. Because the calorimeter is not sealed, the reaction occurs under the essentially constant pressure of the atmosphere.

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 dissolve as well as the calorimeter are part of the surroundings. If we assume that the calorimeter perfectly prevents the gain or loss of heat from the solution, the heat gained by the solution must be produced from the chemical reaction under study. In other words, the heat produced by the reaction, q_{rxn} , is entirely absorbed by the solution; it does not escape the calorimeter. (We also assume that the calorimeter itself does not absorb heat. In the case of the coffee-cup calorimeter, this is a reasonable approximation because the calorimeter has a very low thermal conductivity and heat capacity.) For an exothermic reaction, heat is “lost” by the reaction and “gained” by the solution, so the temperature of the solution rises. The opposite occurs for an endothermic reaction. The heat gained by the solution, q_{soln} , is therefore equal in magnitude to q_{rxn} but opposite in sign: $q_{\text{soln}} = -q_{\text{rxn}}$. The value of q_{soln} is readily calculated from the mass of the solution, its specific heat, and the temperature change:

$$q_{\text{soln}} = (\text{specific heat of solution}) \times (\text{grams of solution}) \times \Delta T = -q_{\text{rxn}} \quad [5.23]$$

For dilute aqueous solutions the specific heat of the solution will be approximately the same as that of water, 4.18 J/g·K.

Equation 5.23 makes it possible to calculate q_{rxn} from the temperature change of the solution in which the reaction occurs. A temperature increase ($\Delta T > 0$) means the reaction is exothermic ($q_{\text{rxn}} < 0$).

GIVE IT SOME THOUGHT

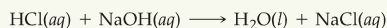
(a) How are the energy changes of a system and its surroundings related? (b) How is the heat gained or lost by a system related to the heat gained or lost by its surroundings?

SAMPLE EXERCISE 5.6 | Measuring ΔH 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 °C 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 5.23. The number of moles of HCl consumed in the reaction must be calculated from the volume and molarity of this substance, and this amount 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 5.23, we have

$$\begin{aligned} q_{\text{rxn}} &= -C_s \times m \times \Delta T \\ &= -(4.18 \text{ J/g}\cdot\text{K})(100 \text{ g})(6.5 \text{ K}) = -2.7 \times 10^3 \text{ J} = -2.7 \text{ kJ} \end{aligned}$$

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 respective solution volumes (50 mL = 0.050 L) and concentrations (1.0 M = 1.0 mol/L):

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

Thus, the enthalpy change per mole of HCl is

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

Check: ΔH is negative (exothermic), which is expected for the reaction of an acid with a base and evidenced by the fact that the reaction causes the temperature of the solution to increase. The molar magnitude of the heat produced seems reasonable.

PRACTICE EXERCISE

When 50.0 mL of 0.100 M AgNO_3 and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 °C to 23.11 °C. The temperature increase is caused by the following reaction:



Calculate ΔH for this reaction in kJ/mol AgNO_3 , assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g °C.

Answer: $-68,000 \text{ J/mol} = -68 \text{ kJ/mol}$

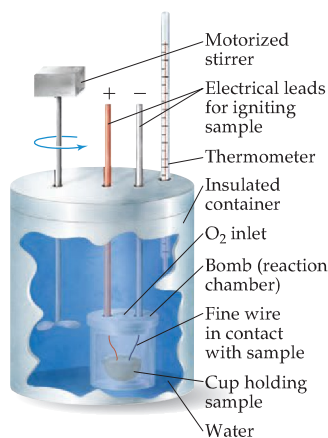
Bomb Calorimetry (Constant-Volume Calorimetry)

One of the most important types of reactions studied using calorimetry is combustion, in which a compound (usually an organic compound) reacts completely with excess oxygen. (Section 3.2) Combustion reactions are most conveniently studied using a **bomb calorimeter**, a device shown schematically in Figure 5.18. The substance to be studied is placed in a small cup within a sealed vessel called a *bomb*. The bomb, which is designed to withstand high pressures, has an inlet valve for adding oxygen and electrical contacts to initiate the combustion. After the sample has been placed in the bomb, the bomb is sealed and pressurized with oxygen. It is then placed in the calorimeter, which is essentially an insulated container, and covered with an accurately measured quantity of water. When all the components within the calorimeter have come to the same temperature, the combustion reaction is initiated by passing an electrical current through a fine wire that is in contact with the sample. When the wire becomes sufficiently hot, the sample ignites.

Heat is released when combustion occurs. This heat is absorbed by the calorimeter contents, causing a rise in the temperature of the water. The temperature of the water is very carefully measured before reaction and then after reaction when the contents of the calorimeter have again arrived at a common temperature.

To calculate the heat of combustion from the measured temperature increase in the bomb calorimeter, we must know the total heat capacity of the calorimeter, C_{cal} . This quantity is determined by combusting a sample that releases a known quantity of heat and measuring the resulting temperature change. For example, the 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, and it increases the temperature by 4.857 °C. The heat capacity of the calorimeter is then given by $C_{\text{cal}} = 26.38 \text{ kJ}/4.857^\circ\text{C} = 5.431 \text{ kJ}/^\circ\text{C}$. Once we know the value of C_{cal} , we can measure temperature changes produced by other reactions, and from these we can calculate the heat evolved in the reaction, q_{rxn} :

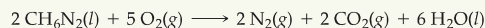
$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T \quad [5.24]$$



▲ Figure 5.18 Bomb calorimeter. This device is used to measure heat accompanying combustion reactions at constant volume.

SAMPLE EXERCISE 5.7 | Measuring q_{rxn} Using a Bomb Calorimeter

Methylhydrazine (CH_6N_2) is used as a liquid rocket fuel. The combustion of methylhydrazine with oxygen produces $\text{N}_2(\text{g})$, $\text{CO}_2(\text{g})$, and $\text{H}_2\text{O}(\text{l})$:



When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 °C to 39.50 °C. In a separate experiment the heat capacity of the calorimeter is measured to be 7.794 kJ/°C. Calculate the heat of reaction for the combustion of a mole of CH_6N_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

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

We can use ΔT and the value for C_{cal} to calculate the heat of reaction (Equation 5.24):

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

We can readily convert this value to the heat of reaction for a mole of CH_6N_2 :

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

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

PRACTICE EXERCISE

A 0.5865-g sample of lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) is burned in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10 °C to 24.95 °C. Calculate the heat of combustion of lactic acid (a) per gram and (b) per mole.

Answers: (a) -15.2 kJ/g , (b) -1370 kJ/mol

Because the reactions in a bomb calorimeter are carried out under constant-volume conditions, the heat transferred corresponds to the change in internal energy, ΔE , rather than the change in enthalpy, ΔH (Equation 5.14). For most reactions, however, the difference between ΔE and ΔH is very small. For the reaction discussed in Sample Exercise 5.7, for example, the difference between ΔE and ΔH is only about 1 kJ/mol—a difference of less than 0.1%. It is possible to correct the measured heat changes to obtain ΔH values, and these form the basis of the tables of enthalpy change that we will see in the following sections. However, we need not concern ourselves with how these small corrections are made.

5.6 HESS'S LAW

Many enthalpies of reaction have been measured and tabulated. In this section and the next we will see that it is often possible to calculate the ΔH for a reaction from the tabulated ΔH values of other reactions. Thus, it is not necessary to make calorimetric measurements for all reactions.

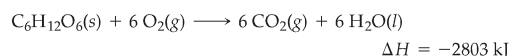
Because enthalpy is a state function, the enthalpy change, ΔH , associated with any chemical process depends only on the amount of matter that undergoes change and on the nature of the initial state of the reactants and the final state of the products. This means that whether a particular reaction is 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, the combustion of methane gas, $\text{CH}_4(\text{g})$, to

For most of us, 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 that something is amiss. In the laboratory you may have tried to maintain a solution at a constant temperature, only to find how difficult it can be. Yet our bodies manage to maintain a near-constant temperature in spite of widely varying weather, levels of physical activity, and periods of high metabolic activity (such as after a meal). How does the human body manage this task, and how does it relate to some of the topics we have discussed in this chapter?

Maintaining a near-constant temperature is one of the primary physiological functions of the human body. Normal body temperature generally ranges from 35.8 °C to 37.2 °C (96.5 °F–99 °F). This very narrow temperature range is essential to proper muscle function and to the control of the rates of the biochemical reactions in the body. You will learn more about the effects of temperature on reaction rates in Chapter 14.

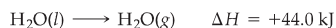
A portion of the human brain stem called the *hypothalamus* regulates the temperature. The hypothalamus acts as a thermostat for body temperature. When body temperature rises above the high end of the normal range, the hypothalamus triggers mechanisms to lower the temperature. It likewise triggers mechanisms to increase the temperature if body temperature drops too low.

To understand qualitatively 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. (Section 5.8) The foods, such as glucose (C₆H₁₂O₆), are metabolized—a process that is essentially controlled oxidation to CO₂ and H₂O:



Roughly 40% of the energy produced is ultimately used to do work in the form of muscle contractions and nerve cell activities. The remainder of the energy 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.

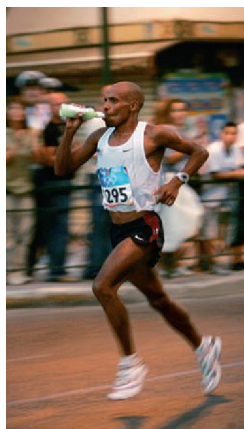
Heat is transferred from the body to its surroundings primarily by *radiation*, *convection*, and *evaporation*. Radiation is the direct loss of heat from the body to cooler surroundings, much as a hot stovetop radiates heat to its surroundings. Convection is heat loss by virtue of heating air that is in contact with the body. The heated air rises and is replaced with cooler air, and the process continues. Warm clothing, which usually consists of insulating layers of material with “dead air” in between, decreases convective heat loss in cold weather. Evaporative cooling occurs when perspiration is generated at the skin surface by the sweat glands. Heat is removed from the body as the perspiration evaporates into the surroundings. Perspiration is predominantly water, so the process involved 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 people seem to be more sweaty and uncomfortable on hot and humid days.

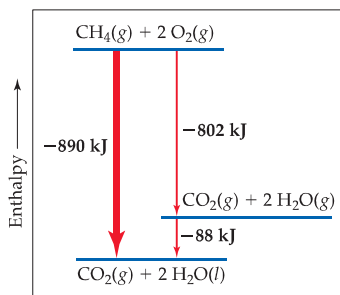
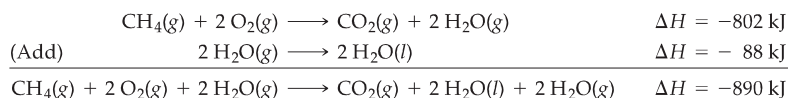
When the hypothalamus senses that the body temperature has risen too high, it increases heat loss from the body in two principal ways. First, it increases the flow of blood near the surface of the skin, which allows for increased radiational and convective cooling. The reddish “flushed” appearance of a hot individual is the result of this increased subsurface blood flow. Second, the hypothalamus stimulates the secretion of perspiration from the sweat glands, which increases evaporative cooling. During periods of extreme activity, the amount of liquid secreted as perspiration can be as high as 2 to 4 liters per hour. As a result, water must be replenished to the body during these periods (Figure 5.19). If the body loses too much fluid through perspiration, it will no longer be able to cool itself and blood volume decreases, which can lead to *heat exhaustion* or the more serious and potentially fatal *heat stroke*, during which the body temperature can rise to as high as 41 °C to 45 °C (106 °F–113 °F). On the other hand, replenishing water without replenishing the electrolytes that are lost during perspiration can also lead to serious problems as pointed out in the “Chemistry in Life” box in Section 4.5.

When body temperature drops too low, the hypothalamus decreases the blood flow to the surface of the skin, thereby decreasing heat loss. It also triggers small involuntary contractions of the muscles; the biochemical reactions that generate the energy to do this work also generate more heat for the body. When these contractions get large enough—as when the body feels a chill—a *shiver* results. If the body is unable to maintain a temperature above 35 °C (95 °F), the very dangerous condition called *hypothermia* can result.



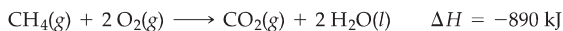
▲ **Figure 5.19 Marathon runner drinking water.** Runners must constantly replenish the water in their bodies that is lost through perspiration.

form $\text{CO}_2(\text{g})$ and liquid water can be thought of as occurring in two steps: (1) the combustion of $\text{CH}_4(\text{g})$ to form $\text{CO}_2(\text{g})$ and gaseous water, $\text{H}_2\text{O}(\text{g})$ and (2) the condensation of gaseous water to form liquid water, $\text{H}_2\text{O}(\text{l})$. The enthalpy change for the overall process is simply the sum of the enthalpy changes for these two steps:



▲ **Figure 5.20** An enthalpy diagram comparing a one-step and a two-step process for a reaction. The enthalpy change of the direct reaction on the left equals the sum of the two steps on the right. That is, ΔH for the overall reaction equals the sum of the ΔH values for the two steps shown.

The net equation is



To obtain the net equation, the sum of the reactants of the two equations is placed on one side of the arrow and the sum of the products on the other side. Because $2 \text{H}_2\text{O}(\text{g})$ occurs on both sides, it can be canceled like an algebraic quantity that appears on both sides of an equal sign. Figure 5.20 ◀ compares the two-step reaction with the direct one.

Hess's law states that if a reaction is carried out in a series of steps, ΔH for the overall reaction will equal the sum of the enthalpy changes for the individual steps. The overall enthalpy change for the process is independent of the number of steps or the particular nature of the path by which the reaction is carried out. This principle is a consequence of the fact that enthalpy is a state function, and ΔH is therefore independent of the path between the initial and final states. We can therefore calculate ΔH for any process, as long as we find a route for which ΔH is known for each step. This means that a relatively small number of experimental measurements can be used to calculate ΔH for a vast number of different reactions.

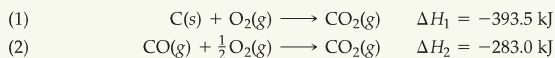
Hess's law provides a useful means of calculating energy changes that are difficult to measure directly. For instance, it is impossible to measure directly the enthalpy for the combustion of carbon to form carbon monoxide. Combustion of 1 mol of carbon with 0.5 mol of O_2 produces both CO and CO_2 , leaving some carbon unreacted. However, solid carbon and carbon monoxide can both be completely burned in O_2 to produce CO_2 . We can use the enthalpy changes of these reactions to calculate the heat of combustion of C to CO , as shown in Sample Exercise 5.8.

GIVE IT SOME THOUGHT

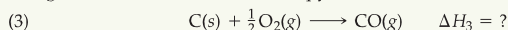
What effect do the following changes have on ΔH for a reaction: (a) reversing a reaction, (b) multiplying coefficients by 2?

SAMPLE EXERCISE 5.8 | Using Hess's Law to Calculate ΔH

The enthalpy of reaction for the combustion of C to CO_2 is -393.5 kJ/mol C , and the enthalpy for the combustion of CO to CO_2 is -283.0 kJ/mol CO :



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

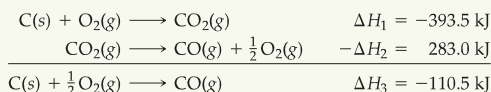


SOLUTION

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 numbers 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 ΔH is reversed. We arrange the two equations so that they can be added to give the desired equation:

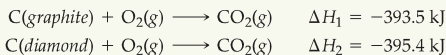


When we add the two equations, CO₂(g) appears on both sides of the arrow and therefore cancels out. Likewise, $\frac{1}{2}$ O₂(g) is eliminated from each side.

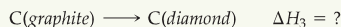
Comment: It is sometimes useful to add subscripts to the enthalpy changes, as we have done here, to keep track of the associations between the chemical reactions and their ΔH values.

PRACTICE EXERCISE

Carbon occurs in two forms, graphite and diamond. The enthalpy of the combustion of graphite is -393.5 kJ/mol and that of diamond is -395.4 kJ/mol :



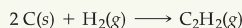
Calculate ΔH for the conversion of graphite to diamond:



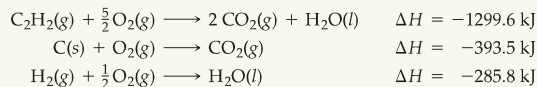
Answer: $\Delta H_3 = +1.9 \text{ kJ}$

SAMPLE EXERCISE 5.9 Using Three Equations with Hess's Law to Calculate ΔH

Calculate ΔH for the reaction



given the following chemical equations and their respective enthalpy changes:

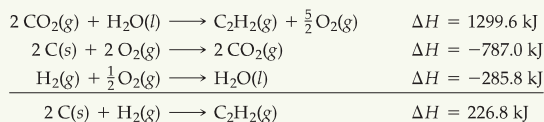


SOLUTION

Analyze: We are given a chemical equation and asked to calculate its ΔH 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 ΔH 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 C₂H₂ as a product, we turn the first equation around; the sign of ΔH is therefore changed. The desired equation has 2 C(s) as a reactant, so we multiply the second equation and its ΔH by 2. Because the target equation has H₂ 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:

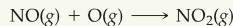


When the equations are added, there are 2 CO₂, $\frac{5}{2}$ O₂, and H₂O on both sides of the arrow. These are canceled in writing the net equation.

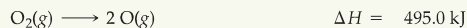
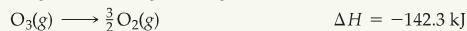
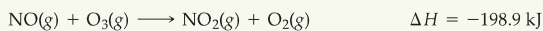
Check: The procedure must be correct because we obtained the correct net equation. In cases like this you should go back over the numerical manipulations of the ΔH values to ensure that you did not make an inadvertent error with signs.

PRACTICE EXERCISE

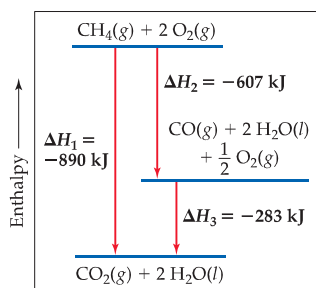
Calculate ΔH for the reaction



given the following information:



Answer: -304.1 kJ



▲ **Figure 5.21** An enthalpy diagram illustrating Hess's law. Because H is a state function, the enthalpy change for the combustion of 1 mol CH_4 is independent of whether the reaction takes place in one or more steps: $\Delta H_1 = \Delta H_2 + \Delta H_3$.

The key point of these examples is that H is a state function, so for a particular set of reactants and products, ΔH is the same whether the reaction takes place in one step or in a series of steps. For example, consider the reaction of methane (CH_4) and oxygen (O_2) to form CO_2 and H_2O . We can envision the reaction forming CO_2 directly or with the initial formation of CO , which is then combusted to CO_2 . These two paths are compared in Figure 5.21. Because H is a state function, both paths *must* produce the same value of ΔH . In the enthalpy diagram, that means $\Delta H_1 = \Delta H_2 + \Delta H_3$.

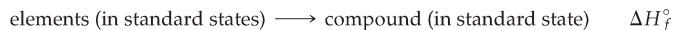
5.7 ENTHALPIES OF FORMATION

By using the methods we have just discussed, we can calculate the enthalpy changes for a great many reactions from tabulated ΔH values. Many experimental data are tabulated according to the type of process. For example, extensive tables exist of *enthalpies of vaporization* (ΔH for converting liquids to gases), *enthalpies of fusion* (ΔH for melting solids), *enthalpies of combustion* (ΔH 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*) and is labeled ΔH_f , where the subscript f indicates that the substance has been *formed* from its component elements.

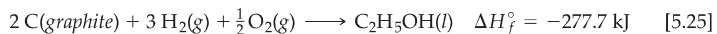
The magnitude of any enthalpy change depends on the conditions of temperature, pressure, and state (gas, liquid, or solid crystalline form) of the reactants and products. To compare the enthalpies of different reactions, we must define a set of conditions, called a *standard state*, at which most enthalpies are tabulated. The standard state of a substance is its pure form at atmospheric pressure (1 atm; [Section 10.2](#)) 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 ΔH° , where the superscript $^\circ$ indicates standard-state conditions.

*The definition of the standard state for gases has been changed to 1 bar (1 atm = 1.013 bar), a slightly lower pressure than the value of 1 atm that is used for the data in this text. For most purposes, this change makes very little difference in the standard changes.

The **standard enthalpy of formation** of a compound, ΔH_f° , 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 ΔH_f° 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, $\text{C}_2\text{H}_5\text{OH}$, is the enthalpy change for the following 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 standard atmospheric pressure. Similarly, the elemental source of carbon is graphite and not diamond, because graphite is more stable (lower energy) at 298 K and standard atmospheric pressure (see Practice Exercise 5.8). Likewise, the most stable form of hydrogen under standard conditions is $\text{H}_2(\text{g})$, 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, enthalpies of formation are reported in kJ/mol of the substance being formed. Several standard enthalpies of formation are given in Table 5.3. A more complete 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 ΔH_f° for C(graphite), $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$, and the standard states of other elements are zero by definition.

GIVE IT SOME THOUGHT

In Table 5.3, the standard enthalpy of formation of $\text{C}_2\text{H}_2(\text{g})$ is listed as 226.7 kJ/mol. Write the thermochemical equation associated with ΔH_f° for this substance.

TABLE 5.3 ■ Standard Enthalpies of Formation, ΔH_f° , at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$\text{C}_2\text{H}_2(\text{g})$	226.7	Hydrogen chloride	$\text{HCl}(\text{g})$	-92.30
Ammonia	$\text{NH}_3(\text{g})$	-46.19	Hydrogen fluoride	$\text{HF}(\text{g})$	-268.60
Benzene	$\text{C}_6\text{H}_6(\text{l})$	49.0	Hydrogen iodide	$\text{HI}(\text{g})$	25.9
Calcium carbonate	$\text{CaCO}_3(\text{s})$	-1207.1	Methane	$\text{CH}_4(\text{g})$	-74.80
Calcium oxide	$\text{CaO}(\text{s})$	-635.5	Methanol	$\text{CH}_3\text{OH}(\text{l})$	-238.6
Carbon dioxide	$\text{CO}_2(\text{g})$	-393.5	Propane	$\text{C}_3\text{H}_8(\text{g})$	-103.85
Carbon monoxide	$\text{CO}(\text{g})$	-110.5	Silver chloride	$\text{AgCl}(\text{s})$	-127.0
Diamond	$\text{C}(\text{s})$	1.88	Sodium bicarbonate	$\text{NaHCO}_3(\text{s})$	-947.7
Ethane	$\text{C}_2\text{H}_6(\text{g})$	-84.68	Sodium carbonate	$\text{Na}_2\text{CO}_3(\text{s})$	-1130.9
Ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.7	Sodium chloride	$\text{NaCl}(\text{s})$	-410.9
Ethylene	$\text{C}_2\text{H}_4(\text{g})$	52.30	Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$	-2221
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1273	Water	$\text{H}_2\text{O}(\text{l})$	-285.8
Hydrogen bromide	$\text{HBr}(\text{g})$	-36.23	Water vapor	$\text{H}_2\text{O}(\text{g})$	-241.8

SAMPLE EXERCISE 5.10 | Identifying Equations Associated with Enthalpies of Formation

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

- (a) $2 \text{Na}(s) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{Na}_2\text{O}(s)$
 (b) $2 \text{K}(l) + \text{Cl}_2(g) \longrightarrow 2 \text{KCl}(s)$
 (c) $\text{C}_6\text{H}_{12}\text{O}_6(s) \longrightarrow 6 \text{C}(\text{diamond}) + 6 \text{H}_2(g) + 3 \text{O}_2(g)$

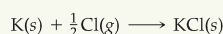
SOLUTION

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.

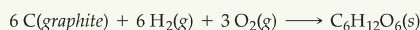
Plan: We need to examine each equation to determine, first, whether the reaction is one in which one mole of substance is formed from the elements. Next, we need to determine whether the reactant elements are in their standard states.

Solve: In (a) 1 mol Na_2O is formed from the elements sodium and oxygen in their proper states, solid Na and O_2 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, two moles of product are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of $\text{KCl}(s)$. The equation for the formation reaction of 1 mol of $\text{KCl}(s)$ 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 1 atm pressure. The equation that correctly represents the enthalpy of formation of glucose from its elements is

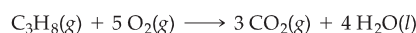

PRACTICE EXERCISE

Write the equation corresponding to the standard enthalpy of formation of liquid carbon tetrachloride (CCl_4).

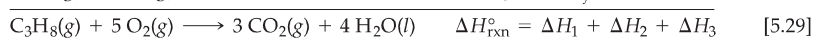
Answer: $\text{C}(\text{graphite}) + 2 \text{Cl}_2(g) \longrightarrow \text{CCl}_4(l)$

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

Tabulations of ΔH_f° , such as those in Table 5.3 and Appendix C, have many important uses. As we will see in this section, we can use Hess's law to calculate the standard enthalpy change for any reaction for which we know the ΔH_f° values for all reactants and products. For example, consider the combustion of propane gas, $\text{C}_3\text{H}_8(g)$, with oxygen to form $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ under standard conditions:



We can write this equation as the sum of three formation reactions:



From Hess's law we can write the standard enthalpy change for the overall reaction, Equation 5.29, as the sum of the enthalpy changes for the processes in

Equations 5.26 through 5.28. We can then use values from Table 5.3 to compute a numerical value for ΔH° for the overall reaction:

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= -\Delta H_f^\circ[\text{C}_3\text{H}_8(\text{g})] + 3\Delta H_f^\circ[\text{CO}_2(\text{g})] + 4\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] \\ &= -(-103.85 \text{ kJ}) + 3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ}) = -2219.9 \text{ kJ}\end{aligned}\quad [5.30]$$

Several aspects of this calculation depend on the guidelines we discussed in Section 5.4.

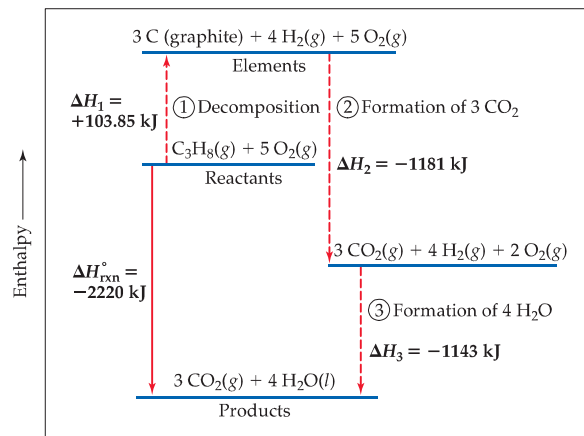
- Equation 5.26 is the reverse of the formation reaction for $\text{C}_3\text{H}_8(\text{g})$, so the enthalpy change for this reaction is $-\Delta H_f^\circ[\text{C}_3\text{H}_8(\text{g})]$.
- Equation 5.27 is the formation reaction for 3 mol of $\text{CO}_2(\text{g})$. Because enthalpy is an extensive property, the enthalpy change for this step is $3\Delta H_f^\circ[\text{CO}_2(\text{g})]$. Similarly, the enthalpy change for Equation 5.28 is $4\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})]$. The reaction specifies that $\text{H}_2\text{O}(\text{l})$, was produced, so be careful to use the value of ΔH_f° for $\text{H}_2\text{O}(\text{l})$, not $\text{H}_2\text{O}(\text{g})$.
- We assume that the stoichiometric coefficients in the balanced equation represent moles. For Equation 5.29, therefore, the value $\Delta H_{\text{rxn}}^\circ = -2220 \text{ kJ}$ represents the enthalpy change for the reaction of 1 mol C_3H_8 and 5 mol O_2 to form 3 mol CO_2 and 4 mol H_2O . The product of the number of moles and the enthalpy change in kJ/mol has the units kJ: (number of moles) \times (ΔH_f° in kJ/mol) = kJ. We therefore report $\Delta H_{\text{rxn}}^\circ$ in kJ.

Figure 5.22 \blacktriangledown presents an enthalpy diagram for Equation 5.29, showing how it can be broken into steps involving formation reactions.

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:

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

The symbol Σ (sigma) means “the sum of,” and n and m are the stoichiometric coefficients of the chemical equation. The first term in Equation 5.31 represents the formation reactions of the products, which are written in the “forward” direction, that is, elements reacting to form products. This term is analogous to Equations 5.27 and 5.28 in the previous example. The second term represents the reverse of the formation reactions of the reactants, as in Equation 5.26, which is why the ΔH_f° values have a minus sign in front of them.



\blacktriangleleft **Figure 5.22 An enthalpy diagram relating the enthalpy change for a reaction to enthalpies of formation.** For the combustion of propane gas, $\text{C}_3\text{H}_8(\text{g})$, the reaction is $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \longrightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$. We can imagine this reaction as occurring in three steps. First, $\text{C}_3\text{H}_8(\text{g})$ is decomposed to its elements, so $\Delta H_1 = \Delta H_f^\circ[\text{C}_3\text{H}_8(\text{g})]$. Second, 3 mol $\text{CO}_2(\text{g})$ are formed, so $\Delta H_2 = 3\Delta H_f^\circ[\text{CO}_2(\text{g})]$. Finally, 4 mol $\text{H}_2\text{O}(\text{l})$ are formed, so $\Delta H_3 = 4\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})]$. Hess’s law tells us that $\Delta H_{\text{rxn}}^\circ = \Delta H_1 + \Delta H_2 + \Delta H_3$. This same result is given by Equation 5.31 because $\Delta H_f^\circ[\text{O}_2(\text{g})] = 0$.

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, $C_6H_6(l)$, to form $CO_2(g)$ and $H_2O(l)$. (b) Compare the quantity of heat produced by combustion of 1.00 g propane to that produced by 1.00 g benzene.

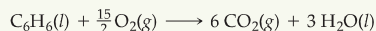
SOLUTION

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, ΔH° . (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 above in the text. (See Equations 5.29 and 5.30.)

Plan: (a) We need to write the balanced equation for the combustion of C_6H_6 . We then look up ΔH_f° 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 above to calculate the enthalpy change per gram of that substance.

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 ΔH° for this reaction by using Equation 5.31 and data in Table 5.3. Remember to multiply the ΔH_f° 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 $\Delta H_f^\circ[O_2(g)] = 0$

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

(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:

$$\begin{aligned}C_3H_8(g): & (-2220 \text{ kJ/mol})(1 \text{ mol}/44.1 \text{ g}) = -50.3 \text{ kJ/g} \\ C_6H_6(l): & (-3267 \text{ kJ/mol})(1 \text{ mol}/78.1 \text{ g}) = -41.8 \text{ kJ/g}\end{aligned}$$

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

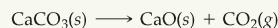
Using the standard enthalpies of formation listed in Table 5.3, calculate the enthalpy change for the combustion of 1 mol of ethanol:



Answer: -1367 kJ

SAMPLE EXERCISE 5.12 | Calculating an Enthalpy of Formation Using an Enthalpy of Reaction

The standard enthalpy change for the reaction



is 178.1 kJ. From the values for the standard enthalpies of formation of $CaO(s)$ and $CO_2(g)$ given in Table 5.3, calculate the standard enthalpy of formation of $CaCO_3(s)$.

SOLUTION

Analyze: We need 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 ΔH_f° values from Table 5.3 or Appendix C, we have

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

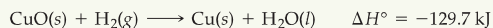
Solving for $\Delta H_f^\circ(CaCO_3)$ gives

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

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

PRACTICE EXERCISE

Given the following standard enthalpy change, use the standard enthalpies of formation in Table 5.3 to calculate the standard enthalpy of formation of CuO(s):



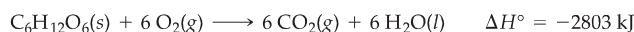
Answer: -156.1 kJ/mol

5.8 FOODS AND FUELS

Most chemical reactions used for the production of heat are combustion reactions. The energy released when one gram of a material is combusted is often called its **fuel value**. Although fuel values represent the heat *released* in a combustion reaction, fuel values are reported as positive numbers. The fuel value of any food or fuel can be measured by calorimetry.

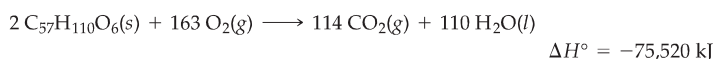
Foods

Most of the energy our bodies need comes from carbohydrates and fats. The forms of carbohydrate known as starch are decomposed in the intestines into glucose, $\text{C}_6\text{H}_{12}\text{O}_6$. 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 $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$, and energy:



The breakdown of carbohydrates is rapid, so 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 (4 kcal/g).

Like carbohydrates, fats produce CO_2 and H_2O when metabolized and when subjected to combustion in a bomb calorimeter. The reaction of tristearin, $\text{C}_{57}\text{H}_{110}\text{O}_6$, a typical fat, is as follows:



The body uses the chemical energy from foods to maintain body temperature (see the “Chemistry and Life” box in Section 5.6), 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 (9 kcal/g).

The metabolism of proteins in the body 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, $(\text{NH}_2)_2\text{CO}$. 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 (4 kcal/g), the same as for carbohydrates.

The fuel values for a variety of common foods are shown in Table 5.4 ▼. 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 5.23 ►). 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 weight per day is required to keep the body functioning at a minimal level. An average 70-kg (154-lb) person expends about 800 kJ/hr when doing light work, such as slow walking or light gardening. Strenuous activity, such as running, often requires 2000 kJ/hr or more. When the energy value, or caloric content, of our food exceeds the energy we expend, our body stores the surplus as fat.



▲ **Figure 5.23 Labels of processed foods showing nutritional information.** Such labels give information about the quantities of different nutrients and the energy value (caloric value) in an average serving.

TABLE 5.4 ■ Compositions and Fuel Values of Some Common Foods

	Approximate Composition (% by mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g (Cal/g)
Carbohydrate	100	–	–	17	4
Fat	–	100	–	38	9
Protein	–	–	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer*	1.2	–	0.3	1.8	0.42
Bread	52	3	9	12	2.8
Cheese	4	37	28	20	4.7
Eggs	0.7	10	13	6.0	1.4
Fudge	81	11	2	18	4.4
Green beans	7.0	–	1.9	1.5	0.38
Hamburger	–	30	22	15	3.6
Milk (whole)	5.0	4.0	3.3	3.0	0.74
Peanuts	22	39	26	23	5.5

*Beers typically contain 3.5% ethanol, which has fuel value.

GIVE IT SOME THOUGHT

Which releases the greatest amount of energy per gram upon metabolism, carbohydrates, proteins, or fats?

SAMPLE EXERCISE 5.13 | Comparing Fuel Values

A plant such as celery contains carbohydrates in the form of starch and cellulose. These two kinds of carbohydrates have essentially the same fuel values when combusted in a bomb calorimeter. When we consume celery, however, our bodies receive fuel value from the starch only. What can we conclude about the difference between starch and cellulose as foods?

SOLUTION

If cellulose does not provide fuel value, we must conclude that it is not converted in the body into CO_2 and H_2O , as starch is. A slight, but critical, difference in the structures of starch and cellulose explains why only starch is broken down into glucose in the body. Cellulose passes through without undergoing significant chemical change. It serves as fiber, or roughage, in the diet, but provides no caloric value.

PRACTICE EXERCISE

The nutritional label on a bottle of canola oil indicates that 10 g of the oil has an energy value of 86 kcal. A similar label on a bottle of pancake syrup indicates that 60 mL (about 60 g) has an energy value of 200 kcal. Account for the difference.

Answer: The oil has a fuel value of 8.6 kcal/g, whereas the syrup has a fuel value of about 3.3 kcal/g. The higher fuel value for the canola oil arises because the oil is essentially pure fat, whereas the syrup is a solution of sugars (carbohydrates) in water. The oil has a higher fuel value per gram; in addition, the syrup is diluted by water.

SAMPLE EXERCISE 5.14 | Estimating the Fuel Value of a Food from Its Composition

(a) A 28-g (1-oz) 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 kinds of substances, estimate the energy value (caloric content) of this serving.

(b) A person of average weight uses about 100 Cal/mi when running or jogging. How many servings of this cereal provide the energy value requirements for running 3 mi?

SOLUTION

(a) **Analyze:** The energy value of the serving will be the sum of the energy values of the protein, carbohydrates, and fat.

Plan: We are given the masses of the protein, carbohydrates, and fat contained in the combined . We can use the data in Table 5.4 to convert these masses to their energy values, which we can sum to get the total energy value.

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

This corresponds to 160 kcal:

$$(650 \text{ kJ})\left(\frac{1 \text{ kcal}}{4.18 \text{ kJ}}\right) = 160 \text{ kcal}$$

Recall that the dietary Calorie is equivalent to 1 kcal. Thus, the serving provides 160 Cal.

(b) Analyze: Here we are faced with the reverse problem, calculating the quantity of food that provides a specific energy value.

Plan: The problem statement provides a conversion factor between Calories and miles. The answer to part (a) provides us with a conversion factor between servings and Calories.

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

$$\text{Servings} = (3 \text{ mi})\left(\frac{100 \text{ Cal}}{1 \text{ mi}}\right)\left(\frac{1 \text{ serving}}{160 \text{ Cal}}\right) = 2 \text{ servings}$$

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 uses 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?

Answers: (a) 15 kJ/g, (b) 95 min

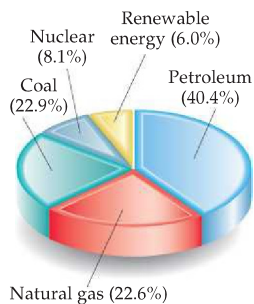
Fuels

The elemental compositions and fuel values of several common fuels are compared in Table 5.5. During the complete combustion of fuels, carbon is converted to CO_2 and hydrogen is converted to H_2O , 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. Compare, for example, the compositions and fuel values of bituminous coal and wood. The coal has a higher fuel value because of its greater carbon content.

In 2005 the United States consumed 1.05×10^{17} kJ of energy. This value corresponds to an average daily energy consumption per person of 9.6×10^5 kJ which is roughly 100 times greater than the per capita food-energy needs.

TABLE 5.5 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



▲ **Figure 5.24 Sources of energy consumed in the United States.** In 2005 the United States consumed a total of 1.05×10^{17} kJ of energy.

Although the population of the United States is only about 4.5% of the world's population, the U.S. accounts for nearly one-fourth of the world's total energy consumption. Figure 5.24 illustrates the sources of this energy.

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 (CH_4), with small amounts of ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). We determined the fuel value of propane in Sample Exercise 5.11. **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; it constitutes 80% of the fossil fuel reserves of the United States and 90% of those of the world. 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, SO_2 , a very 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.

One promising way to utilize coal reserves is to use them to produce a mixture of gaseous hydrocarbons called *syngas* (for "synthesis gas"). In this process, called *coal gasification*, the coal typically is pulverized and treated with superheated steam. Sulfur-containing compounds, water, and carbon dioxide can be removed from the products, leading to a gaseous mixture of CH_4 , H_2 , and CO , all of which have high fuel values:



Chemistry Put to Work

THE HYBRID CAR

The hybrid cars now entering the automobile marketplace nicely illustrate the convertibility of energy from one form to another. Hybrid cars run on either gasoline or electricity. The so-called "full hybrids" are cars capable of running at low speeds on a battery-powered electrical engine alone (Figure 5.25). The "mild hybrid" cars are best described as electrically assisted gasoline engines.

Full hybrid cars are more efficient than the mild hybrid designs but are more costly to produce and require more technological advances than the mild hybrid versions. The mild hybrids are likely to be more widely produced and sold within the next several years. Let's consider how they operate and some of the interesting thermodynamic considerations they incorporate.

Figure 5.26 shows a schematic diagram of the power system for a mild hybrid car. In addition to the 12-volt battery that is standard on conventional autos, the hybrid car typically carries a 48-volt battery pack. The electrical energy from this battery pack is not employed to move the car directly; an electrical engine capable of doing that, as in the full hybrids, requires from 150 to 300 volts. (The popular Toyota Prius has a battery pack consisting of 228 cells of 1.2 V each, thereby generating a nominal voltage of 270 V.)



▲ **Figure 5.25 A hybrid car.** The Lexus GS450h is the first rear-drive full hybrid luxury car, evidence of the widespread movement of hybrid cars into the marketplace.

In the mild hybrid cars the added electrical source is employed to run various auxiliary devices that would otherwise be run off the gasoline engine, such as water pump, power steering, and air systems. To save on energy, when the hybrid

Because it is gaseous, syngas can be easily transported in pipelines. Additionally, because much of the sulfur in coal is removed during the gasification process, combustion of syngas causes less air pollution than burning coal. For these reasons, the economical conversion of coal and petroleum into “cleaner” fuels such as syngas and hydrogen is a very active area of current research in chemistry and engineering.

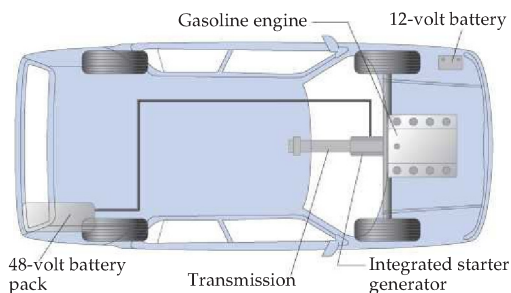
Other Energy Sources

Nuclear energy is energy that is released in either the splitting or the fusion (combining) of the nuclei of atoms. Nuclear power is currently used to produce about 22% of the electric power in the United States and comprises about 8% of the total U.S. energy production (Figure 5.24). Nuclear energy is, in principle, free of the polluting emissions that are a major problem in the generation of energy from fossil fuels. However, nuclear power plants produce radioactive waste products, and their use has therefore been fraught with controversy. We will discuss issues related to the production of nuclear energy in Chapter 21.

Fossil fuel and nuclear energy are *nonrenewable* sources of energy; they are limited resources that we are consuming at a much greater rate than they are being regenerated. Eventually these fuels will be expended, although estimates vary greatly as to when this will occur. Because nonrenewable sources of energy will eventually be used up, a great deal of research is being conducted into sources of **renewable energy**, energy 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 in the mass of Earth, *hydroelectric energy* from flowing rivers, and *biomass energy* from crops, such as trees and corn, and from biological waste matter. Currently, renewable sources provide about 6.0% of the U.S. annual energy consumption, with hydroelectric and biomass sources as the major contributors.

Providing our future energy needs will most certainly depend on developing the 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

car comes to a stop, the engine shuts off. It restarts automatically when the driver presses the accelerator. This feature saves fuel that would otherwise be used to keep the engine idling at traffic lights and other stopping situations.



▲ **Figure 5.26 Schematic diagram of a mild hybrid car.** The 48-volt battery pack provides energy for operating several auxiliary functions. It is recharged from the engine and through the braking system.

The idea is that the added electrical system will improve overall fuel efficiency of the car. The added battery, moreover, is not supposed to need recharging from an external power source. Where, then, can the improved fuel efficiency come from? Clearly, if the battery pack is to continue to operate auxiliary devices such as the water pump, it must be recharged. We can think of it this way: The source of the voltage that the battery develops is a chemical reaction. Recharging the battery thus represents a conversion of mechanical energy into chemical potential energy. The recharging occurs in part through the agency of an alternator, which runs off the engine and provides a recharging voltage. In the mild hybrid car, the braking system serves as an additional source of mechanical energy for recharging. When the brakes are applied in a conventional car, the car’s kinetic energy is converted through the brake pads in the wheels into heat, so no useful work is done. In the hybrid car, some of the car’s kinetic energy is used to recharge the battery when the brakes are applied. Thus, kinetic energy that would otherwise be dissipated as heat is partially converted into useful work. Overall, the mild hybrid cars are expected to yield 10–20% improvements in fuel economy as compared with similar conventional cars.

reaches each square meter of Earth's surface every second. The average solar energy that falls on only 0.1% of U.S. land area is equivalent to all the energy that this nation currently uses. Harnessing this energy is difficult because it is dilute (it is distributed over a wide area) and it varies with time of day and weather conditions. The effective use of solar energy will depend on the development of some means of storing the collected energy for use at a later time. Any practical means for doing this will almost certainly involve use of an endothermic chemical process that can be later reversed to release heat. One such reaction is the following:



This reaction proceeds in the forward direction at high temperatures, which can be obtained in a solar furnace. The CO and H₂ formed in the reaction could then be stored and allowed to react later, with the heat released being put to useful work.

A survey taken about 25 years ago at Walt Disney's EPCOT Center revealed that nearly 30% of the visitors expected that solar energy would be the principal source of energy in the United States in the year 2000. The future of solar energy has proven to be a lot like the Sun itself: big and bright but farther away than it seems. Nevertheless, important progress has been made in recent years. Perhaps the most direct way to make use of the Sun's energy is to convert it directly into electricity by use of photovoltaic devices, sometimes called *solar cells*. The efficiencies of solar energy conversion by use of such devices have increased dramatically during the past few years because of intensive research efforts. Photovoltaics are vital to the generation of power for the space station. More significant for our Earth-bound concerns, the unit costs of solar panels have been steadily declining, even as their efficiencies have improved dramatically.

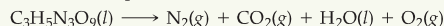
In 2006 construction was started in southern Portugal on what the builders claim will be the world's biggest solar energy power station. The first module of the station is planned to cover about 150 acres and is capable of generating 11 MW (megawatts) of electrical power—enough for 8000 homes. When fully constructed, the plant is projected to cover 620 acres and supply over 100 MW of power. Several other large solar plants with capacities over 100 MW have also been announced in Australia, Israel, and China.

■ SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

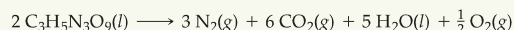
Trinitrolycerin, C₃H₅N₃O₉ (usually referred to simply as nitrolycerin), has been widely used as an explosive. Alfred Nobel used it to make dynamite in 1866. Rather surprisingly, it also is used as a medication, to relieve angina (chest pains resulting from partially blocked arteries to the heart) by dilating the blood vessels. The enthalpy of decomposition at 1 atm pressure of trinitrolycerin to form nitrogen gas, carbon dioxide gas, liquid water, and oxygen gas at 25 °C is -1541.4 kJ/mol. (a) Write a balanced chemical equation for the decomposition of trinitrolycerin. (b) Calculate the standard heat of formation of trinitrolycerin. (c) A standard dose of trinitrolycerin 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 number of calories is released? (d) One common form of trinitrolycerin 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 trinitrolycerin is used as an explosive to break rockfaces in highway construction.

SOLUTION

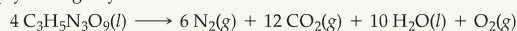
(a) The general form of the equation we must balance is



We go about balancing in the usual way. To obtain an even number of nitrogen atoms on the left, we multiply the formula for C₃H₅N₃O₉ by 2. This then gives us 3 mol of N₂, 6 mol of CO₂ and 5 mol of H₂O. Everything is balanced except for oxygen. We have an odd number of oxygen atoms on the right. We can balance the oxygen by adding $\frac{1}{2}$ mol of O₂ on the right:

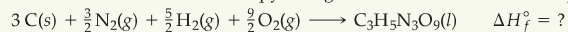


We multiply through by 2 to convert all coefficients to whole numbers:

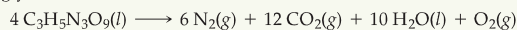


(At the temperature of the explosion, water is a gas. The rapid expansion of the gaseous products creates the force of an explosion.)

(b) The heat of formation is the enthalpy change in the balanced chemical equation:



We can obtain the value of ΔH_f° by using the equation for the heat of decomposition of trinitrolycerin:



The enthalpy change in this reaction is $4(-1541.4 \text{ kJ}) = -6165.6 \text{ kJ}$. [We need to multiply by 4 because there are 4 mol of $\text{C}_3\text{H}_5\text{N}_3\text{O}_9(l)$ in the balanced equation.] This enthalpy change is given by 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 ΔH_f° values for $\text{N}_2(g)$ and $\text{O}_2(g)$ are zero, by definition. We look up the values for $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ from Table 5.3 and find that

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

$$\Delta H_f^\circ(\text{C}_3\text{H}_5\text{N}_3\text{O}_9(l)) = -353.6 \text{ kJ/mol}$$

(c) We know that on oxidation 1 mol of $\text{C}_3\text{H}_5\text{N}_3\text{O}_9(l)$ yields 1541.4 kJ. We need to calculate the number of moles of in $\text{C}_3\text{H}_5\text{N}_3\text{O}_9(l)$ in 0.60 mg:

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

$$= 4.1 \text{ J}$$

(d) Because trinitrolycerin 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. [∞ \(Sections 2.5 and 2.6\)](#) Also, the molecular formula suggests that it is likely to be a molecular substance. All the elements of which it is composed are nonmetals.

(e) The energy stored in trinitrolycerin is chemical potential energy. When the substance reacts explosively, it forms substances such as 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 very high heat energy is transferred to the surroundings; the gases expand against the surroundings, which may be solid materials. Work is done in 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.

CHAPTER REVIEW

SUMMARY AND KEY TERMS

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** is the energy due to the motion of the object; and (2) **potential energy** is the energy that an object possesses by virtue of its position relative to other objects. An electron in motion near a proton, for example, has kinetic energy because of its motion and potential energy because of its electrostatic attraction to the proton. The SI unit of ener-

gy is the **joule** (J): $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$. Another common energy unit is the **calorie** (cal), which was originally defined as the quantity of energy necessary to increase the temperature of 1 g of water by 1°C : $1 \text{ cal} = 4.184 \text{ J}$. 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. Energy can be transferred between the system and the surroundings as work or

heat. **Work** is the energy expended to move an object against a **force**. **Heat** is the energy that is transferred from a hotter object to a colder one. **Energy** is the capacity to do work or to transfer heat.

Section 5.2 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, ΔE , 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. The heat, q , and the work, w , are not state functions; their values depend on the particular way in which a system changes its state.

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. 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 that is due to gases is involved, the change in the enthalpy of a system, ΔH , equals the heat gained or lost by the system at constant pressure, $\Delta H = q_p$. For an endothermic process, $\Delta H > 0$; for an exothermic process, $\Delta H < 0$. Every substance has a characteristic enthalpy. In a chemical process, the **enthalpy of reaction** is the enthalpy of the products minus the enthalpy of the reactants: $\Delta H_{\text{rxn}} = H(\text{products}) - H(\text{reactants})$. 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 ΔH . (3) The enthalpy of reaction depends on the physical states of the reactants and products.

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 J/g·K. The amount of heat, q , absorbed by a substance is the product of its specific heat (C_s), its mass, and its temperature change: $q = C_s \times m \times \Delta T$. 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**. Bomb calorimeters are used to measure the heat evolved in combustion reactions. The heat transferred under constant-volume conditions is equal to ΔE . However, corrections can be applied to ΔE values to yield enthalpies of combustion.

Section 5.6 Because enthalpy is a state function, ΔH 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, ΔH for the reaction will be equal to the sum of the enthalpy changes for the steps. We can therefore calculate ΔH for any process, as long as we can write the process as a series of steps for which ΔH is known.

Section 5.7 The **enthalpy of formation**, ΔH_f° , of a substance is the enthalpy change for the reaction in which the substance is formed from its constituent elements. The **standard enthalpy change** of a reaction, ΔH° , is the enthalpy change when all reactants and products are at 1 atm pressure and a specific temperature, usually 298 K (25 °C). Combining these ideas, the **standard enthalpy of formation**, ΔH_f° , of a substance is the change in enthalpy for the reaction that forms one mole of the substance from its elements in their most stable form with all reactants and products at 1 atm pressure and usually 298 K. For any element in its most stable state at 298 K and 1 atm pressure, $\Delta H_f^\circ = 0$. 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:

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

Section 5.8 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**. Coal is the most abundant fossil fuel, but the sulfur present in most coals causes air pollution. Coal gasification is one possible way to use existing resources as sources of cleaner energy in the future. Sources of **renewable energy** include solar energy, wind energy, biomass, and hydroelectric energy. Nuclear power does not utilize fossil fuels but does create serious waste-disposal problems.

KEY SKILLS

- Interconvert energy units.
- Express the relationships among the quantities q , w , ΔE , and ΔH . Understand their sign conventions, including how the signs of q and ΔH relate to whether a process is exothermic or endothermic.

- State the first law of thermodynamics.
- Understand the concept of a state function and be able to give examples.
- Use thermochemical equations to relate the amount of heat energy transferred in reactions at constant pressure (ΔH) to the amount of substance involved in the reaction.
- Calculate the heat transferred in a process from temperature measurements together with heat capacities or specific heats (calorimetry).
- Use Hess's law to determine enthalpy changes for reactions.
- Use standard enthalpies of formation to calculate ΔH° for reactions.

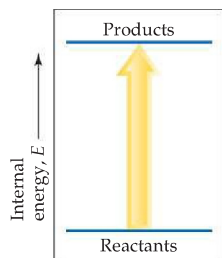
KEY EQUATIONS

- $E_k = \frac{1}{2}mv^2$ [5.1] Kinetic energy
- $\Delta E = E_{\text{final}} - E_{\text{initial}}$ [5.4] The change in internal energy
- $\Delta E = q + w$ [5.5] Relates the change in internal energy to heat and work (the first law of thermodynamics)
- $w = -P \Delta V$ [5.7] The work done by an expanding gas at constant pressure
- $\Delta H = \Delta E + P \Delta V = q_p$ [5.10] Enthalpy change at constant pressure
- $q = C_s \times m \times \Delta T$ [5.22] Heat gained or lost based on specific heat, mass, and temperature change.
- $\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants})$ [5.31] Standard enthalpy change of a reaction

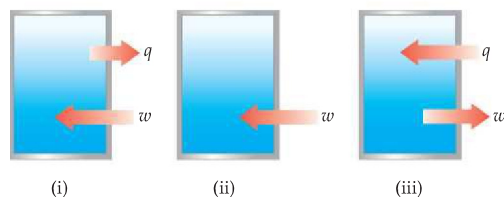
VISUALIZING CONCEPTS

5.1 Imagine a book that is falling from a shelf. At a particular moment during its fall, the book has a kinetic energy of 13 J and a potential energy with respect to the floor of 72 J. How does the book's kinetic energy and its potential energy change as it continues to fall? What is its total kinetic energy at the instant just before it strikes the floor? [Section 5.1]

5.2 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 ΔE for this process? (c) If there is no work associated with the process, is it exothermic or endothermic? [Section 5.2]



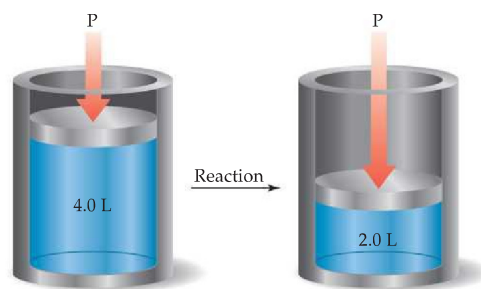
5.3 The contents of the closed box in each of the following illustrations represent a system, and the arrows show the changes to the system during some process. The



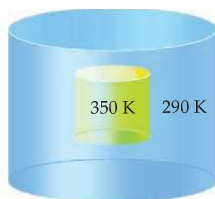
lengths of the arrows represent the relative magnitudes of q and w (a) Which of these processes is endothermic? (b) For which of these processes, if any, is $\Delta E < 0$? (c) For which process, if any, is there a net gain in internal energy? [Section 5.2]

5.4 Imagine that you are climbing a mountain. (a) Is the distance you travel to the top a state function? Why or why not? (b) Is the change in elevation between your base camp and the peak a state function? Why or why not? [Section 5.2]

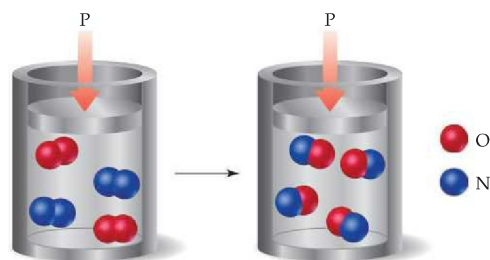
5.5 In the cylinder diagrammed below, a chemical process occurs at constant temperature and pressure. (a) Is the sign of w indicated by this change positive or negative? (b) If the process is endothermic, does the internal energy of the system within the cylinder increase or decrease during the change and is ΔE positive or negative? [Sections 5.2 and 5.3]



- 5.6 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? What is the sign of q associated with each change? 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]

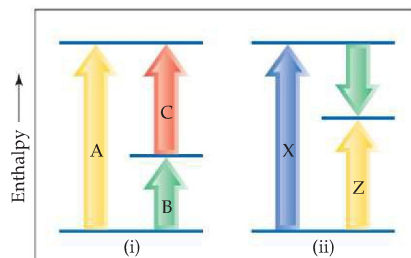


- 5.7 Which will release more heat as it cools from 50 °C to 25 °C, 1 kg of water or 1 kg of aluminum? How do you know? [Section 5.5]
- 5.8 A gas-phase reaction was run in an apparatus designed to maintain a constant pressure. (a) Write a balanced

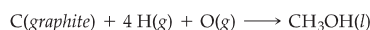


chemical equation for the reaction depicted, and predict whether w is positive, negative, or zero. (b) Using data from Appendix C, determine ΔH for the formation of one mole of the product. Why is this enthalpy change called the enthalpy of formation of the involved product? [Sections 5.3 and 5.7]

- 5.9 Consider the two diagrams below. (a) Based on (i), write an equation showing how ΔH_A is related to ΔH_B and ΔH_C . How do both diagram (i) and your equation relate to the fact that enthalpy is a state function? (b) Based on (ii), write an equation relating ΔH_Z to the other enthalpy changes in the diagram. (c) How do these diagrams relate to Hess's law? [Section 5.6]



- 5.10 Does ΔH_{rxn} for the reaction represented by the following equation equal the standard enthalpy of formation for $\text{CH}_3\text{OH}(l)$? Why or why not? [Section 5.7]



EXERCISES

The Nature of Energy

- 5.11 In what two ways can an object possess energy? How do these two ways differ from one another?
- 5.12 Suppose you toss a tennis ball upward. (a) Does the kinetic energy of the ball increase or decrease as it moves higher? (b) What happens to the potential energy of the ball as it moves higher? (c) If the same amount of energy were imparted to a ball the same size as a tennis ball, but of twice the mass, how high would it go in comparison to the tennis ball? Explain your answers.
- 5.13 (a) Calculate the kinetic energy in joules of a 45-g golf ball moving at 61 m/s. (b) Convert this energy to calories. (c) What happens to this energy when the ball lands in a sand trap?
- 5.14 (a) What is the kinetic energy in joules of an 850-lb motorcycle moving at 66 mph? (b) By what factor will the kinetic energy change if the speed of the motorcycle is decreased to 33 mph? (c) Where does the kinetic energy of the motorcycle go when the rider brakes to a stop?
- 5.15 The use of the British thermal unit (Btu) is common in much engineering work. A Btu is the amount of heat required to raise the temperature of 1 lb of water by 1 °F. Calculate the number of joules in a Btu.
- 5.16 A watt is a measure of power (the rate of energy change) equal to 1 J/s. (a) Calculate the number of joules in a kilowatt-hour. (b) An adult person radiates heat to the surroundings at about the same rate as a 100-watt electric incandescent lightbulb. What is the total amount of energy in kcal radiated to the surroundings by an adult in 24 hours?
- 5.17 (a) What is meant by the term *system* in thermodynamics? (b) What is a *closed system*?
- 5.18 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? Explain your choice. (b) If it is not a closed system, what could be done to make it a closed system?



- 5.19 (a) What is work? (b) How do we determine the amount of work done, given the force associated with the work?
- 5.20 (a) What is heat? (b) Under what conditions is heat transferred from one object to another?
- 5.21 Identify the force present, and explain whether work is being performed in the following cases: (a) You lift a

pencil off the top of a desk. (b) A spring is compressed to half its normal length.

- 5.22 Identify the force present, and explain whether work is done when (a) a positively charged particle moves in a circle at a fixed distance from a negatively charged particle; (b) an iron nail is pulled off a magnet.

The First Law of Thermodynamics

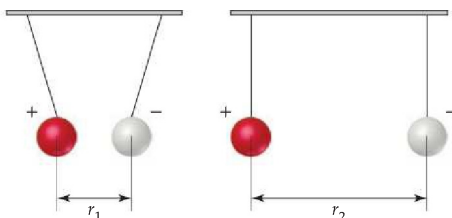
- 5.23 (a) State the first law of thermodynamics. (b) What is meant by the *internal energy* of a system? (c) By what means can the internal energy of a closed system increase?
- 5.24 (a) Write an equation that expresses the first law of thermodynamics in terms of heat and work. (b) Under what conditions will the quantities q and w be negative numbers?
- 5.25 Calculate ΔE , and determine whether the process is endothermic or exothermic for the following cases: (a) A system absorbs 105 kJ of heat from its surroundings while doing 29 kJ of work on the surroundings; (b) $q = 1.50$ kJ and $w = -657$ J; (c) the system releases 57.5 kJ of heat while doing 22.5 kJ of work on the surroundings.
- 5.26 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 heated by adding 850 J of heat. It expands, doing 382 J of work on the atmosphere. (b) A 50-g sample of water is cooled from 30 °C to 15 °C, thereby losing approximately 3140 J of heat. (c) A chemical reaction releases 6.47 kJ of heat and does no work on the surroundings.

- 5.27 A gas is confined to a cylinder fitted with a piston and an electrical heater, as shown in the accompanying illustration. 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? Explain.



(b) What can you say about the values of q and w in each of these cases? (c) What can you say about the relative values of ΔE for the system (the gas in the cylinder) in the two cases?

- 5.28 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 along a track. (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 ΔE ? (c) What can you say about q and w for this process?



- 5.29 (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 work a state function? Why or why not?
- 5.30 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 $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, (c) the work accomplished in burning a gallon of gasoline.

Enthalpy

- 5.31 (a) Why is the change in enthalpy usually easier to measure than the change in internal energy? (b) For a given process at constant pressure, ΔH is negative. Is the process endothermic or exothermic?
- 5.32 (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 absorbs heat from the surroundings. Does the enthalpy of the system increase or decrease during the process?
- 5.33 You are given ΔH for a process that occurs at constant pressure. What additional information do you need to determine ΔE for the process?

- 5.34 Suppose that the gas-phase reaction $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ were carried out in a constant-volume container at constant temperature. Would the measured heat change represent ΔH or ΔE ? If there is a difference, which quantity is larger for this reaction? Explain.

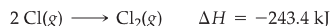
- 5.35 A gas is confined to a cylinder under constant atmospheric pressure, as illustrated in Figure 5.3. When the gas undergoes a particular chemical reaction, it releases 79 kJ of heat to its surroundings and does 18 kJ of P - V work on its surroundings. What are the values of ΔH and ΔE for this process?
- 5.36 A gas is confined to a cylinder under constant atmospheric pressure, as illustrated in Figure 5.3. When 378 J

of heat is added to the gas, it expands and does 56 J of work on the surroundings. What are the values of ΔH and ΔE for this process?

5.37 The complete combustion of acetic acid, $\text{CH}_3\text{COOH}(l)$, to form $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ at constant pressure releases 871.7 kJ of heat per mole of CH_3COOH . (a) Write a balanced thermochemical equation for this reaction. (b) Draw an enthalpy diagram for the reaction.

5.38 The decomposition of zinc carbonate, $\text{ZnCO}_3(s)$, into zinc oxide, $\text{ZnO}(s)$, and $\text{CO}_2(g)$ at constant pressure requires the addition of 71.5 kJ of heat per mole of ZnCO_3 . (a) Write a balanced thermochemical equation for the reaction. (b) Draw an enthalpy diagram for the reaction.

5.39 Consider the following reaction, which occurs at room temperature and pressure:



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

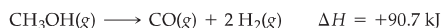
5.40 Without referring to tables, predict which of the following has the higher enthalpy in each case: (a) 1 mol $\text{CO}_2(s)$ or 1 mol $\text{CO}_2(g)$ at the same temperature, (b) 2 mol of hydrogen atoms or 1 mol of H_2 , (c) 1 mol $\text{H}_2(g)$ and 0.5 mol $\text{O}_2(g)$ at 25 °C or 1 mol $\text{H}_2\text{O}(g)$ at 25 °C, (d) 1 mol $\text{N}_2(g)$ at 100 °C or 1 mol $\text{N}_2(g)$ at 300 °C.

5.41 Consider the following reaction:



(a) Is this reaction exothermic or endothermic? (b) Calculate the amount of heat transferred when 2.4 g of $\text{Mg}(s)$ reacts at constant pressure. (c) How many grams of MgO are produced during an enthalpy change of -96.0 kJ ? (d) How many kilojoules of heat are absorbed when 7.50 g of $\text{MgO}(s)$ is decomposed into $\text{Mg}(s)$ and $\text{O}_2(g)$ at constant pressure?

5.42 Consider the following reaction:



(a) Is heat absorbed or released in the course of this reaction? (b) Calculate the amount of heat transferred when 45.0 g of $\text{CH}_3\text{OH}(g)$ is decomposed by this reaction at constant pressure. (c) For a given sample of CH_3OH , the enthalpy change on reaction is 25.8 kJ. How many grams of hydrogen gas are produced? What is the value of ΔH for the reverse of the previous reaction? (d) How

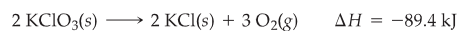
many kilojoules of heat are released when 50.9 g of $\text{CO}(g)$ reacts completely with $\text{H}_2(g)$ to form $\text{CH}_3\text{OH}(g)$ at constant pressure?

5.43 When solutions containing silver ions and chloride ions are mixed, silver chloride precipitates:



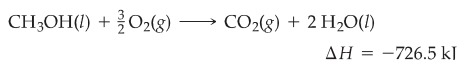
(a) Calculate ΔH for production of 0.200 mol of AgCl by this reaction. (b) Calculate ΔH for the production of 2.50 g of AgCl . (c) Calculate ΔH when 0.150 mmol of AgCl dissolves in water.

5.44 At one time, a common means of forming small quantities of oxygen gas in the laboratory was to heat KClO_3 :



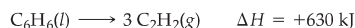
For this reaction, calculate ΔH for the formation of (a) 0.632 mol of O_2 and (b) 8.57 g of KCl . (c) The decomposition of KClO_3 proceeds spontaneously when it is heated. Do you think that the reverse reaction, the formation of KClO_3 from KCl and O_2 , is likely to be feasible under ordinary conditions? Explain your answer.

5.45 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 ΔH 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 ΔH to increase, decrease, or stay the same? Explain.

5.46 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 ΔH 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 ΔH to increase, decrease, or stay the same? Explain.

Calorimetry

5.47 (a) What are the units of molar heat capacity? (b) What are the units of specific heat? (c) If you know the specific heat of copper, what additional information do you need to calculate the heat capacity of a particular piece of copper pipe?

5.48 Two solid objects, A and B, are placed in boiling water and allowed to come to temperature there. Each is then lifted out and placed in separate beakers containing 1000 g 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?

5.49 (a) What is the specific heat of liquid water? (b) What is the molar heat capacity of liquid water? (c) What is the heat capacity of 185 g of liquid water? (d) How many kJ of heat are needed to raise the temperature of 10.00 kg of liquid water from 24.6 °C to 46.2 °C?

5.50 (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.

5.51 The specific heat of iron metal is 0.450 J/g·K. How many J of heat are necessary to raise the temperature of a 1.05-kg block of iron from 25.0 °C to 88.5 °C?

- 5.52 The specific heat of ethylene glycol is 2.42 J/g·K. How many J of heat are needed to raise the temperature of 62.0 g of ethylene glycol from 13.1 °C to 40.5 °C?
- 5.53 When a 9.55-g sample of solid sodium hydroxide dissolves in 100.0 g of water in a coffee-cup calorimeter (Figure 5.17), the temperature rises from 23.6 °C to 47.4 °C. Calculate ΔH (in kJ/mol NaOH) for the solution process
- $$\text{NaOH}(s) \longrightarrow \text{Na}^+(aq) + \text{OH}^-(aq)$$
- Assume that the specific heat of the solution is the same as that of pure water.
- 5.54 (a) When a 3.88-g sample of solid ammonium nitrate dissolves in 60.0 g of water in a coffee-cup calorimeter (Figure 5.17), the temperature drops from 23.0 °C to 18.4 °C. Calculate ΔH (in kJ/mol NH_4NO_3) for the solution process
- $$\text{NH}_4\text{NO}_3(s) \longrightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)$$
- Assume that the specific heat of the solution is the same as that of pure water. (b) Is this process endothermic or exothermic?
- 5.55 A 2.200-g sample of quinone ($\text{C}_6\text{H}_4\text{O}_2$) is burned in a bomb calorimeter whose total heat capacity is 7.854 kJ/°C. The temperature of the calorimeter increases from 23.44 °C to 30.57 °C. What is the heat of combustion per gram of quinone? Per mole of quinone?
- 5.56 A 1.800-g sample of phenol ($\text{C}_6\text{H}_5\text{OH}$) was burned in a bomb calorimeter whose total heat capacity is 11.66 kJ/°C. The temperature of the calorimeter plus contents increased from 21.36 °C to 26.37 °C. (a) Write a balanced chemical equation for the bomb calorimeter reaction. (b) What is the heat of combustion per gram of phenol? Per mole of phenol?
- 5.57 Under constant-volume conditions the heat of combustion of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is 15.57 kJ/g. A 2.500-g sample of glucose is burned in a bomb calorimeter. The temperature of the calorimeter increased from 20.55 °C to 23.25 °C. (a) What is the total heat capacity of the calorimeter? (b) If the size of the glucose sample had been exactly twice as large, what would the temperature change of the calorimeter have been?
- 5.58 Under constant-volume conditions the heat of combustion of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is 26.38 kJ/g. A 1.640-g sample of benzoic acid is burned in a bomb calorimeter. The temperature of the calorimeter increases from 22.25 °C to 27.20 °C. (a) What is the total heat capacity of the calorimeter? (b) A 1.320-g sample of a new organic substance is combusted in the same calorimeter. The temperature of the calorimeter increases from 22.14 °C to 26.82 °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

- 5.59 What is the connection between Hess's law and the fact that H is a state function?
- 5.60 Consider the following hypothetical reactions:
- $$\begin{aligned} \text{A} &\longrightarrow \text{B} & \Delta H &= +30 \text{ kJ} \\ \text{B} &\longrightarrow \text{C} & \Delta H &= +60 \text{ kJ} \end{aligned}$$
- (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.
- 5.61 Calculate the enthalpy change for the reaction
- $$\text{P}_4\text{O}_6(s) + 2 \text{O}_2(g) \longrightarrow \text{P}_4\text{O}_{10}(s)$$
- given the following enthalpies of reaction:
- $$\begin{aligned} \text{P}_4(s) + 3 \text{O}_2(g) &\longrightarrow \text{P}_4\text{O}_6(s) & \Delta H &= -1640.1 \text{ kJ} \\ \text{P}_4(s) + 5 \text{O}_2(g) &\longrightarrow \text{P}_4\text{O}_{10}(s) & \Delta H &= -2940.1 \text{ kJ} \end{aligned}$$
- 5.62 From the enthalpies of reaction
- $$\begin{aligned} 2 \text{H}_2(g) + \text{O}_2(g) &\longrightarrow 2 \text{H}_2\text{O}(g) & \Delta H &= -483.6 \text{ kJ} \\ 3 \text{O}_2(g) &\longrightarrow 2 \text{O}_3(g) & \Delta H &= +284.6 \text{ kJ} \end{aligned}$$
- calculate the heat of the reaction
- $$3 \text{H}_2(g) + \text{O}_3(g) \longrightarrow 3 \text{H}_2\text{O}(g)$$
- 5.63 From the enthalpies of reaction
- $$\begin{aligned} \text{H}_2(g) + \text{F}_2(g) &\longrightarrow 2 \text{HF}(g) & \Delta H &= -537 \text{ kJ} \\ \text{C}(s) + 2 \text{F}_2(g) &\longrightarrow \text{CF}_4(g) & \Delta H &= -680 \text{ kJ} \\ 2 \text{C}(s) + 2 \text{H}_2(g) &\longrightarrow \text{C}_2\text{H}_4(g) & \Delta H &= +52.3 \text{ kJ} \end{aligned}$$
- calculate ΔH for the reaction of ethylene with F_2 :
- $$\text{C}_2\text{H}_4(g) + 6 \text{F}_2(g) \longrightarrow 2 \text{CF}_4(g) + 4 \text{HF}(g)$$
- 5.64 Given the data
- $$\begin{aligned} \text{N}_2(g) + \text{O}_2(g) &\longrightarrow 2 \text{NO}(g) & \Delta H &= +180.7 \text{ kJ} \\ 2 \text{NO}(g) + \text{O}_2(g) &\longrightarrow 2 \text{NO}_2(g) & \Delta H &= -113.1 \text{ kJ} \\ 2 \text{N}_2\text{O}(g) &\longrightarrow 2 \text{N}_2(g) + \text{O}_2(g) & \Delta H &= -163.2 \text{ kJ} \end{aligned}$$
- use Hess's law to calculate ΔH for the reaction
- $$\text{N}_2\text{O}(g) + \text{NO}_2(g) \longrightarrow 3 \text{NO}(g)$$

Enthalpies of Formation

- 5.65 (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*?
- 5.66 (a) Why are tables of standard enthalpies of formation so useful? (b) What is the value of the standard enthalpy of formation of an element in its most stable form? (c) Write the chemical equation for the reaction whose enthalpy change is the standard enthalpy of formation of glucose, $\text{C}_6\text{H}_{12}\text{O}_6(s)$, $\Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6]$.

5.67 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 use Appendix C to obtain the value of ΔH_f° : (a) $\text{NH}_3(\text{g})$, (b) $\text{SO}_2(\text{g})$, (c) $\text{RbClO}_3(\text{s})$, (d) $\text{NH}_4\text{NO}_3(\text{s})$.

5.68 Write balanced equations that describe the formation of the following compounds from elements in their standard states, and use Appendix C to obtain the values of their standard enthalpies of formation: (a) $\text{HBr}(\text{g})$, (b) $\text{AgNO}_3(\text{s})$, (c) $\text{Fe}_2\text{O}_3(\text{s})$, (d) $\text{CH}_3\text{COOH}(\text{l})$.

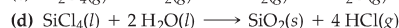
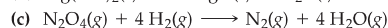
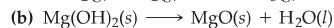
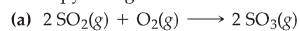
5.69 The following is known as the thermite reaction [Figure 5.7(b)]:



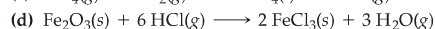
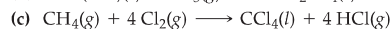
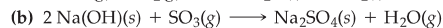
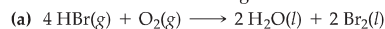
This highly exothermic reaction is used for welding massive units, such as propellers for large ships. Using standard enthalpies of formation in Appendix C, calculate ΔH° for this reaction.

5.70 Many cigarette lighters contain liquid butane, $\text{C}_4\text{H}_{10}(\text{l})$. Using standard enthalpies of formation, calculate the quantity of heat produced when 5.00 g of butane is completely combusted in air under standard conditions.

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



5.72 Using values from Appendix C, calculate the value of ΔH° for each of the following reactions:



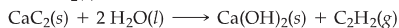
5.73 Complete combustion of 1 mol of acetone ($\text{C}_3\text{H}_6\text{O}$) liberates 1790 kJ:



$$\Delta H^\circ = -1790 \text{ kJ}$$

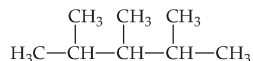
Using this information together with data from Appendix C, calculate the enthalpy of formation of acetone.

5.74 Calcium carbide (CaC_2) reacts with water to form acetylene (C_2H_2) and $\text{Ca}(\text{OH})_2$. From the following enthalpy of reaction data and data in Appendix C, calculate ΔH_f° for $\text{CaC}_2(\text{s})$:



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

5.75 Gasoline 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 $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ leads to $\Delta H^\circ = -5064.9 \text{ kJ/mol}$.

(a) Write a balanced equation for the combustion of 1 mol of $\text{C}_8\text{H}_{18}(\text{l})$. (b) Write a balanced equation for the formation of $\text{C}_8\text{H}_{18}(\text{l})$ from its elements. (c) By using the information in this problem and data in Table 5.3, calculate ΔH_f° for 2,3,4-trimethylpentane.

5.76 Naphthalene (C_{10}H_8) is a solid aromatic compound often sold as mothballs. The complete combustion of this substance to yield $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ at 25 °C yields 5154 kJ/mol. (a) Write balanced equations for the formation of naphthalene from the elements and for its combustion. (b) Calculate the standard enthalpy of formation of naphthalene.

5.77 Ethanol ($\text{C}_2\text{H}_5\text{OH}$) is currently blended with gasoline as an automobile fuel. (a) Write a balanced equation for the combustion of liquid ethanol in air. (b) Calculate the standard enthalpy change for the reaction, assuming $\text{H}_2\text{O}(\text{g})$ 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 g/mL. (d) Calculate the mass of CO_2 produced per kJ of heat emitted.

5.78 Methanol (CH_3OH) 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 $\text{H}_2\text{O}(\text{g})$ 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 CO_2 produced per kJ of heat emitted.

Foods and Fuels

5.79 (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?

5.80 (a) Why are fats well suited for energy storage in the human body? (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?

5.81 A serving of condensed cream of mushroom soup contains 7 g fat, 9 g carbohydrate, and 1 g protein. Estimate the number of Calories in a serving.

5.82 A pound of plain M&M[®] candies contains 96 g fat, 320 g carbohydrate, and 21 g protein. What is the fuel value in kJ in a 42-g (about 1.5 oz) serving? How many Calories does it provide?

5.83 The heat of combustion of fructose, $\text{C}_6\text{H}_{12}\text{O}_6$, is -2812 kJ/mol . If a fresh golden delicious apple weighing 4.23 oz (120 g) contains 16.0 g of fructose, what caloric content does the fructose contribute to the apple?

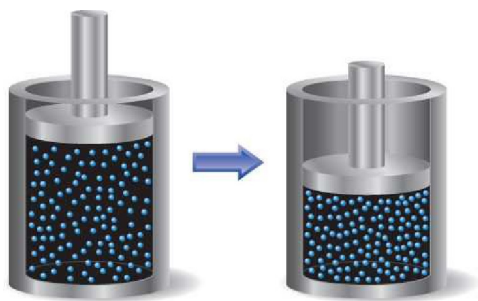
5.84 The heat of combustion of ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$, is -1367 kJ/mol . A batch of Sauvignon Blanc wine contains 10.6% ethanol by mass. Assuming the density of

the wine to be 1.0 g/mL, what caloric content does the alcohol (ethanol) in a 6-oz glass of wine (177 mL) have?

- 5.85 The standard enthalpies of formation of gaseous propyne (C_3H_4), propylene (C_3H_6), and propane (C_3H_8) are +185.4, +20.4, and -103.8 kJ/mol, respectively. (a) Calculate the heat evolved per mole on combustion of each substance to yield $CO_2(g)$ and $H_2O(g)$. (b) Calculate the heat evolved on combustion of 1 kg of each substance.

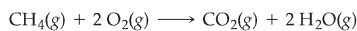
ADDITIONAL EXERCISES

- 5.87 At 20 °C (approximately room temperature) the average velocity of N_2 molecules in air is 1050 mph. (a) What is the average speed in m/s? (b) What is the kinetic energy (in J) of an N_2 molecule moving at this speed? (c) What is the total kinetic energy of 1 mol of N_2 molecules moving at this speed?
- 5.88 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.
- 5.89 When a mole of dry ice, $CO_2(s)$, is converted to $CO_2(g)$ at atmospheric pressure and -78 °C, the heat absorbed by the system exceeds the increase in internal energy of the CO_2 . Why is this so? What happens to the remaining energy?
- 5.90 The air bags that provide protection in autos 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?
- [5.91] An aluminum can of a soft drink is placed in a freezer. Later, you find that the can is split open and its contents frozen. Work was done on the can in splitting it open. Where did the energy for this work come from?
- [5.92] A sample of gas is contained in a cylinder-and-piston arrangement. It 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



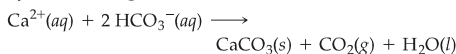
(c) Which is the most efficient fuel in terms of heat evolved per unit mass?

- 5.86 It is interesting to compare the “fuel value” of a hydrocarbon in a world where fluorine rather than oxygen is the combustion agent. The enthalpy of formation of $CF_4(g)$ is -679.9 kJ/mol. Which of the following two reactions is the more exothermic?



change? What is the sign of w for the state change? What can be said about ΔE 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 warmer 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 ΔE ?

- [5.93] Limestone stalactites and stalagmites are formed in caves by the following reaction:



If 1 mol of $CaCO_3$ forms at 298 K under 1 atm pressure, the reaction performs 2.47 kJ of P - V work, pushing back the atmosphere as the gaseous CO_2 forms. At the same time, 38.95 kJ of heat is absorbed from the environment. What are the values of ΔH and of ΔE for this reaction?

- [5.94] Consider the systems shown in Figure 5.9. In one case the battery becomes completely discharged by running the current through a heater, and in the other by running a fan. Both processes occur at constant pressure. In both cases the change in state of the system is the same: The battery goes from being fully charged to being fully discharged. Yet in one case the heat evolved is large, and in the other it is small. Is the enthalpy change the same in the two cases? If not, how can enthalpy be considered a state function? If it is, what can you say about the relationship between enthalpy change and q in this case, as compared with others that we have considered?
- 5.95 The enthalpy change for melting ice at 0 °C and constant atmospheric pressure is 6.01 kJ/mol. Calculate the quantity of energy required to melt a moderately large iceberg with a mass of 1.25 million metric tons. (A metric ton is 1000 kg.)
- 5.96 Comparing the energy associated with the rainstorm and that of a conventional explosive gives some idea of the immense amount of energy associated with a storm. (a) The heat of vaporization of water is 44.0 kJ/mol. Calculate the quantity of energy released when enough water vapor condenses to form 0.50 inches of rain over an area of one square mile. (b) The energy released when one ton of dynamite explodes is 4.2×10^6 kJ. Calculate the number of tons of dynamite needed to provide the energy of the storm in part (a).
- 5.97 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 1.7×10^3 gal of water?

[5.98] A coffee-cup calorimeter of the type shown in Figure 5.17 contains 150.0 g of water at 25.1 °C. A 121.0-g block of copper metal is heated to 100.4 °C by putting it in a beaker of boiling water. The specific heat of Cu(s) is 0.385 J/g·K. The Cu is added to the calorimeter, and after a time the contents of the cup reach a constant temperature of 30.1 °C. (a) Determine the amount of heat, in J, lost by the copper block. (b) Determine the amount of heat gained by the water. The specific heat of water is 4.18 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 copper block were absorbed by the water in the calorimeter?

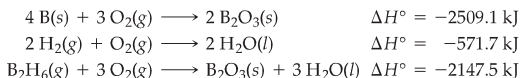
[5.99] (a) When a 0.235-g sample of benzoic acid is combusted in a bomb calorimeter, the temperature rises 1.642 °C. When a 0.265-g sample of caffeine, $C_8H_{10}O_2N_4$, is burned, the temperature rises 1.525 °C. Using the value 26.38 kJ/g for the heat of combustion of benzoic acid, calculate the heat 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?

5.100 How many grams of methane [$CH_4(g)$] must be combusted to heat 1.00 kg of water from 25.0 °C to 90.0 °C, assuming $H_2O(l)$ as a product and 100% efficiency in heat transfer?

5.101 Meals-ready-to-eat (MREs) are military meals that can be heated on a flameless heater. The heat is produced by the following reaction: $Mg(s) + 2 H_2O(l) \longrightarrow Mg(OH)_2(s) + H_2(g)$. (a) Calculate the standard enthalpy change for this reaction. (b) Calculate the number of grams of Mg needed for this reaction to release enough energy to increase the temperature of 25 mL of water from 15 °C to 85 °C.

5.102 Burning methane in oxygen can produce three different carbon-containing products: soot (very fine particles of graphite), $CO(g)$, and $CO_2(g)$. (a) Write three balanced equations for the reaction of methane gas with oxygen to produce these three products. In each case assume that $H_2O(l)$ 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 $CO_2(g)$ the predominant carbon-containing product of the combustion of methane?

5.103 (a) Calculate the standard enthalpy of formation of gaseous diborane (B_2H_6) using the following thermochemical information:



(b) Pentaborane (B_5H_9) is another boron hydride. What experiment or experiments would you need to perform to yield the data necessary to calculate the heat of formation of $B_5H_9(l)$? Explain by writing out and summing any applicable chemical reactions.

5.104 From the following data for three prospective fuels, calculate which could provide the most energy per unit volume:

Fuel	Density at 20 °C (g/cm ³)	Molar Enthalpy of Combustion (kJ/mol)
Nitroethane, $C_2H_5NO_2(l)$	1.052	-1368
Ethanol, $C_2H_5OH(l)$	0.789	-1367
Methylhydrazine, $CH_6N_2(l)$	0.874	-1305

5.105 The hydrocarbons acetylene (C_2H_2) and benzene (C_6H_6) have the same empirical formula. Benzene is an "aromatic" hydrocarbon, one that is unusually stable because of its structure. (a) By using the data in Appendix C, determine the standard enthalpy change for the reaction $3 C_2H_2(g) \longrightarrow C_6H_6(l)$. (b) Which has greater enthalpy, 3 mol of acetylene gas or 1 mol of liquid benzene? (c) Determine the fuel value in kJ/g for acetylene and benzene.

[5.106] Ammonia (NH_3) boils at -33 °C; at this temperature it has a density of 0.81 g/cm³. The enthalpy of formation of $NH_3(g)$ is -46.2 kJ/mol, and the enthalpy of vaporization of $NH_3(l)$ is 23.2 kJ/mol. Calculate the enthalpy change when 1 L of liquid NH_3 is burned in air to give $N_2(g)$ and $H_2O(g)$. How does this compare with ΔH for the complete combustion of 1 L of liquid methanol, $CH_3OH(l)$? For $CH_3OH(l)$, the density at 25 °C is 0.792 g/cm³, and ΔH_f° equals -239 kJ/mol.

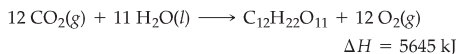
[5.107] Three common hydrocarbons that contain four carbons are listed here, along with their standard enthalpies of formation:

Hydrocarbon	Formula	ΔH_f° (kJ/mol)
1,3-Butadiene	$C_4H_6(g)$	111.9
1-Butene	$C_4H_8(g)$	1.2
<i>n</i> -Butane	$C_4H_{10}(g)$	-124.7

(a) For each of these substances, calculate the molar enthalpy of combustion to $CO_2(g)$ and $H_2O(l)$. (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.

5.108 The two common sugars, glucose ($C_6H_{12}O_6$) and sucrose ($C_{12}H_{22}O_{11}$), are both carbohydrates. Their standard enthalpies of formation are given in Table 5.3. Using these data, (a) calculate the molar enthalpy of combustion to $CO_2(g)$ and $H_2O(l)$ for the two sugars; (b) calculate the enthalpy of combustion per gram of each sugar; (c) determine how your answers to part (b) compare to the average fuel value of carbohydrates discussed in Section 5.8.

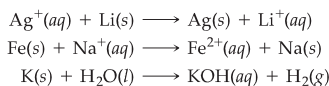
- 5.109** A 200-lb man decides to add to his exercise routine by walking up three flights of stairs (45 ft) 20 times per day. He figures that the work required to increase his potential energy in this way will permit him to eat an extra order of French fries, at 245 Cal, without adding to his weight. Is he correct in this assumption?
- 5.110** The sun supplies about 1.0 kilowatt of energy for each square meter of surface area (1.0 kW/m^2 , where a watt = 1 J/s). Plants produce the equivalent of about 0.20 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) per hour per square meter. Assuming that the sucrose is produced as follows, calculate the percentage of sunlight used to produce sucrose.



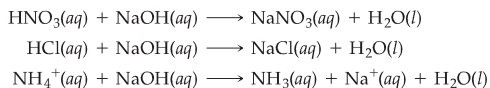
- [5.111]** It is estimated that the net amount of carbon dioxide fixed by photosynthesis on the landmass of Earth is $5.5 \times 10^{16} \text{ g/yr}$ of CO_2 . Assume that all this carbon is converted into glucose. **(a)** Calculate the energy stored by photosynthesis on land per year in kJ. **(b)** Calculate the average rate of conversion of solar energy into plant energy in MW ($1 \text{ W} = 1 \text{ J/s}$). A large nuclear power plant produces about 10^3 MW . The energy of how many such nuclear power plants is equivalent to the solar energy conversion?

INTEGRATIVE EXERCISES

- 5.112** Consider the combustion of a single molecule of $\text{CH}_4(\text{g})$ forming $\text{H}_2\text{O}(\text{l})$ as a product. **(a)** How much energy, in J, is produced during this reaction? **(b)** A typical X-ray photon has an energy of 8 keV. How does the energy of combustion compare to the energy of the X-ray photon?
- 5.113** Consider the dissolving of NaCl in water, illustrated in Figure 4.3. Assume the system consists of 0.1 mol NaCl and 1 L of water. Considering that the NaCl readily dissolves in the water and that the ions are strongly stabilized by the water molecules, as shown in the figure, is it safe to conclude that the dissolution of NaCl in water results in a lower enthalpy for the system? Explain your response. What experimental evidence would you examine to test this question?
- 5.114** Consider the following unbalanced oxidation-reduction reactions in aqueous solution:



- (a)** Balance each of the reactions. **(b)** By using data in Appendix C, calculate ΔH° for each of the reactions. **(c)** Based on the values you obtain for ΔH° , which of the reactions would you expect to be thermodynamically favored? (That is, which would you expect to be spontaneous?) **(d)** Use the activity series to predict which of these reactions should occur. ∞ (Section 4.4) Are these results in accord with your conclusion in part (c) of this problem?
- [5.115]** Consider the following acid-neutralization reactions involving the strong base $\text{NaOH}(\text{aq})$:



- (a)** By using data in Appendix C, calculate ΔH° 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 ΔH° for the first two reactions. What can you conclude? **(d)** In the third equation $\text{NH}_4^+(\text{aq})$ is acting as an acid. Based on the value of ΔH° for this reaction, do you think it is a strong or a weak acid? Explain.
- 5.116** Consider two solutions, the first being 50.0 mL of 1.00 M CuSO_4 and the second 50.0 mL of 2.00 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°C to 27.7°C . **(a)** Before mixing, how many grams of Cu are present in the solution of 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 ΔH 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 that of pure water.

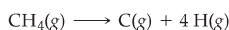
- 5.117** The precipitation reaction between $\text{AgNO}_3(\text{aq})$ and $\text{NaCl}(\text{aq})$ proceeds as follows:



(a) By using Appendix C, calculate ΔH° for the net ionic equation of this reaction. **(b)** What would you expect for the value of ΔH° 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 ΔH_f° for $\text{AgNO}_3(\text{aq})$.

- [5.118]** A sample of a hydrocarbon is combusted completely in $\text{O}_2(\text{g})$ to produce 21.83 g $\text{CO}_2(\text{g})$, 4.47 g $\text{H}_2\text{O}(\text{g})$, 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 ΔH_f° 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.

- 5.119** The methane molecule, CH_4 , has the geometry shown in Figure 2.21. 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. **(b)** Calculate the enthalpy change in each case. Which is the more endothermic process? What accounts for the difference in ΔH° values? **(c)** Suppose that 3.45 g $\text{CH}_4(\text{g})$ is reacted with 1.22 g $\text{F}_2(\text{g})$, forming $\text{CF}_4(\text{g})$ and $\text{HF}(\text{g})$ as sole products. What is the limiting reagent in this reaction? If the reaction occurs at constant pressure, what amount of heat is evolved?