7

Thermochemistry

Potassium reacts with water, liberating sufficient heat to ignite the hydrogen evolved. The transfer of heat between substances in chemical reactions is an important aspect of thermochemistry.

CONTENTS

Natural gas consists mostly of methane, CH_4. As we learned in Chapter 4, the complete combustion of a hydrocarbon, such as methane, yields carbon dioxide and water as products. More important, however, is another "product" of this reaction, which we have not previously mentioned: heat. This heat can be used to produce hot water in a water heater, to heat a house, or to cook food.

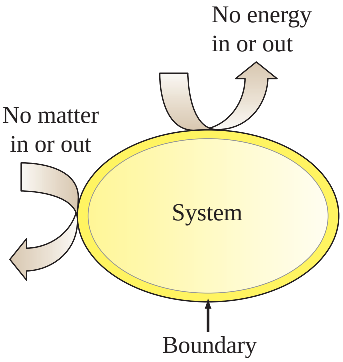
◀ Thermochemistry is a subfield of a larger discipline called *thermodynamics*. The broader aspects of thermodynamics are considered in Chapters 19 and 20.

Thermochemistry is the branch of chemistry concerned with the heat effects that accompany chemical reactions. To understand the relationship between heat and chemical and physical changes, we must start with some basic definitions. We will then explore the concept of heat and the methods used to measure the transfer of energy across boundaries. Another form of energy transfer is work, and, in combination with heat, we will define the first law of thermodynamics. At this point, we will establish the relationship between heats of reaction and changes in internal energy and enthalpy. We will see that the tabulation of the change in internal energy and change in enthalpy can be used to calculate, directly or indirectly, energy changes during chemical and physical changes. Finally, concepts introduced in this chapter will answer a host of practical questions, such as why natural gas is a better fuel than coal and why the energy value of fats is greater than that of carbohydrates and proteins.

7-1 Getting Started: Some Terminology

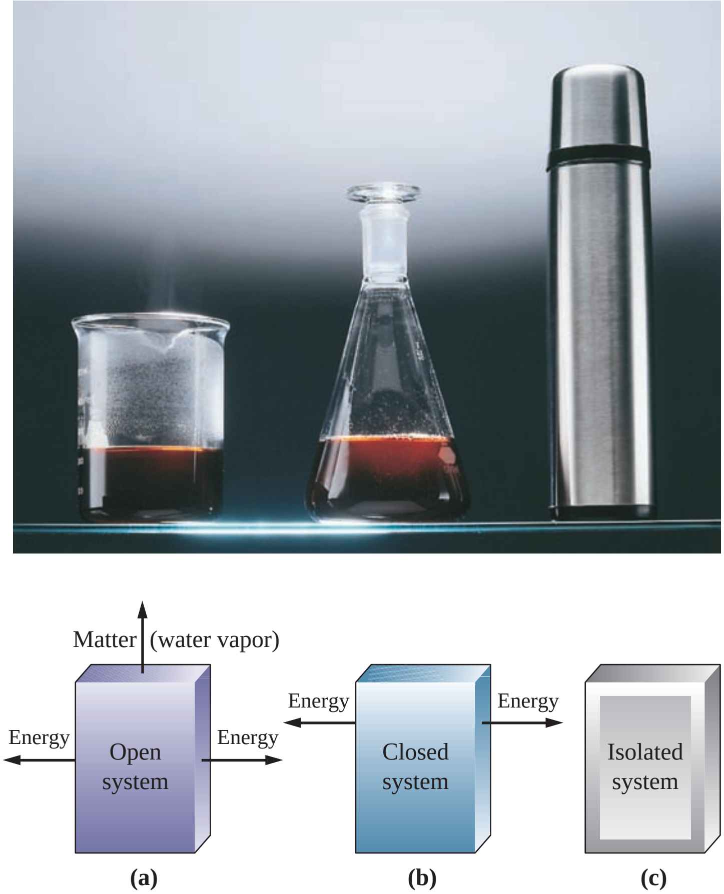
In this section, we introduce and define some very basic terms. Most are discussed in greater detail in later sections, and your understanding of these terms should grow as you proceed through the chapter.

A **system** is the part of the universe chosen for study, and it can be as large as all the oceans on Earth or as small as the contents of a beaker. Most of the systems we will examine will be small and we will look, particularly, at the transfer of *energy* (as heat and work) and *matter* between the system and its surroundings. The **surroundings** are that part of the universe outside the system with which the system interacts. Figure 7-1 pictures three common systems: first, as we see them and, then, in an abstract form that chemists commonly use. An **open system** freely exchanges energy and matter with its surroundings (Fig. 7-1a). A **closed system** can exchange energy, but not matter, with its surroundings (Fig. 7-1b). An **isolated system** does not interact with its surroundings (approximated in Figure 7-1c).

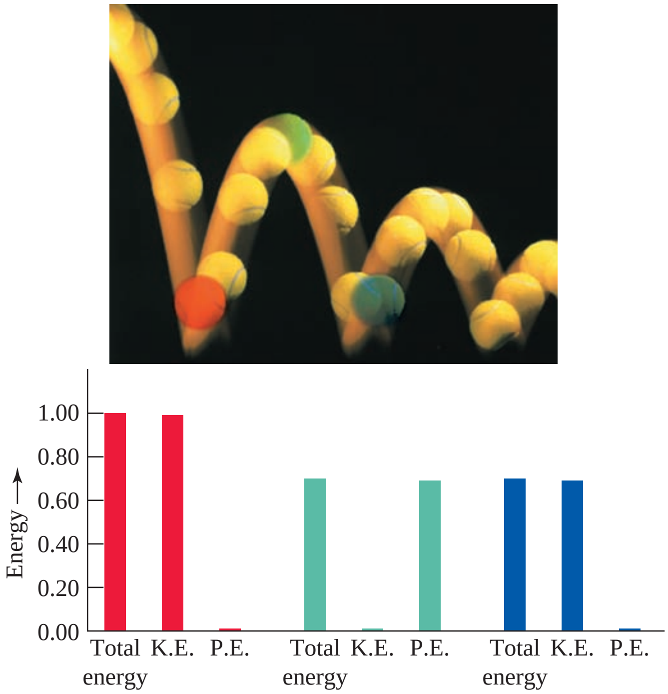


▲ **Isolated system**
No interactions occur across the system boundary with the surroundings.

The remainder of this section says more, in a general way, about energy and its relationship to work. Like many other scientific terms, *energy* is derived from Greek. It means "work within." **Energy** is the capacity to do work. **Work** is done when a force acts through a distance. Moving objects do work when they slow down or are stopped. Thus, when one billiard ball strikes another and sets it in motion, work is done. The energy of a moving object is called **kinetic energy** (the word *kinetic* means "motion" in Greek). We can see the relationship between work and energy by comparing the units for these two quantities. The kinetic energy of an object is based on its mass (m) and



▶ FIGURE 7-1
Systems and their surroundings
(a) *Open system*. The beaker of hot coffee transfers energy to the surroundings—it loses heat as it cools. Matter is also transferred in the form of water vapor. (b) *Closed system*. The flask of hot coffee transfers energy (heat) to the surroundings as it cools. Because the flask is stoppered, no water vapor escapes and no matter is transferred. (c) *Isolated system*. Hot coffee in an insulated container approximates an isolated system. No water vapor escapes, and, for a time at least, little heat is transferred to the surroundings. (Eventually, though, the coffee in the container cools to room temperature.)



◀ FIGURE 7-2
Potential energy (P.E.) and kinetic energy (K.E.)
The energy of the bouncing tennis ball changes continuously from potential to kinetic energy and back again. The maximum potential energy is at the top of each bounce, and the maximum kinetic energy occurs at the moment of impact. The sum of P.E. and K.E. decreases with each bounce as the thermal energies of the ball and the surroundings increase. The ball soon comes to rest. The bar graph below the bouncing balls illustrates the relative contributions that the kinetic and potential energy make to the total energy for each ball position. The red bars correspond to the red ball, green bars correspond to the green ball and the blue bars correspond to the blue ball.

velocity (u) through the first equation below; work (w) is related to force $[\text{mass } (m) \times \text{acceleration } (a)]$ and distance (d) by the second equation.

$$\text{kinetic energy} = \frac{1}{2} \times m(\text{kg}) \times [u(\text{m/s})]^2 \tag{7.1}$$

$$\text{work} = \text{force} \times \text{distance} = [m(\text{kg}) \times a(\text{m s}^{-2})] \times d(\text{m})$$

When the units for the expressions for work and energy are collected together, in both cases, the resultant unit is $\text{kg m}^2\,\text{s}^{-2}$. This corresponds to the SI unit of energy called the joule (J). That is, 1 *joule* (J) $= 1\,\text{kg m}^2\,\text{s}^{-2}$.

The bouncing ball in Figure 7-2 suggests something about the nature of energy and work. First, to lift the ball to the starting position, we have to apply a force through a distance (to overcome the force of gravity). The work we do is "stored" in the ball as energy. This stored energy has the potential to do work when released and is therefore called potential energy. **Potential energy** is energy resulting from condition, position, or composition; it is an energy associated with forces of attraction or repulsion between objects.

When we release the ball, it is pulled toward Earth's center by the force of gravity—it falls. Potential energy is converted to kinetic energy during this fall. The kinetic energy reaches its maximum just as the ball strikes the surface. On its rebound, the kinetic energy of the ball decreases (the ball slows down), and its potential energy increases (the ball rises). If the collision of the ball with the surface were perfectly *elastic*, like collisions between molecules in the kinetic-molecular theory, the sum of the potential and kinetic energies of the ball would remain constant. The ball would reach the same maximum height on each rebound, and it would bounce forever. But we know this doesn't happen—the bouncing ball soon comes to rest. All the energy originally invested in the ball as potential energy (by raising it to its initial position) eventually appears as additional kinetic energy of the atoms and molecules that make up the ball, the surface, and the surrounding air. This kinetic energy associated with random molecular motion is called **thermal energy**.

◀ A unit of work, heat and energy is the joule, but work and heat are not forms of energy but *processes* by which the energy of a system is changed.

In general, thermal energy is proportional to the temperature of a system, as suggested by the kinetic theory of gases. The more vigorous the motion of the molecules in the system, the hotter the sample and the greater is its thermal energy. However, the thermal energy of a system also depends on the number of particles present, so that a small sample at a high temperature (for example, a cup of coffee at 75 °C) may have less thermal energy than a larger sample at a lower temperature (for example, a swimming pool at 30 °C). Thus, temperature and thermal energy must be carefully distinguished. Equally important, we need to distinguish between energy changes produced by the action of forces through distances—*work*—and those involving the transfer of thermal energy—*heat*.

7-1 CONCEPT ASSESSMENT

Consider the following situations: a stick of dynamite exploding deep within a mountain cavern, the titration of an acid with base in a laboratory, and a cylinder of a steam engine with all of its valves closed. To what type of thermodynamic systems do these situations correspond?

7-2 Heat

▲ James Joule (1818–1889)—an amateur scientist
Joule's primary occupation was running a brewery, but he also conducted scientific research in a home laboratory. His precise measurements of quantities of heat formed the basis of the law of conservation of energy.

Heat is energy transferred between a system and its surroundings as a result of a temperature difference. Energy that passes from a warmer body (with a higher temperature) to a colder body (with a lower temperature) is transferred as heat. At the molecular level, molecules of the warmer body, through collisions, lose kinetic energy to those of the colder body. Thermal energy is transferred—"heat flows"—until the average molecular kinetic energies of the two bodies become the same, until the temperatures become equal. Heat, like work, describes energy in transit between a system and its surroundings.

Not only can heat transfer cause a change in temperature but, in some instances, it can also change a state of matter. For example, when a solid is heated, the molecules, atoms, or ions of the solid move with greater vigor and eventually break free from their neighbors by overcoming the attractive forces between them. Energy is required to overcome these attractive forces. During the process of melting, the temperature remains constant as a thermal energy transfer (heat) is used to overcome the forces holding the solid together. A process occurring at a constant temperature is said to be *isothermal*. Once a solid has melted completely, any further heat flow will raise the temperature of the resulting liquid.

Although we commonly use expressions like "heat is lost," "heat is gained," "heat flows," and "the system loses heat to the surroundings," you should not take these statements to mean that a system contains heat. It does not. The energy content of a system, as we shall see in Section 7-5, is a quantity called the *internal energy*. Heat is simply a form in which a quantity of energy may be *transferred* across a boundary between a system and its surroundings.

It is reasonable to expect that the quantity of heat, q, required to change the temperature of a substance depends on

- how much the temperature is to be changed
- the quantity of substance
- the nature of the substance (type of atoms or molecules)

Historically, the quantity of heat required to change the temperature of one gram of water by one degree Celsius has been called the **calorie** (**cal**). The calorie is a small unit of energy, and the unit *kilocalorie* (kcal) has also been widely used. The SI unit for heat is simply the basic SI energy unit, the joule (J).

$$1\ \text{cal} = 4.184\ \text{J} \qquad \textbf{(7.2)}$$

Although the joule is used almost exclusively in this text, the calorie is widely encountered in older scientific literature. In the United States, the kilocalorie is commonly used for measuring the energy content of foods (see Focus On 7 on www.masteringchemistry.com).

The quantity of heat required to change the temperature of a system by one degree is called the **heat capacity** of the system. If the system is a mole of substance, the term *molar heat capacity* is applicable. If the system is one gram of substance, the applicable term is *specific heat capacity*, or more commonly, **specific heat** (sp ht).* The specific heats of substances are somewhat temperature dependent. Over the range from 0 to 100 °C, the specific heat of water averages about

$$\frac{4.18\ \text{J}}{\text{g}\ ^\circ\text{C}} = 4.18\ \text{J g}^{-1}\ {}^\circ\text{C}^{-1} \qquad \textbf{(7.3)}$$

In Example 7-1, the objective is to calculate a quantity of heat based on the amount of a substance, the specific heat of that substance, and its temperature change.

EXAMPLE 7-1 Calculating a Quantity of Heat

How much heat is required to raise the temperature of 7.35 g of water from 21.0 to 98.0 °C? (Assume the specific heat of water is $4.18\ \text{J g}^{-1}\ {}^\circ\text{C}^{-1}$ throughout this temperature range.)

Analyze

To answer this question, we begin by multiplying the specific heat capacity by the mass of water to obtain the heat capacity of the system. To find the amount of heat required to produce the desired temperature change we multiply the heat capacity by the temperature difference.

Solve

The specific heat is the heat capacity of 1.00 g water:

$$\frac{4.18\ \text{J}}{\text{g water}\ ^\circ\text{C}}$$

The heat capacity of the system (7.35 g water) is

$$7.35\ \cancel{\text{g water}} \times \frac{4.18\ \text{J}}{\cancel{\text{g water}}\ ^\circ\text{C}} = 30.7\,\frac{\text{J}}{^\circ\text{C}}$$

The required temperature change in the system is

$$(98.0 - 21.0)\ ^\circ\text{C} = 77.0\ ^\circ\text{C}$$

The heat required to produce this temperature change is

$$30.7\,\frac{\text{J}}{\cancel{^\circ\text{C}}} \times 77.0\ \cancel{^\circ\text{C}} = 2.36 \times 10^3\ \text{J}$$

Assess

Remember that specific heat is a quantity that depends on the amount of material. Also note that the change in temperature is determined by subtracting the initial temperature from the final temperature. This will be important in determining the sign on the value you determine for heat, as will become apparent in the next section.

PRACTICE EXAMPLE A: How much heat, in kilojoules (kJ), is required to raise the temperature of 237 g of cold water from 4.0 to 37.0 °C (body temperature)?

PRACTICE EXAMPLE B: How much heat, in kilojoules (kJ), is required to raise the temperature of 2.50 kg Hg(l) from −20.0 to −6.0 °C? Assume a density of 13.6 g/mL and a molar heat capacity of $28.0\ \text{J mol}^{-1}\ {}^\circ\text{C}^{-1}$ for Hg(l).

The line of reasoning used in Example 7-1 can be summarized in equation (7.5), which relates a quantity of heat to the mass of a substance, its specific heat, and the temperature change.

$$\text{quantity of heat} = \underbrace{\text{mass of substance} \times \text{specific heat}}_{\text{heat capacity } = \ C} \times \text{temperature change} \qquad \textbf{(7.4)}$$

$$q = m \times \text{specific heat} \times \Delta T = C \times \Delta T \qquad \textbf{(7.5)}$$

◀ The Greek letter delta, Δ, indicates a *change* in some quantity.

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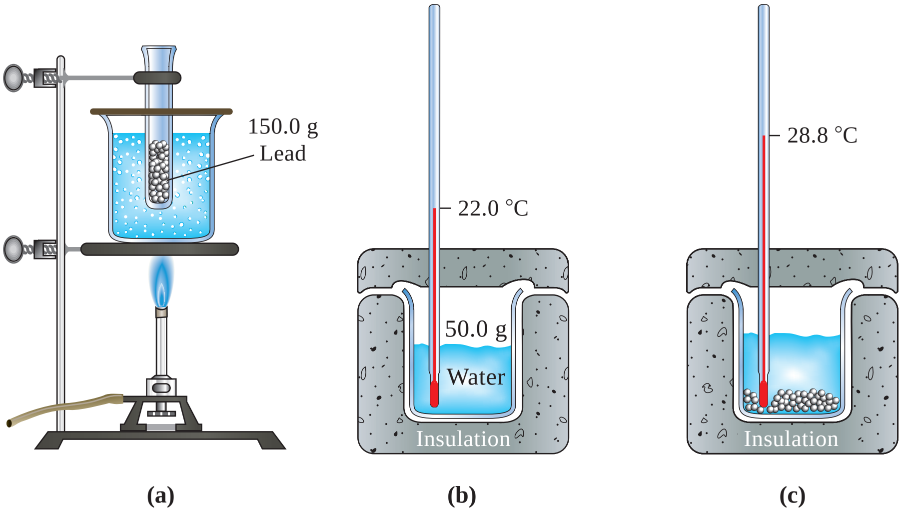
*The original meaning of specific heat was that of a *ratio*: the quantity of heat required to change the temperature of a mass of substance divided by the quantity of heat required to produce the same temperature change in the same mass of water—this definition would make specific heat dimensionless. The meaning given here is more commonly used.

▶ FIGURE 7-3
Determining the specific heat of lead—Example 7-2 illustrated
(a) A 150.0 g sample of lead is heated to the temperature of boiling water (100.0 °C). (b) A 50.0 g sample of water is added to a thermally insulated beaker, and its temperature is found to be 22.0 °C. (c) The hot lead is dumped into the cold water, and the temperature of the final lead–water mixture is 28.8 °C.



▶ The symbol > means "greater than," and < means "less than."

In equation (7.5), the temperature change is expressed as $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature. When the temperature of a system increases ($T_f > T_i$), ΔT is *positive*. A positive q signifies that heat is absorbed or *gained* by the system. When the temperature of a system decreases ($T_f < T_i$), ΔT is *negative*. A negative q signifies that heat is evolved or *lost* by the system.

Another idea that enters into calculations of quantities of heat is the **law of conservation of energy**: In interactions between a system and its surroundings, the total energy remains *constant*—energy is neither created nor destroyed. Applied to the exchange of heat, this means that

$$q_{\text{system}} + q_{\text{surroundings}} = 0 \qquad \textbf{(7.6)}$$

Thus, heat *gained* by a system is *lost* by its surroundings, and vice versa.

$$q_{\text{system}} = -q_{\text{surroundings}} \qquad \textbf{(7.7)}$$

Experimental Determination of Specific Heats

Let us consider how the law of conservation of energy is used in the experiment outlined in Figure 7-3. The object is to determine the specific heat of lead. The transfer of energy, as heat, from the lead to the cooler water causes the temperature of the lead to decrease and that of the water to increase, until the lead and water are at the same temperature. Either the lead or the water can be considered the system. If we consider lead to be the system, we can write $q_{\text{lead}} = q_{\text{system}}$. Furthermore, if the lead and water are maintained in a thermally insulated enclosure, we can assume that $q_{\text{water}} = q_{\text{surroundings}}$. Then, applying equation (7.7), we have

$$q_{\text{lead}} = -q_{\text{water}} \qquad \textbf{(7.8)}$$

We complete the calculation in Example 7-2.

EXAMPLE 7-2 Determining a Specific Heat from Experimental Data

Use data presented in Figure 7-3 to calculate the specific heat of lead.

Analyze

Keep in mind that if we know any four of the five quantities—q, m, specific heat, T_f, T_i—we can solve equation (7.5) for the remaining one. We know from Figure 7-3 that a known quantity of lead is heated and then dumped into a known amount of water at a known temperature, which is the initial temperature. Once the system comes to equilibrium, the water temperature is the final temperature. In this type of question, we will use equation (7.5).

Solve

First, use equation (7.5) to calculate q_{water}.

$$q_{\text{water}} = 50.0\text{ g water} \times \frac{4.18\text{ J}}{\text{g water °C}} \times (28.8 - 22.0)\text{ °C} = 1.4 \times 10^3\text{ J}$$

From equation (7.8) we can write

$$q_{\text{lead}} = -q_{\text{water}} = -1.4 \times 10^3\text{ J}$$

Now, from equation (7.5) again, we obtain

$$q_{\text{lead}} = 150.0\text{ g lead} \times \text{specific heat of lead} \times (28.8 - 100.0)\text{ °C} = -1.4 \times 10^3\text{ J}$$

$$\text{specific heat of lead} = \frac{-1.4 \times 10^3\text{ J}}{150.0\text{ g lead} \times (28.8 - 100.0)\text{ °C}} = \frac{-1.4 \times 10^3\text{ J}}{150.0\text{ g lead} \times -71.2\text{ °C}} = 0.13\text{ J g}^{-1}\text{ °C}^{-1}$$

Assess

The key concept to recognize is that energy, in the form of heat, flowed from the lead, which is our system, to the water, which is the surroundings. A quick way to make sure that we have done the problem correctly is to check the sign on the final answer. For specific heat, the sign should always be positive and have the units of $\text{J g}^{-1}\text{ °C}^{-1}$.

PRACTICE EXAMPLE A: When 1.00 kg lead (specific heat $= 0.13\text{ J g}^{-1}\text{ °C}^{-1}$) at 100.0 °C is added to a quantity of water at 28.5 °C, the final temperature of the lead–water mixture is 35.2°C. What is the mass of water present?

PRACTICE EXAMPLE B: A 100.0 g copper sample (specific heat $= 0.385\text{ J g}^{-1}\text{ °C}^{-1}$) at 100.0 °C is added to 50.0 g water at 26.5 °C. What is the final temperature of the copper–water mixture?

7-2 CONCEPT ASSESSMENT

With a minimum of calculation, estimate the final temperature reached when 100.0 mL of water at 10.00 °C is added to 200.0 mL of water at 70.00 °C. What basic principle did you use and what assumptions did you make in arriving at this estimate?

Significance of Specific-Heat Values

Table 7.1 lists the specific heats of several materials. The range of values in Table 7.1 is relatively large: 0.128 to $4.187\text{ J g}^{-1}\text{ °C}^{-1}$.

Because of their greater complexity at the molecular level, compounds generally have more ways of storing internal energy than do the elements; they tend to have higher specific heats. Water, for example, has a specific heat that is more than 30 times as great as that of lead. We need a much larger quantity of heat to change the temperature of a sample of water than of an equal mass of a metal.

An environmental consequence of the high specific heat of water is found in the effect of large lakes on local climates. Because a lake takes much longer to heat up in summer and cool down in winter than other types of terrain, lakeside communities tend to be cooler in summer and warmer in winter than communities more distant from the lake.

TABLE 7.1 Specific Heats of Several Elements, Compounds $\text{J g}^{-1}\text{ °C}^{-1}$

Metals	
Lead(s)	0.128
Copper(s)	0.385
Iron(s)	0.449
Aluminum(s)	0.903
Magnesium(s)	1.024
Nonmetals	
Selenium(s)	0.321
Sulfur(s)	0.706
Phosphorus(s)	0.777
Metalloids	
Tellurium(s)	0.202
Arsenic(s)	0.329
Compounds	
$H_2O(s)$	2.108
$H_2O(l)$	4.187
$H_2O(g)$	1.996
$O_2(g)$	0.918
$N_2(g)$	1.040

7-3 CONCEPT ASSESSMENT

Two objects of the same mass absorb the same amount of heat when heated in a flame, but the temperature of one object increases more than the temperature of the other. Which object has the greater specific heat?

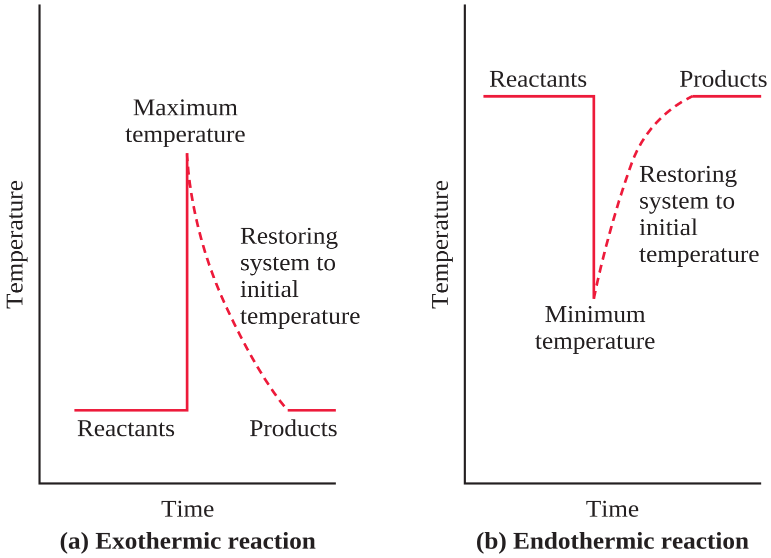
7-3 Heats of Reaction and Calorimetry

▶ Although no perfectly reversible process exists, the melting and freezing of a substance at its transition temperature is an example of a process that is nearly reversible: pump in heat (melts), take out heat (freezes).

In Section 7-1, we introduced the notion of *thermal energy*—kinetic energy associated with random molecular motion. Another type of energy that contributes to the internal energy of a system is **chemical energy**. This is energy associated with chemical bonds and intermolecular attractions. If we think of a chemical reaction as a process in which some chemical bonds are broken and others are formed, then, in general, we expect the chemical energy of a system to change as a result of a reaction. Furthermore, we might expect some of this energy change to appear as heat. A **heat of reaction**, q_{rxn}, is the quantity of heat exchanged between a system and its surroundings when a chemical reaction occurs within the system at *constant temperature*. One of the most common reactions studied is the combustion reaction. This is such a common reaction that we often refer to the *heat of combustion* when describing the heat released by a combustion reaction.

If a reaction occurs in an *isolated* system, that is, one that exchanges no matter or energy with its surroundings, the reaction produces a change in the thermal energy of the system—the temperature either increases or decreases. Imagine that the previously isolated system is allowed to interact with its surroundings. The heat of reaction is the quantity of heat exchanged between the system and its surroundings as the system is restored to its initial temperature (Fig. 7-4). In actual practice, we do not physically restore the system to its initial temperature. Instead, we calculate the quantity of heat that *would be* exchanged in this restoration. To do this, a probe (thermometer) is placed within the system to record the temperature change produced by the reaction. Then, we use the temperature change and other system data to calculate the heat of reaction that would have occurred at constant temperature.

Two widely used terms related to heats of reaction are exothermic and endothermic reactions. An **exothermic reaction** is one that produces a temperature increase in an isolated system or, in a nonisolated system, gives off heat to the surroundings. For an exothermic reaction, the heat of reaction is a negative quantity ($q_{\text{rxn}} < 0$). In an **endothermic reaction**, the corresponding situation is a temperature decrease in an isolated system or a gain of heat from the surroundings by a nonisolated system. In this case, the heat of reaction is a positive quantity ($q_{\text{rxn}} > 0$). Heats of reaction are experimentally determined in a **calorimeter**, a device for measuring quantities of heat. We will consider two types of calorimeters in this section, and we will treat both of them as *isolated* systems.



(a) Exothermic reaction (b) Endothermic reaction

▶ FIGURE 7-4
Conceptualizing a heat of reaction at constant temperature
The solid lines indicate the initial temperature and the (a) maximum and (b) minimum temperature reached in an isolated system, in an exothermic and an endothermic reaction, respectively. The broken lines represent pathways to restoring the system to the initial temperature. The heat of reaction is the heat lost or gained by the system in this restoration.

(a)

(b)

◀ **Exothermic and endothermic reactions**
(a) An exothermic reaction. Slaked lime, $Ca(OH)_2$, is produced by the action of water on quicklime, (CaO). The reactants are mixed at room temperature, but the temperature of the mixture rises to 40.5 °C.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

(b) An endothermic reaction. $Ba(OH)_2 \cdot 8\,H_2O(s)$ and $NH_4Cl(s)$ are mixed at room temperature, and the temperature falls to 5.8 °C in the reaction.

$$Ba(OH)_2 \cdot 8\,H_2O(s) + 2\,NH_4Cl(s) \longrightarrow BaCl_2 \cdot 2H_2O(s) + 2\,NH_3(aq) + 8\,H_2O(l)$$

Bomb Calorimetry

Figure 7-5 shows a **bomb calorimeter**, which is ideally suited for measuring the heat evolved in a combustion reaction. The system is everything within the double-walled outer jacket of the calorimeter. This includes the bomb and its contents, the water in which the bomb is immersed, the thermometer, the stirrer, and so on. The system is *isolated* from its surroundings. When the combustion reaction occurs, chemical energy is converted to thermal energy, and the temperature of the system rises. The heat of reaction, as described earlier, is the quantity of heat that the system would have to *lose* to its surroundings to be restored to its initial temperature. This quantity of heat, in turn, is just the *negative* of the thermal energy gained by the calorimeter and its contents (q_{calorim}).

KEEP IN MIND

that the temperature of a reaction mixture usually changes during a reaction, so the mixture must be returned to the initial temperature (actually or hypothetically) before we assess how much heat is exchanged with the surroundings.

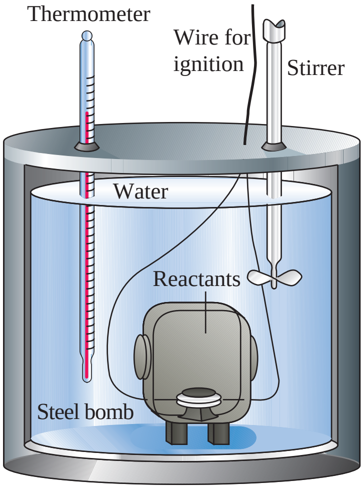
$$q_{\text{rxn}} = -q_{\text{calorim}} \text{ (where } q_{\text{calorim}} = q_{\text{bomb}} + q_{\text{water}} \cdots) \qquad \textbf{(7.9)}$$

If the calorimeter is assembled in exactly the same way each time we use it—that is, use the same bomb, the same quantity of water, and so on—we can define a *heat capacity of the calorimeter*. This is the quantity of heat required to raise the temperature of the calorimeter assembly by one degree Celsius. When this heat capacity is multiplied by the observed temperature change, we get q_{calorim}.

◀ The heat capacity of a bomb calorimeter must be determined by experiment.

$$q_{\text{calorim}} = \text{heat capacity of calorim} \times \Delta T \qquad \textbf{(7.10)}$$

And from q_{calorim}, we then establish q_{rxn}, as in Example 7-3, where we determine the heat of combustion of sucrose (table sugar).



◀ FIGURE 7-5
A bomb calorimeter assembly
An iron wire is embedded in the sample in the lower half of the bomb. The bomb is assembled and filled with $O_2(g)$ at high pressure. The assembled bomb is immersed in water in the calorimeter, and the initial temperature is measured. A short pulse of electric current heats the sample, causing it to ignite. The final temperature of the calorimeter assembly is determined after the combustion. Because the bomb confines the reaction mixture to a fixed volume, the reaction is said to occur at *constant volume*. The significance of this fact is discussed on page 259.

EXAMPLE 7-3 Using Bomb Calorimetry Data to Determine a Heat of Reaction

The combustion of 1.010 g sucrose, $C_{12}H_{22}O_{11}$, in a bomb calorimeter causes the temperature to rise from 24.92 to 28.33 °C. The heat capacity of the calorimeter assembly is 4.90 kJ/°C. **(a)** What is the heat of combustion of sucrose expressed in kilojoules per mole of $C_{12}H_{22}O_{11}$? **(b)** Verify the claim of sugar producers that one teaspoon of sugar (about 4.8 g) contains only 19 Calories.

Analyze

We are given a specific heat and two temperatures, the initial and the final, which indicate that we are to use equation (7.5). In these kinds of experiments one obtains the amount of heat generated by the reaction by measuring the temperature change in the surroundings. This means that $q_{\text{rxn}} = -q_{\text{calorim}}$.

Solve

(a) Calculate q_{calorim} with equation (7.10).

$$q_{\text{calorim}} = 4.90\ \text{kJ/°C} \times (28.33 - 24.92)\ \text{°C} = (4.90 \times 3.41)\ \text{kJ} = 16.7\ \text{kJ}$$

Now, using equation (7.9), we get

$$q_{\text{rxn}} = -q_{\text{calorim}} = -16.7\ \text{kJ}$$

This is the heat of combustion of the 1.010 g sample.
Per gram $C_{12}H_{22}O_{11}$:

$$q_{\text{rxn}} = \frac{-16.7\ \text{kJ}}{1.010\ \text{g}\ C_{12}H_{22}O_{11}} = -16.5\ \text{kJ/g}\ C_{12}H_{22}O_{11}$$

Per mole $C_{12}H_{22}O_{11}$:

$$q_{\text{rxn}} = \frac{-16.5\ \text{kJ}}{\text{g}\ C_{12}H_{22}O_{11}} \times \frac{342.3\ \text{g}\ C_{12}H_{22}O_{11}}{1\ \text{mol}\ C_{12}H_{22}O_{11}} = -5.65 \times 10^3\ \text{kJ/mol}\ C_{12}H_{22}O_{11}$$

(b) To determine the caloric content of sucrose, we can use the heat of combustion per gram of sucrose determined in part **(a)**, together with a factor to convert from kilojoules to kilocalories. (Because 1 cal = 4.184 J, 1 kcal = 4.184 kJ.)

$$?\ \text{kcal} = \frac{4.8\ \text{g}\ C_{12}H_{22}O_{11}}{\text{tsp}} \times \frac{-16.5\ \text{kJ}}{\text{g}\ C_{12}H_{22}O_{11}} \times \frac{1\ \text{kcal}}{4.184\ \text{kJ}} = \frac{-19\ \text{kcal}}{\text{tsp}}$$

1 food Calorie (1 Calorie with a capital C) is actually 1000 cal, or 1 kcal. Therefore, 19 kcal = 19 Calories. The claim is justified.

Assess

A combustion reaction is an exothermic reaction, which means that energy flows, in the form of heat, from the reaction to the surroundings. Therefore, the q for a combustion reaction is negative.

PRACTICE EXAMPLE A: Vanillin is a natural constituent of vanilla. It is also manufactured for use in artificial vanilla flavoring. The combustion of 1.013 g of vanillin, $C_8H_8O_3$, in the same bomb calorimeter as in Example 7-3 causes the temperature to rise from 24.89 to 30.09 °C. What is the heat of combustion of vanillin, expressed in kilojoules per mole?

PRACTICE EXAMPLE B: The heat of combustion of benzoic acid is −26.42 kJ/g. The combustion of a 1.176 g sample of benzoic acid causes a temperature *increase* of 4.96°C in a bomb calorimeter assembly. What is the heat capacity of the assembly?

The "Coffee-Cup" Calorimeter

In the general chemistry laboratory you are much more likely to run into the simple calorimeter pictured in Figure 7-6 (on page 252) than a bomb calorimeter. We mix the reactants (generally in aqueous solution) in a Styrofoam cup and measure the temperature change. Styrofoam is a good heat insulator, so there is very little heat transfer between the cup and the surrounding air. We treat the system—the cup and its contents—as an *isolated* system.

As with the bomb calorimeter, the heat of reaction is defined as the quantity of heat that would be exchanged with the surroundings in restoring the calorimeter to its initial temperature. But, again, the calorimeter is not physically restored to its initial conditions. We simply take the heat of reaction to be the *negative* of the quantity of heat producing the temperature change in the calorimeter. That is, we use equation (7.9): $q_{\text{rxn}} = -q_{\text{calorim}}$.

In Example 7-4, we make certain assumptions to simplify the calculation, but for more precise measurements, these assumptions would not be made (see Exercise 25).

EXAMPLE 7-4 Determining a Heat of Reaction from Calorimetric Data

In the neutralization of a strong acid with a strong base, the essential reaction is the combination of $H^+(aq)$ and $OH^-(aq)$ to form water (recall page 165).

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Two solutions, 25.00 mL of 2.50 M HCl(aq) and 25.00 mL of 2.50 M NaOH(aq), both initially at 21.1 °C, are added to a Styrofoam-cup calorimeter and allowed to react. The temperature rises to 37.8 °C. Determine the heat of the neutralization reaction, expressed per mole of H_2O formed. Is the reaction endothermic or exothermic?

Analyze

In addition to assuming that the calorimeter is an isolated system, assume that all there is in the system to absorb heat is 50.00 mL of water. This assumption ignores the fact that 0.0625 mol each of NaCl and H_2O are formed in the reaction, that the density of the resulting NaCl(aq) is not exactly 1.00 g/mL, and that its specific heat is not exactly $4.18\ \text{J g}^{-1}\,°\text{C}^{-1}$. Also, ignore the small heat capacity of the Styrofoam cup itself.

Because the reaction is a neutralization reaction, let us call the heat of reaction q_{neutr}. Now, according to equation (7.9), $q_{\text{neutr}} = -q_{\text{calorim}}$, and if we make the assumptions described above, we can solve the problem.

Solve

We begin with

$$q_{\text{calorim}} = 50.00\ \text{mL} \times \frac{1.00\ \text{g}}{\text{mL}} \times \frac{4.18\ \text{J}}{\text{g}\ °\text{C}} \times (37.8 - 21.1)\ °\text{C} = 3.5 \times 10^3\ \text{J}$$

$$q_{\text{neutr}} = -q_{\text{calorim}} = -3.5 \times 10^3\ \text{J} = -3.5\ \text{kJ}$$

In 25.00 mL of 2.50 M HCl, the amount of H^+ is

$$?\ \text{mol H}^+ = 25.00\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{2.50\ \text{mol}}{1\ \text{L}} \times \frac{1\ \text{mol H}^+}{1\ \text{mol HCl}} = 0.0625\ \text{mol H}^+$$

Similarly, in 25.00 mL of 2.50 M NaOH there is 0.0625 mol OH^-. Thus, the H^+ and the OH^- combine to form 0.0625 mol H_2O. (The two are in *stoichiometric* proportions; neither is in excess.)

The amount of heat produced per mole of H_2O is

$$q_{\text{neutr}} = \frac{-3.5\ \text{kJ}}{0.0625\ \text{mol H}_2\text{O}} = -56\ \text{kJ/mol H}_2\text{O}$$

Assess

Because q_{neutr} is a *negative* quantity, the neutralization reaction is *exothermic*. In this example, relatively small quantities of acid and base were mixed yet a comparatively large temperature change occurred. The large temperature rise was due to the relatively large negative heat of neutralization.

PRACTICE EXAMPLE A: Two solutions, 100.0 mL of 1.00 M $AgNO_3$(aq) and 100.0 mL of 1.00 M NaCl(aq), both initially at 22.4 °C, are added to a Styrofoam-cup calorimeter and allowed to react. The temperature rises to 30.2 °C. Determine q_{rxn} per mole of AgCl(s) in the reaction.

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

PRACTICE EXAMPLE B: Two solutions, 100.0 mL of 1.020 M HCl and 50.0 mL of 1.988 M NaOH, both initially at 24.52 °C, are mixed in a Styrofoam-cup calorimeter. What will be the final temperature of the mixture? Make the same assumptions, and use the heat of neutralization established in Example 7-4. [*Hint:* Which is the limiting reactant?]

▲ FIGURE 7-6
A Styrofoam "coffee-cup" calorimeter
The reaction mixture is in the inner cup. The outer cup provides additional thermal insulation from the surrounding air. The cup is closed off with a cork stopper through which a thermometer and a stirrer are inserted and immersed into the reaction mixture. The reaction in the calorimeter occurs under the *constant pressure* of the atmosphere. We consider the difference between constant-volume and constant-pressure reactions in Section 7-6.

7-4 CONCEPT ASSESSMENT

How do we determine the specific heat of the bomb calorimeter or the solution calorimeter (coffee-cup calorimeter)?

7-4 Work

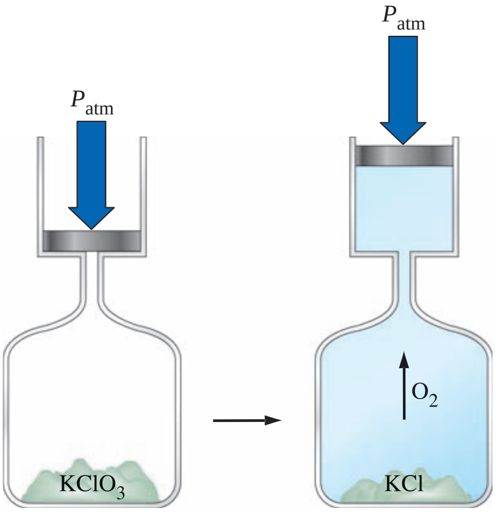
We have just learned that heat effects generally accompany chemical reactions. In some reactions, work is also involved—that is, the system may do work on its surroundings or vice versa. Consider the decomposition of potassium chlorate to potassium chloride and oxygen. Suppose that this decomposition is carried out in the strange vessel pictured in Figure 7-7. The walls of the container resist moving under the pressure of the expanding $O_2(g)$ except for the piston that closes off the cylindrical top of the vessel. The pressure of the $O_2(g)$ exceeds the atmospheric pressure and the piston is lifted—the system does work on the surroundings. Can you see that even if the piston were removed, work still would be done as the expanding $O_2(g)$ pushed aside other atmospheric gases? Work involved in the expansion or compression of gases is called **pressure–volume work**. Pressure–volume, or P–V, work is the type of work performed by explosives and by the gases formed in the combustion of gasoline in an automobile engine.

Now let us switch to a somewhat simpler situation to see how to calculate a quantity of P–V work.

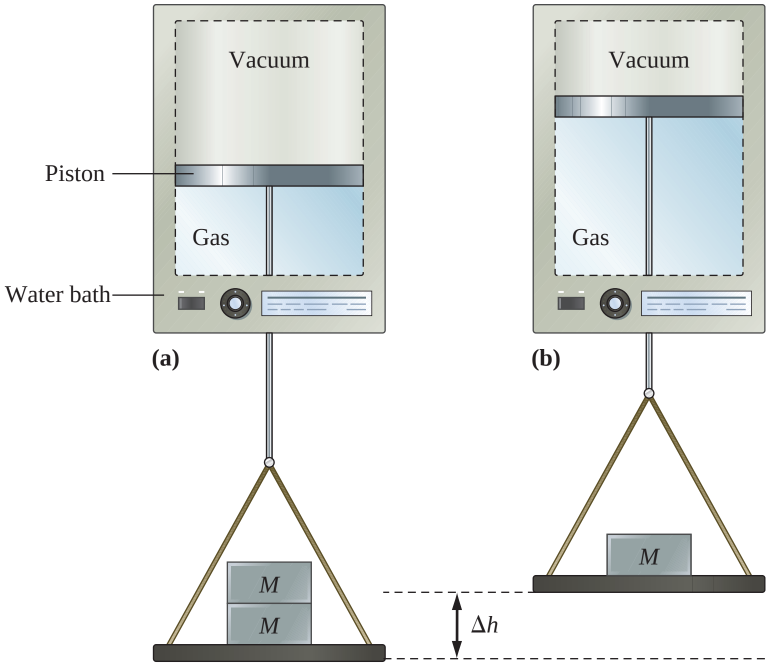
In the hypothetical apparatus pictured in Figure 7-8(a), a weightless piston is attached to a weightless wire support, to which is attached a weightless pan. On the pan are two identical weights just sufficient to stop the gas from expanding. The gas is confined by the cylinder walls and piston, and the space above the piston is a vacuum. The cylinder is contained in a constant-temperature water bath, which keeps the temperature of the gas constant. Now imagine that one of the two weights is removed, leaving half the original mass on the pan. Let us call this remaining mass M. The gas will expand and the remaining weight will move against gravity, the situation represented by Figure 7-8(b). After the expansion, we find that the piston has risen through a vertical distance, Δh; that the volume of gas has doubled; and that the pressure of the gas has decreased.

Now let us see how pressure and volume enter into calculating how much *pressure–volume* work the expanding gas does. First we can calculate the work done by the gas in moving the weight of mass M through a displacement Δh. Recall from equation (7.1) that the work can be calculated by

$$\text{work}\ (w) = \text{force}\ (M \times g) \times \text{distance}\ (\Delta h) = -M \times g \times \Delta h$$



▶ FIGURE 7-7
Illustrating work (expansion) during the chemical reaction
$2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$
The oxygen gas that is formed pushes back the weight and, in doing so, does work on the surroundings.



▲ FIGURE 7-8
Pressure–volume work
(a) In this hypothetical apparatus, a gas is confined by a massless piston of area A. A massless wire is attached to the piston and the gas is held back by two weights with a combined mass of $2M$ resting on the massless pan. The cylinder is immersed in a large water bath in order to keep the gas temperature constant. The initial state of the gas is $P_i = 2\,Mg/A$ with a volume V_i at temperature, T. (b) When the external pressure on the confined gas is suddenly lowered by removing one of the weights the gas expands, pushing the piston up by the distance, Δh. The increase in volume of the gas (ΔV) is the product of the cross-sectional area of the cylinder (A) and the distance (Δh). The final state of the gas is $P_f = Mg/A$, V_f, and T.

The magnitude of the force exerted by the weight is $M \times g$, where g is the acceleration due to gravity. The negative sign appears because the force is acting in a direction opposite to the piston's direction of motion.

Now recall equation (6.1)—pressure = force $(M \times g)$/area (A)—so that if the expression for work is multiplied by A/A we get

$$w = -\frac{M \times g}{A} \times \Delta h \times A = -P_{ext}\Delta V \qquad \textbf{(7.11)}$$

The "pressure" part of the pressure–volume work is seen to be the external pressure (P_{ext}) on the gas, which in our thought experiment is due to the weight pulling down on the piston and is given by Mg/A. Note that the product of the area (A) and height (Δh) is equal to a volume—the volume change, ΔV, produced by the expansion.

Two significant features to note in equation (7.11) are the *negative* sign and the term P_{ext}. The negative sign is necessary to conform to sign conventions that we will introduce in the next section. When a gas expands, ΔV is positive and w is negative, signifying that energy leaves the system as work. When a gas is compressed, ΔV is negative and w is positive, signifying that energy (as work) enters the system. The term P_{ext} is the *external* pressure—the pressure against which a system expands or the applied pressure that compresses a system. In many instances the internal pressure in a system will be essentially equal to the external pressure, in which case the pressure in equation (7.11) is expressed simply as P.

◀ Work is negative when energy is transferred out of the system and is positive when energy is transferred into the system. This is consistent with the signs associated with the heat of a reaction (q) during endothermic and exothermic processes.

If pressure is stated in atmospheres and volume in liters, the unit of work is the liter-atmosphere, L atm; while the SI unit of work is the joule. The conversion factor between these two units of work can be obtained from the gas constant, R.

$$8.3145\ \text{m}^3\ \text{Pa mol}^{-1}\ \text{K}^{-1} = 8.3145\ \text{m}^3\ \text{N m}^{-2}\ \text{mol}^{-1}\ \text{K}^{-1} = 8.3145\ \text{kg m}^2\ \text{s}^{-2}\text{mol}^{-1}\ \text{K}^{-1}$$
$$8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} = 0.082057\ \text{L atm mol}^{-1}\ \text{K}^{-1} = 0.083145\ \text{L bar mol}^{-1}\ \text{K}^{-1}$$

and

$$\frac{8.3145\ \text{J}}{0.082057\ \text{L atm}} = 101.33\ \frac{\text{J}}{\text{L atm}}$$

EXAMPLE 7-5 Calculating Pressure–Volume Work

Suppose the gas in Figure 7-8 is 0.100 mol He at 298 K, the two weights correspond to an external pressure of 2.40 atm in Figure 7-8(a), and the single weight in Figure 7-8(b) corresponds to an external pressure of 1.20 atm. How much work, in joules, is associated with the gas expansion at constant temperature?

Analyze

We are given enough data to calculate the initial and final gas volumes (note that the identity of the gas does not enter into the calculations because we are assuming ideal gas behavior). With these volumes, we can obtain ΔV. The external pressure term in the pressure–volume work is the *final* pressure: 1.20 atm. The product $-P_{\text{ext}} \times \Delta V$ must be multiplied by a factor to convert work in liter-atmospheres to work in joules.

Solve

First calculate the initial and final volumes.

$$V_{\text{initial}} = \frac{nRT}{P_i} = \frac{0.100\ \text{mol} \times 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{2.40\ \text{atm}} = 1.02\ \text{L}$$
$$V_{\text{final}} = \frac{nRT}{P_f} = \frac{0.100\ \text{mol} \times 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{1.20\ \text{atm}} = 2.04\ \text{L}$$
$$\Delta V = V_f - V_i = 2.04\ \text{L} - 1.02\ \text{L} = 1.02\ \text{L}$$
$$w = -P_{\text{ext}} \times \Delta V = -1.20\ \text{atm} \times 1.02\ \text{L} \times \frac{101\ \text{J}}{1\ \text{L atm}} = -1.24 \times 10^2\ \text{J}$$

Assess

The negative value signifies that the expanding gas (i.e., the system) does work on its surroundings. Keep in mind that the ideal gas equation embodies Boyle's law: The volume of a fixed amount of gas at a fixed temperature is inversely proportional to the pressure. Thus, in Example 7-5 we could simply write that

$$V_f = 1.02\ \text{L} \times \frac{2.40\ \text{atm}}{1.20\ \text{atm}}$$
$$V_f = 2.04\ \text{L}$$

PRACTICE EXAMPLE A: How much work, in joules, is involved when 0.225 mol N_2 at a constant temperature of 23°C is allowed to expand by 1.50 L in volume against an external pressure of 0.750 atm? [*Hint:* How much of this information is required?]

PRACTICE EXAMPLE B: How much work is done, in joules, when an external pressure of 2.50 atm is applied, at a constant temperature of 20.0 °C, to 50.0 g $N_2(g)$ in a 75.0 L cylinder? The cylinder is like that shown in Figure 7-8.

7-5 CONCEPT ASSESSMENT

A gas in a 1.0 L closed cylinder has an initial pressure of 10.0 bar. It has a final pressure of 5.0 bar. The volume of the cylinder remained constant during this time. What form of energy was transferred across the boundary to cause this change? In which direction did the energy flow?

7-5 The First Law of Thermodynamics

The absorption or evolution of heat and the performance of work require changes in the energy of a system and its surroundings. When considering the energy of a system, we use the concept of internal energy and how heat and work are related to it.

Internal energy, U, is the total energy (both kinetic and potential) in a system, including *translational kinetic energy* of molecules, the energy associated with molecular rotations and vibrations, the energy stored in chemical bonds and intermolecular attractions, and the energy associated with electrons in atoms. Some of these forms of internal energy are illustrated in Figure 7-9. Internal energy also includes energy associated with the interactions of protons and neutrons in atomic nuclei, although this component is unchanged in chemical reactions. A system contains *only* internal energy. A system does not contain energy in the form of heat or work. Heat and work are the means by which a system exchanges energy with its surroundings. *Heat and work exist only during a change in the system.* The relationship between heat (q), work (w), and changes in internal energy (ΔU) is dictated by the law of conservation of energy, expressed in the form known as the **first law of thermodynamics**.

$$\Delta U = q + w \tag{7.12}$$

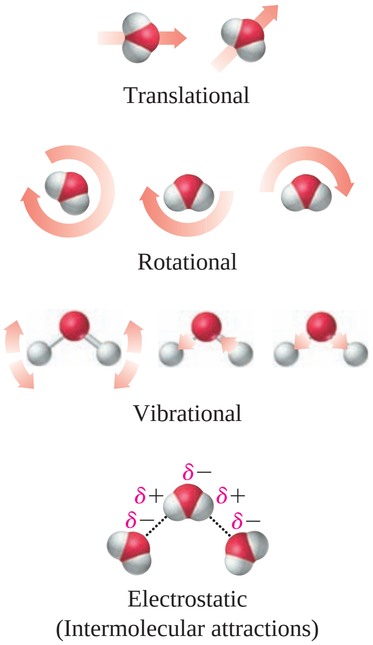
An isolated system is unable to exchange either heat or work with its surroundings, so that $\Delta U_{\text{isolated system}} = 0$, and we can say

The energy of an isolated system is constant.

In using equation (7.12) we must keep these important points in mind.

- Any energy *entering* the system carries a *positive* sign. Thus, if heat is *absorbed* by the system, $q > 0$. If work is done *on* the system, $w > 0$.
- Any energy *leaving* the system carries a *negative* sign. Thus, if heat is *given off* by the system, $q < 0$. If work is done *by* the system, $w < 0$.
- In general, the internal energy of a system changes as a result of energy entering or leaving the system as heat and/or work. If, on balance, more energy enters the system than leaves, ΔU is *positive*. If more energy leaves than enters, ΔU is *negative*.
- A consequence of $\Delta U_{\text{isolated system}} = 0$ is that $\Delta U_{\text{system}} = -\Delta U_{\text{surroundings}}$; that is, energy is conserved.

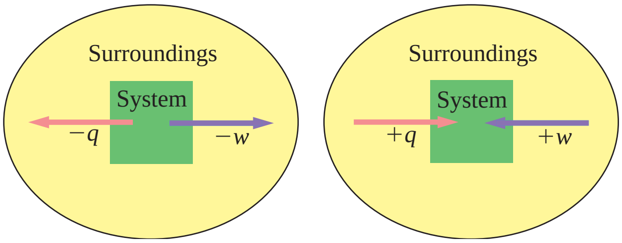
These ideas are summarized in Figure 7-10 and illustrated in Example 7-6.



▲ FIGURE 7-9
Some contributions to the internal energy of a system
The models represent water molecules, and the arrows represent the types of motion they can undergo. In the intermolecular attractions between water molecules, the symbols δ+ and δ− signify a separation of charge, producing centers of positive and negative charge that are smaller than ionic charges. These intermolecular attractions are discussed in Chapter 12.

KEEP IN MIND

that heat is the disordered flow of energy and work is the ordered flow of energy.



◀ FIGURE 7-10
Illustration of sign conventions used in thermodynamics
Arrows represent the direction of heat flow (⟶) and work (⟶). In the left diagram, the minus (−) signs signify energy leaving the system and entering the surroundings. In the right diagram the plus (+) signs refer to energy entering the system from the surroundings. These sign conventions are consistent with the expression $\Delta U = q + w$.

EXAMPLE 7-6 Relating ΔU, q, and w Through the First Law of Thermodynamics

A gas, while expanding (recall Figure 7-8), absorbs 25 J of heat and does 243 J of work. What is ΔU for the gas?

Analyze

The key to problems of this type lies in assigning the correct signs to the quantities of heat and work. Because heat is absorbed by (enters) the system, q is *positive*. Because work done *by* the system represents energy *leaving* the system, w is *negative*. You may find it useful to represent the values of q and w, with their correct signs, within parentheses. Then complete the algebra.

Solve

$$\Delta U = q + w = (+25\,\text{J}) + (-243\,\text{J}) = 25\,\text{J} - 243\,\text{J} = -218\,\text{J}$$

Assess

The negative sign for the change in internal energy, ΔU, signifies that the system, in this case the gas, has lost energy.

PRACTICE EXAMPLE A: In compressing a gas, 355 J of work is done on the system. At the same time, 185 J of heat escapes from the system. What is ΔU for the system?

PRACTICE EXAMPLE B: If the internal energy of a system *decreases* by 125 J at the same time that the system *absorbs* 54 J of heat, does the system do work or have work done on it? How much?

7-6 CONCEPT ASSESSMENT

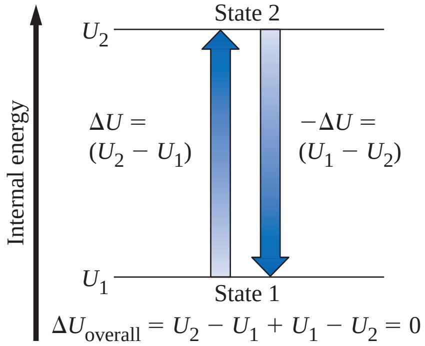
When water is injected into a balloon filled with ammonia gas, the balloon shrinks and feels warm. What are the sources of heat and work, and what are the signs of q and w in this process?

Functions of State

To describe a system completely, we must indicate its temperature, its pressure, and the kinds and amounts of substances present. When we have done this, we have specified the *state* of the system. Any property that has a unique value for a specified state of a system is said to be a **function of state**, or a **state function**. For example, a sample of pure water at 20 °C (293.15 K) and under a pressure of 100 kPa is in a specified state. The density of water in this state is 0.99820 g/mL. We can establish that this density is a unique value—a function of state—in the following way: Obtain three different samples of water—one purified by extensive distillation of groundwater; one synthesized by burning pure $H_2(g)$ in pure $O_2(g)$; and one prepared by driving off the water of hydration from $CuSO_4 \cdot 5\,H_2O$ and condensing the gaseous water to a liquid. The densities of the three different samples for the state that we specified will all be the same: 0.99820 g/mL. Thus, the value of a function of state depends on the state of the system, and not on how that state was established.

The internal energy of a system is a function of state, although there is no simple measurement or calculation that we can use to establish its value. That is, we cannot write down a value of U for a system in the same way that we can write $d = 0.99820$ g/mL for the density of water at 20 °C. Fortunately, we don't need to know actual values of U. Consider, for example, heating 10.0 g of ice at 0 °C to a final temperature of 50 °C. The internal energy of the ice at 0 °C has one unique value, U_1, while that of the liquid water at 50 °C has another, U_2. The *difference* in internal energy between these two states also has a unique value, $\Delta U = U_2 - U_1$, and this difference *is* something that we can precisely measure. It is the quantity of energy (as heat) that must be transferred from the surroundings to the system during the change from state 1 to state 2. As a further illustration, consider the scheme outlined here and illustrated by the diagram on page 257. Imagine that a system changes from state 1 to state 2 and then back to state 1.

$$\text{State 1 } (U_1) \xrightarrow{\Delta U} \text{State 2 } (U_2) \xrightarrow{-\Delta U} \text{State 1 } (U_1)$$



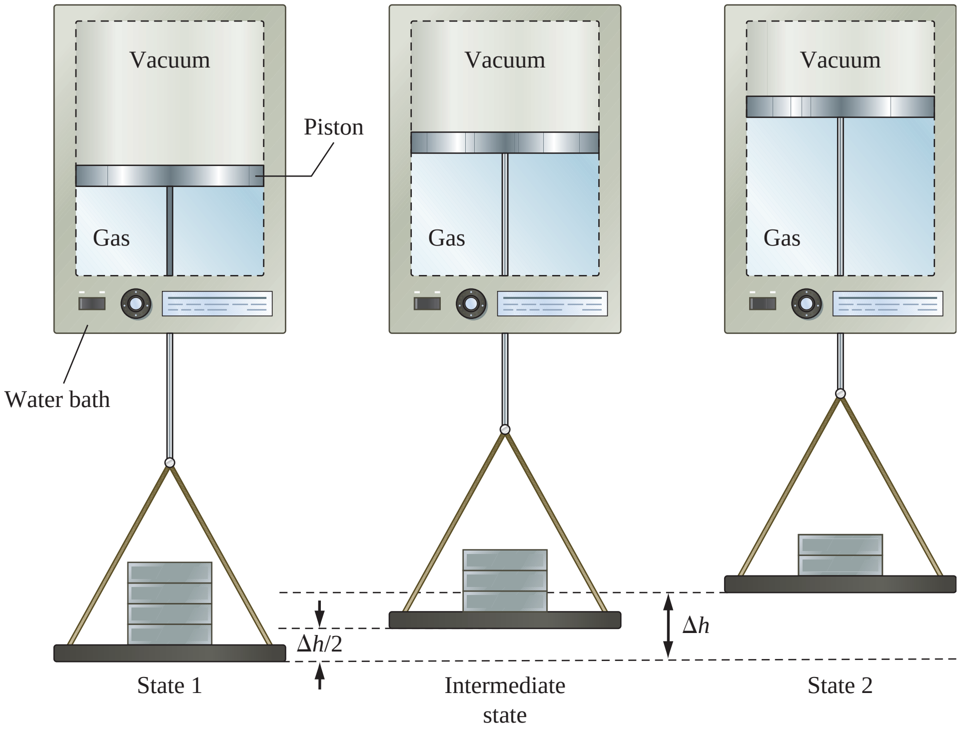
Because U has a unique value in each state, ΔU also has a unique value; it is $U_2 - U_1$. The change in internal energy when the system is returned from state 2 to state 1 is $-\Delta U = U_1 - U_2$. Thus, the *overall* change in internal energy is

$$\Delta U + (-\Delta U) = (U_2 - U_1) + (U_1 - U_2) = 0$$

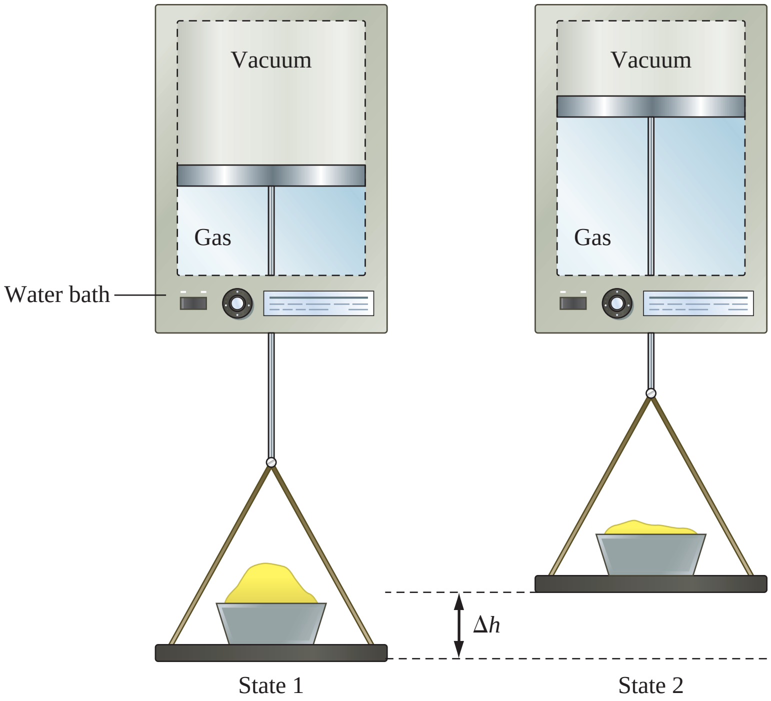
This means that the internal energy returns to its initial value of U_1, which it must do, since it is a function of state. It is important to note here that when we reverse the direction of change, we change the sign of ΔU.

Path-Dependent Functions

Unlike internal energy and changes in internal energy, heat (q) and work (w) are *not* functions of state. Their values depend on the path followed when a system undergoes a change. We can see why this is so by considering again the process described by Figure 7-8 and Example 7-5. Think of the 0.100 mol of He at 298 K and under a pressure of 2.40 atm as *state 1*, and under a pressure of 1.20 atm as *state 2*. The change from state 1 to state 2 occurred in a single step. Suppose that in another instance, we allowed the expansion to occur through an intermediate stage pictured in Figure 7-11. That is, suppose the external pressure on the gas was first reduced from 2.40 atm to 1.80 atm (at which point, the gas volume would be 1.36 L). Then, in a second stage, reduced from 1.80 atm to 1.20 atm, thereby arriving at state 2.



◀ FIGURE 7-11
A two-step expansion for the gas shown in Figure 7-8
In the initial state there are four weights of mass $M/2$ holding the gas back. In the intermediate state one of these weights has been removed and in the final state a second weight of mass $M/2$ has been removed. The initial and final states in this figure are the same as in Figure 7-8. This two-step expansion helps us to establish that the work of expansion depends on the path taken.



▶ FIGURE 7-12
A different method of achieving the expansion of a gas
In this expansion process, the weights in Figures 7-8 and 7-11 have been replaced by a pan containing sand, which has a mass of 2*M*, equivalent to that of the weights in the initial state. In the final state the mass of the sand has been reduced to *M*.

We calculated the amount of work done by the gas in a single-stage expansion in Example 7-5; it was $w = -1.24 \times 10^2$ J. The amount of work done in the two-stage process is the sum of two terms: the pressure–volume work for each stage of the expansion.

$$\begin{aligned} w &= -1.80\ \text{atm} \times (1.36\ \text{L} - 1.02\ \text{L}) - 1.20\ \text{atm} \times (2.04\ \text{L} - 1.36\ \text{L}) \\ &= -0.61\ \text{L atm} - 0.82\ \text{L atm} \\ &= -1.43\ \text{L atm} \times \frac{101\ \text{J}}{1\ \text{L atm}} = -1.44 \times 10^2\ \text{J} \end{aligned}$$

The value of ΔU is the same for the single- and two-stage expansion processes because internal energy is a function of state. However, we see that slightly more work is done in the two-stage expansion. Work is not a function of state; it is path dependent. In the next section, we will stress that heat is also path dependent.

KEEP IN MIND

that if w differs in the two expansion processes, q must also differ, and in such a way that $q + w = \Delta U$ has a unique value, as required by the first law of thermodynamics.

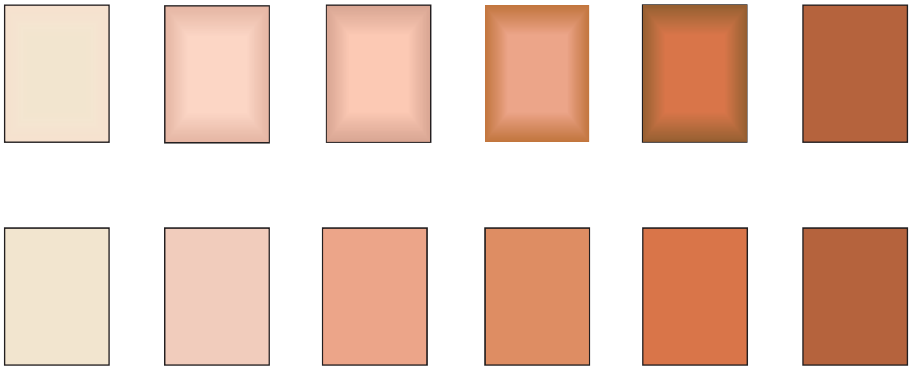
Now consider a different way to carry out the expansion from state 1 to state 2 (see Figure 7-12). The weights in Figures 7-8 and 7-11 have now been replaced by an equivalent amount of sand so that the gas is in state 1. Imagine sand is removed very slowly from this pile—say, one grain at a time. When exactly half the sand has been removed, the gas will have reached state 2. This very slow expansion proceeds in a nearly reversible fashion. A **reversible process** is one that can be made to reverse its direction when an infinitesimal change is made in a system variable. For example, adding a grain of sand rather than removing one would reverse the expansion we are describing. However, the process is not quite reversible because grains of sand have more than an infinitesimal mass. In this approximately reversible process we have made a very large number of intermediate expansions. This process provides more work than when the gas expands directly from state 1 to state 2.

The important difference between the expansion in a finite number of steps and the reversible expansion is that the gas in the reversible process is always in equilibrium with its surroundings whereas in a stepwise process this is never the case. The stepwise processes are said to be **irreversible** because the system is not in equilibrium with the surroundings, and the process cannot be reversed by an infinitesimal change in a system variable.

In comparing the quantity of work done in the two different expansions (Figs. 7-8 and 7-11), we found them to be different, thereby proving that work is not a state function. Additionally, the quantity of work performed is greater in the two-step expansion (Fig. 7-11) than in the single-step expansion (Fig. 7-8). We leave it to the interested student to demonstrate, through Feature Problem 125, that the maximum possible work is that done in a reversible expansion (Fig. 7-12).

7-7 CONCEPT ASSESSMENT

A sample can be heated very slowly or very rapidly. The darker shading in the illustration indicates a higher temperature. Which of the two sets of diagrams do you think corresponds to reversible heating and which to spontaneous, or irreversible, heating?



7-6 Heats of Reaction: ΔU and ΔH

Think of the reactants in a chemical reaction as the initial state of a system and the products as the final state.

$$\begin{array}{ccc} \text{reactants} & \longrightarrow & \text{products} \\ \text{(initial state)} & & \text{(final state)} \\ U_i & & U_f \end{array}$$

$$\Delta U = U_f - U_i$$

According to the first law of thermodynamics, we can also say that $\Delta U = q + w$. We have previously identified a heat of reaction as q_{rxn}, and so we can write

$$\Delta U = q_{\text{rxn}} + w$$

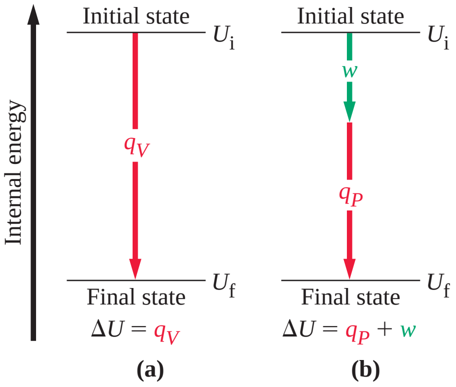
Now consider again a combustion reaction carried out in a bomb calorimeter (see Figure 7-5). The original reactants and products are confined within the bomb, and we say that the reaction occurs at *constant volume*. Because the volume is constant, $\Delta V = 0$, and no work is done. That is, $w = -P\Delta V = 0$. Denoting the heat of reaction for a constant-volume reaction as q_V, we see that $\Delta U = q_V$.

$$\Delta U = q_{\text{rxn}} + w = q_{\text{rxn}} + 0 = q_{\text{rxn}} = q_V \qquad \textbf{(7.13)}$$

The heat of reaction measured in a bomb calorimeter is equal to ΔU.

Chemical reactions are not ordinarily carried out in bomb calorimeters. The metabolism of sucrose occurs under the conditions present in the human body. The combustion of methane (natural gas) in a water heater occurs in an open flame. This question then arises: How does the heat of a reaction measured in a

▶ FIGURE 7-13
Two different paths leading to the same internal energy change in a system
In path (a), the volume of the system remains constant and no internal energy is converted into work—think of burning gasoline in a bomb calorimeter. In path (b), the system does work, so some of the internal energy change is used to do work—think of burning gasoline in an automobile engine to produce heat and work.



bomb calorimeter compare with the heat of reaction if the reaction is carried out in some other way? The usual other way is in beakers, flasks, and other containers open to the atmosphere and under the *constant pressure* of the atmosphere. We live in a world of constant pressure! The neutralization reaction of Example 7-4 is typical of this more common method of conducting chemical reactions.

In many reactions carried out at constant pressure, a small amount of pressure–volume work is done as the system expands or contracts (recall Figure 7-7). In these cases, the heat of reaction, q_P, is different from q_V. We know that the change in internal energy (ΔU) for a reaction carried out between a given initial and a given final state has a unique value. Furthermore, for a reaction at constant volume, $\Delta U = q_V$. From Figure 7-13 and the first law of thermodynamics, we see that for the same reaction at constant pressure $\Delta U = q_P + w$, which means $\Delta U = q_V = q_P + w$. Thus, unless $w = 0$, q_V and q_P must be different. The fact that q_V and q_P for a reaction may differ, even though ΔU has the same value, underscores that U is a function of state and q and w are not.

The relationship between q_V and q_P can be used to devise another state function that represents the heat flow for a process at constant pressure. To do this, we begin by writing

$$q_V = q_P + w$$

Now, using $\Delta U = q_V$, $w = -P\Delta V$ and rearranging terms, we obtain

$$\Delta U = q_P - P\Delta V$$
$$q_P = \Delta U + P\Delta V$$

The quantities U, P, and V are all state functions, so it should be possible to derive the expression $\Delta U + P\Delta V$ from yet another state function. This state function, called **enthalpy**, ***H***, is the sum of the internal energy and the pressure–volume product of a system: $H = U + PV$. The **enthalpy change**, ΔH, for a process between initial and final states is

$$\Delta H = H_f - H_i = (U_f + P_f V_f) - (U_i + P_i V_i)$$
$$\Delta H = (U_f - U_i) + (P_i V_f - P_i V_i)$$
$$\Delta H = \Delta U + \Delta PV$$

If the process is carried out at a constant temperature and pressure $(P_i = P_f)$ and with work limited to pressure–volume work, the enthalpy change is

$$\Delta H = \Delta U + P\Delta V$$

and the heat flow for the process under these conditions is

$$\Delta H = q_P \tag{7.14}$$

7-8 CONCEPT ASSESSMENT

Suppose a system is subjected to the following changes: a 40 kJ quantity of heat is added and the system does 15 kJ of work; then the system is returned to its original state by cooling and compression. What is the value of ΔH?

Enthalpy (ΔH) and Internal Energy (ΔU) Changes in a Chemical Reaction

We have noted that the heat of reaction at constant pressure, ΔH, and the heat of reaction at constant volume, ΔU, are related by the expression

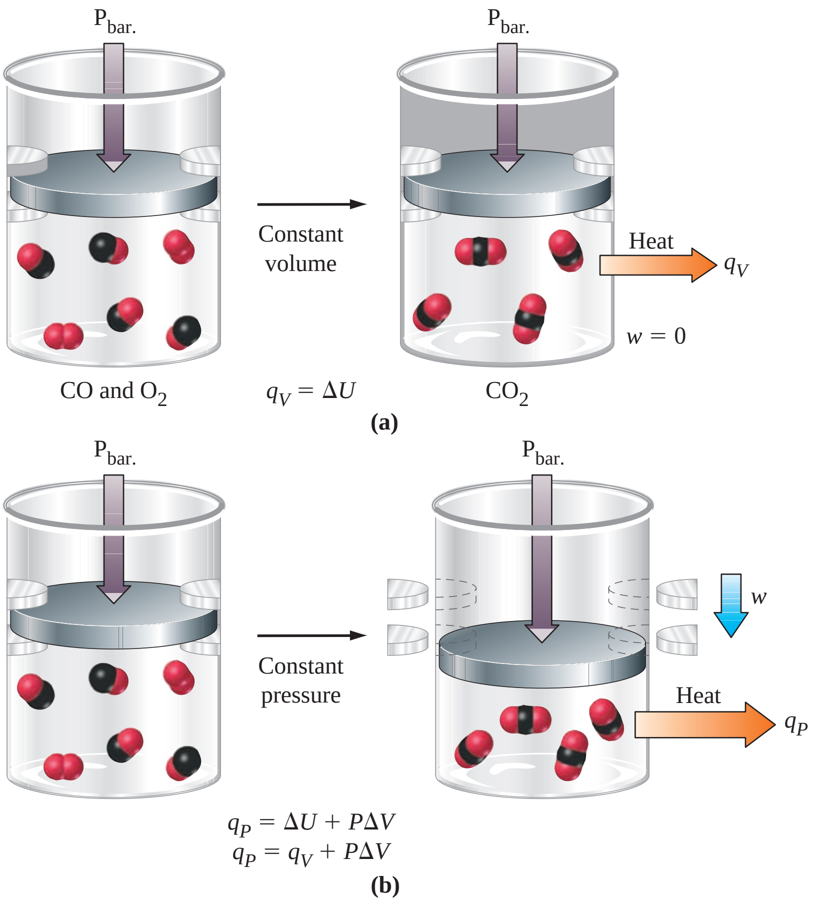
$$\Delta U = \Delta H - P\Delta V \tag{7.15}$$

The last term in this expression is the energy associated with the change in volume of the system under a constant external pressure. To assess just how significant pressure–volume work is, consider the following reaction, which is also illustrated in Figure 7-14.

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$

If the heat of this reaction is measured under constant-pressure conditions at a constant temperature of 298 K, we get −566.0 kJ, indicating that 566.0 kJ of energy has left the system as heat: $\Delta H = -566.0$ kJ. To evaluate the pressure–volume work, we begin by writing

$$P\Delta V = P(V_f - V_i)$$



◀ FIGURE 7-14
Comparing heats of reaction at constant volume and constant pressure for the reaction $2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$
(a) No work is performed at constant volume because the piston cannot move because of the stops placed through the cylinder walls; $q_V = \Delta U = -563.5$ kJ. (b) When the reaction is carried out at constant pressure, the stops are removed. This allows the piston to move and the surroundings do work on the system, causing it to shrink into a smaller volume. More heat is evolved than in the constant-volume reaction; $q_P = \Delta H = -566.0$ kJ.

Then we can use the ideal gas equation to write this alternative expression.

$$P\Delta V = RT(n_f - n_i)$$

Here, n_f is the number of moles of gas in the products (2 mol CO_2) and n_i is the number of moles of gas in the reactants (2 mol CO + 1 mol O_2). Thus,

$$P\Delta V = 0.0083145\ \text{kJ mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K} \times [2 - (2 + 1)]\ \text{mol} = -2.5\ \text{kJ}$$

The change in internal energy is

$$\begin{aligned}\Delta U &= \Delta H - P\Delta V \\ &= -566.0\ \text{kJ} - (-2.5\ \text{kJ}) \\ &= -563.5\ \text{kJ}\end{aligned}$$

This calculation shows that the $P\Delta V$ term is quite small compared to ΔH and that ΔU and ΔH are almost the same. An additional interesting fact here is that the volume of the system decreases as a consequence of the work done on the system by the surroundings.

In the combustion of sucrose at a fixed temperature, the heat of combustion turns out to be the same, whether at constant volume (q_V) or constant pressure (q_P). Only heat is transferred between the reaction mixture and the surroundings; no pressure–volume work is done. This is because the volume of a system is almost entirely determined by the volume of gas and because 12 mol $CO_2(g)$ occupies the same volume as 12 mol $O_2(g)$. There is no change in volume in the combustion of sucrose: $q_P = q_V$. Thus, the result of Example 7-3 can be represented as

$$C_{12}H_{22}O_{11}(s) + 12\,O_2(g) \longrightarrow 12\,CO_2(g) + 11\,H_2O(l) \quad \Delta H = -5.65 \times 10^3\ \text{kJ} \qquad \textbf{(7.16)}$$

That is, 1 mol $C_{12}H_{22}O_{11}(s)$ reacts with 12 mol $O_2(g)$ to produce 12 mol $CO_2(g)$, 11 mol $H_2O(l)$, and 5.65×10^3 kJ of evolved heat. Strictly speaking, the unit for ΔH should be kilojoules per mole, meaning per mole of reaction. "One mole of reaction" relates to the amounts of reactants and products in the equation as written. Thus, reaction (7.16) involves 1 mol $C_{12}H_{22}O_{11}(s)$, 12 mol $O_2(g)$, 12 mol $CO_2(g)$, 11 mol $H_2O(l)$, and -5.65×10^3 kJ of enthalpy change *per mol reaction*. The mol^{-1} part of the unit of ΔH is often dropped, but there are times we need to carry it to achieve the proper cancellation of units. We will find this to be the case in Chapters 19 and 20.

In summary, in most reactions, the heat of reaction we measure is ΔH. In some reactions, notably combustion reactions, we measure ΔU (that is, q_V). In reaction (7.16), $\Delta U = \Delta H$, but this is not always the case. Where it is not, a value of ΔH can be obtained from ΔU by the method illustrated in the discussion of expression (7.15), but even in those cases, ΔH and ΔU will be nearly equal. In this text, all heats of reactions are treated as ΔH values unless there is an indication to the contrary.

Example 7-7 shows how enthalpy changes can provide conversion factors for problem solving.

You may be wondering why the term ΔH is used instead of ΔU, q, and w. It's mainly a matter of convenience. Think of an analogous situation from daily life—buying gasoline at a gas station. The gasoline price posted on the pump is actually the sum of a base price and various taxes that must be paid to different levels of government. This breakdown is important to the accountants who must determine how much tax is to be paid to which agencies. To the consumer, however, it's easier to be given just the total cost per gallon or liter. After all, this determines what he or she must pay. In thermochemistry, our chief interest is generally in heats of reaction, not pressure–volume work. And because most reactions are carried out under atmospheric pressure, it's

EXAMPLE 7-7 Stoichiometric Calculations Involving Quantities of Heat

How much heat is associated with the complete combustion of 1.00 kg of sucrose, $C_{12}H_{22}O_{11}$?

Analyze

Equation (7.16) represents the combustion of 1 mol of sucrose. In that reaction the amount of heat generated is given as an enthalpy, $\Delta H = -5.65 \times 10^3$ kJ/mol. The first step is to determine the number of moles in 1.00 kg of sucrose, and then use that value with the change in enthalpy for the reaction.

Solve

Express the quantity of sucrose in moles.

$$?\,\text{mol} = 1.00\,\text{kg}\ C_{12}H_{22}O_{11} \times \frac{1000\,\text{g}\ C_{12}H_{22}O_{11}}{1\,\text{kg}\ C_{12}H_{22}O_{11}} \times \frac{1\,\text{mol}\ C_{12}H_{22}O_{11}}{342.3\,\text{g}\ C_{12}H_{22}O_{11}} = 2.92\,\text{mol}\ C_{12}H_{22}O_{11}$$

Formulate a conversion factor (shown in blue) based on the information in equation (7.16)—that is, -5.65×10^3 kJ of heat is associated with the combustion of 1 mol $C_{12}H_{22}O_{11}$.

$$?\,\text{kJ} = 2.92\,\text{mol}\ C_{12}H_{22}O_{11} \times \frac{-5.65 \times 10^3\,\text{kJ}}{1\,\text{mol}\ C_{12}H_{22}O_{11}} = -1.65 \times 10^4\,\text{kJ}$$

The negative sign denotes that heat is given off in the combustion.

Assess

The negative sign denotes that heat is given off in the combustion. Variations of this type of calculation should make intuitive sense. For example, doubling the amount of sucrose in the combustion reaction should double the amount of heat.

PRACTICE EXAMPLE A: What mass of sucrose must be burned to produce 1.00×10^3 kJ of heat?

PRACTICE EXAMPLE B: A 25.0 mL sample of 0.1045 M HCl(aq) was neutralized by NaOH(aq). Use the result of Example 7-4 to determine the heat evolved in this neutralization.

helpful to have a function of state, enthalpy, H, whose change is exactly equal to something we can measure: q_P.

Enthalpy Change (ΔH) Accompanying a Change in State of Matter

When a liquid is in contact with the atmosphere, energetic molecules at the surface of the liquid can overcome forces of attraction to their neighbors and pass into the gaseous, or vapor, state. We say that the liquid *vaporizes*. If the temperature of the liquid is to remain constant, the liquid must absorb heat from its surroundings to replace the energy carried off by the vaporizing molecules. The heat required to vaporize a fixed quantity of liquid is called the enthalpy (or heat) of vaporization. Usually the fixed quantity of liquid chosen is one mole, and we can call this quantity the *molar enthalpy of vaporization*. For example,

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H = 44.0\ \text{kJ at 298 K}$$

We described the melting of a solid in a similar fashion (page 244). The energy requirement in this case is called the enthalpy (or heat) of fusion. For the melting of one mole of ice, we can write

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = 6.01\ \text{kJ at 273.15 K}$$

We can use the data represented in these equations, together with other appropriate data, to answer questions like those posed in Example 7-8 and its accompanying Practice Examples.

EXAMPLE 7-8 Enthalpy Changes Accompanying Changes in States of Matter

Calculate ΔH for the process in which 50.0 g of water is converted from liquid at 10.0 °C to vapor at 25.0 °C.

Analyze

The key to this calculation is to view the process as proceeding in two steps: first raising the temperature of liquid water from 10.0 to 25.0 °C, and then completely vaporizing the liquid at 25.0 °C. The total enthalpy change is the sum of the changes in the two steps. For a process at constant pressure, $\Delta H = q_P$, so we need to calculate the heat absorbed in each step.

Solve

HEATING WATER FROM 10.0 TO 25.0°C

This heat requirement can be determined by the method shown in Example 7-1; that is, we apply equation (7.5).

$$? \text{ kJ} = 50.0 \text{ g } H_2O \times \frac{4.18 \text{ J}}{\text{g } H_2O \text{ °C}} \times (25.0 - 10.0) \text{ °C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 3.14 \text{ kJ}$$

VAPORIZING WATER AT 25.0°C

For this part of the calculation, the quantity of water must be expressed in moles so that we can then use the molar enthalpy of vaporization at 25 °C: 44.0 kJ/mol.

$$? \text{ kJ} = 50.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{44.0 \text{ kJ}}{1 \text{ mol } H_2O} = 122 \text{ kJ}$$

TOTAL ENTHALPY CHANGE

$$\Delta H = 3.14 \text{ kJ} + 122 \text{ kJ} = 125 \text{ kJ}$$

Assess

Note that the sign of the enthalpy change is positive, which reflects that the system (i.e., the water) gains energy. The reverse would be true for condensation of water at this temperature.

PRACTICE EXAMPLE A: What is the enthalpy change when a cube of ice 2.00 cm on edge is brought from −10.0 °C to a final temperature of 23.2 °C? For ice, use a density of 0.917 g/cm^3, a specific heat of 2.01 J g^{-1} °C^{-1}, and an enthalpy of fusion of 6.01 kJ/mol.

PRACTICE EXAMPLE B: What is the maximum mass of ice at −15.0 °C that can be completely converted to water vapor at 25.0 °C if the available heat for this transition is 5.00×10^3 kJ?

Standard States and Standard Enthalpy Changes

The measured enthalpy change for a reaction has a unique value *only* if the initial state (reactants) and final state (products) are precisely described. If we define a particular state as *standard* for the reactants and products, we can then say that the standard enthalpy change is the enthalpy change in a reaction in which the reactants and products are in their standard states. This so-called **standard enthalpy of reaction** is denoted with a degree symbol, $\Delta H°$.

The **standard state** of a solid or liquid substance is the pure element or compound at a pressure of *1 bar* (10^5 Pa)* and at the temperature of interest. For a gas, the standard state is the pure gas behaving as an (hypothetical) ideal gas at a pressure of 1 bar and the temperature of interest. Although temperature is not part of the definition of a standard state, it still must be specified in tabulated values of $\Delta H°$, because $\Delta H°$ depends on temperature. The values given in this text are all for 298.15 K (25 °C) unless otherwise stated.

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*The International Union of Pure and Applied Chemistry (IUPAC) recommended that the standard-state pressure be changed from 1 atm to 1 bar about 25 years ago, but some data tables are still based on the 1 atm standard. Fortunately, the differences in values resulting from this change in standard-state pressure are very small—almost always small enough to be ignored.

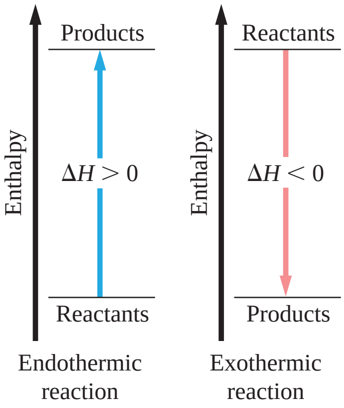
In the rest of this chapter, we will mostly use standard enthalpy changes. We will explore the details of nonstandard conditions in Chapter 19.

Enthalpy Diagrams

The negative sign of ΔH in equation (7.16) means that the enthalpy of the products is lower than that of the reactants. This *decrease* in enthalpy appears as heat evolved to the surroundings. The combustion of sucrose is an exothermic reaction. In the reaction

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \qquad \Delta H^\circ = 180.50\ \text{kJ} \qquad \textbf{(7.17)}$$

the products have a *higher* enthalpy than the reactants; ΔH is positive. To produce this increase in enthalpy, heat is absorbed from the surroundings. The reaction is endothermic. An **enthalpy diagram** is a diagrammatic representation of enthalpy changes in a process. Figure 7-15 shows how exothermic and endothermic reactions can be represented through such diagrams.

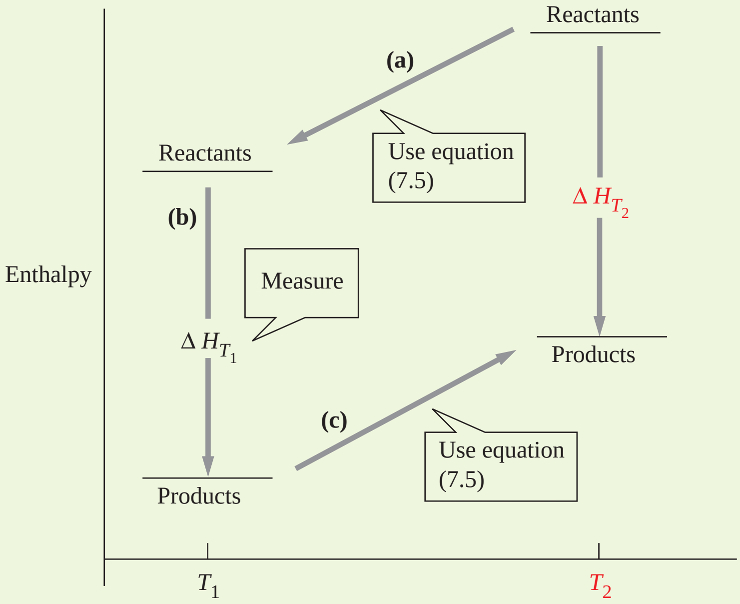


▲ FIGURE 7-15
Enthalpy diagrams
Horizontal lines represent absolute values of enthalpy. The higher a horizontal line, the greater the value of H that it represents. Vertical lines or arrows represent changes in enthalpy (ΔH). Arrows pointing up signify increases in enthalpy—endothermic reactions. Arrows pointing down signify decreases in enthalpy—exothermic reactions.

7-1 ARE YOU WONDERING...

Why ΔH depends on temperature?

The difference in ΔH for a reaction at two different temperatures is determined by the amount of heat involved in changing the reactants and products from one temperature to the other under constant pressure. These quantities of heat can be calculated with the help of equation (7.5): q_P = heat capacity × temperature change = $C_P \times \Delta T$. We write an expression of this type for each reactant and product and combine these expressions with the measured ΔH value at one temperature to obtain the value of ΔH at another. This method is illustrated in Figure 7-16 and applied in Exercise 117.



▲ FIGURE 7-16
Conceptualizing ΔH as a function of temperature
In the three-step process outlined here, (a) the reactants are cooled from the temperature T_2 to T_1. (b) The reaction is carried out at T_1, and (c) the products are warmed from T_1 to T_2. When the quantities of heat associated with each step are combined, the result is the same as if the reaction had been carried out at T_2, that is, ΔH_{T_2}.

7-7 Indirect Determination of ΔH: Hess's Law

One of the reasons that the enthalpy concept is so useful is that a large number of heats of reaction can be calculated from a small number of measurements. The following features of enthalpy change (ΔH) make this possible.

- **ΔH Is an Extensive Property.** Consider the standard enthalpy change in the formation of NO(g) from its elements at 25 °C.

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \qquad \Delta H^\circ = 180.50\text{ kJ}$$

To express the enthalpy change in terms of *one mole* of NO(g), we divide all coefficients *and the ΔH value* by *two*.

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \qquad \Delta H^\circ = \frac{1}{2} \times 180.50 = 90.25\text{ kJ}$$

Enthalpy change is directly proportional to the amounts of substances in a system.

▶ Although we have avoided fractional coefficients previously, we need them here. The coefficient of NO(g) must be one.

- **ΔH Changes Sign When a Process Is Reversed.** As we learned on page 257 if a process is reversed, the change in a function of state reverses sign. Thus, ΔH for the *decomposition* of one mole of NO(g) is $-\Delta H$ for the *formation* of one mole of NO(g).

$$NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H^\circ = -90.25\text{ kJ}$$

- **Hess's Law of Constant Heat Summation.** To describe the standard enthalpy change for the formation of $NO_2(g)$ from $N_2(g)$ and $O_2(g)$,

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H^\circ = ?$$

we can think of the reaction as proceeding in two steps: First we form NO(g) from $NO_2(g)$ and $O_2(g)$, and then $NO_2(g)$ from NO(g) and $O_2(g)$. When the equations for these two steps are added together with their individual and distinctive ΔH° values, we get the overall equation and ΔH° value that we are seeking.

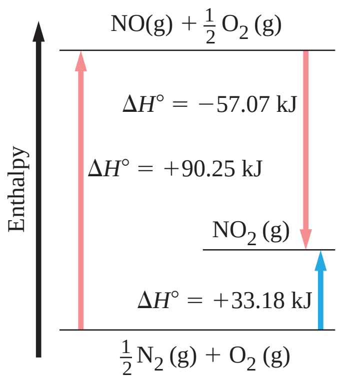
$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow \cancel{NO(g)}\ \cancel{\frac{1}{2}O_2(g)} \qquad \Delta H^\circ = +90.25\text{ kJ}$$

$$\cancel{NO(g)} + \cancel{\frac{1}{2}O_2(g)} \longrightarrow NO_2(g) \qquad \Delta H^\circ = -57.07\text{ kJ}$$

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H^\circ = +33.18\text{ kJ}$$

Note that in summing the two equations NO(g), a species that would have appeared on both sides of the overall equation was canceled out. Figure 7-17 uses an enthalpy diagram to illustrate what we just did. **Hess's law** states the principle we used:

> If a process occurs in stages or steps (even if only hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.



▲ FIGURE 7-17
An enthalpy diagram illustrating Hess's law
Whether the reaction occurs through a single step (blue arrow) or in two steps (red arrows), the enthalpy change is $\Delta H^\circ = 33.18$ kJ for the overall reaction $\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)$.

Hess's law is simply a consequence of the state function property of enthalpy. Regardless of the path taken in going from the initial state to the final state, ΔH (or ΔH° if the process is carried out under standard conditions) has the same value.

Suppose we want the standard enthalpy change for the reaction

$$3\,C(\text{graphite}) + 4\,H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H^\circ = ? \qquad (7.18)$$

KEEP IN MIND

that ΔH° is an extensive property. In a chemical equation, the stoichiometric coefficients specify the amounts involved, and the unit kJ suffices for ΔH°. When ΔH° is not accompanied by an equation, the amount involved must somehow be specified, such as per mole of $C_3H_8(g)$ in the expression $\Delta H^\circ_{comb} = -2219.9\text{ kJ/mol } C_3H_8(g)$.

How should we proceed? If we try to get graphite and hydrogen to react, a slight reaction will occur, but it will not go to completion. Furthermore, the product will not be limited to propane (C_3H_8); several other hydrocarbons will form as well. The fact is that we cannot directly measure ΔH° for reaction (7.18). Instead, we must resort to an *indirect calculation* from ΔH° values that can be established by experiment. Here is where Hess's law is of greatest value. It permits us to calculate ΔH values that we cannot measure directly. In Example 7-9,

EXAMPLE 7-9 Applying Hess's Law

Use the heat of combustion data from page 268 to determine ΔH° for reaction (7.18)
$3\,C(\text{graphite}) + 4\,H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H^\circ = ?$

Analyze

To determine an enthalpy change with Hess's law, we need to combine the appropriate chemical equations. A good starting point is to write chemical equations for the given combustion reactions based on *one mole* of the indicated reactant. Recall from Section 3-4 that the products of the combustion of carbon–hydrogen–oxygen compounds are $CO_2(g)$ and $H_2O(l)$.

Solve

Begin by writing the following reactions

$$\begin{array}{lll}
\textbf{(a)} & C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) & \Delta H^\circ = -2219.9\text{ kJ} \\
\textbf{(b)} & C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ = -393.5\text{ kJ} \\
\textbf{(c)} & H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) & \Delta H^\circ = -285.8\text{ kJ}
\end{array}$$

Because our objective in reaction (7.18) is to *produce* $C_3H_8(g)$, the next step is to find a reaction in which $C_3H_8(g)$ is formed—the *reverse* of reaction **(a)**.

$$-\textbf{(a)}:\ 3\,CO_2(g) + 4\,H_2O(l) \longrightarrow C_3H_8(g) + 5\,O_2(g) \qquad \Delta H^\circ = -(-2219.9)\text{ kJ} = +2219.9\text{ kJ}$$

Now, we turn our attention to the reactants, C(graphite) and $H_2(g)$. To get the proper number of moles of each, we must multiply equation **(b)** by three and equation **(c)** by four.

$$\begin{array}{lll}
3\times\textbf{(b)}: & 3\,C(\text{graphite}) + 3\,O_2(g) \longrightarrow 3\,CO_2(g) & \Delta H^\circ = 3(-393.5\text{ kJ}) = -1181\text{ kJ} \\
4\times\textbf{(c)}: & 4\,H_2(g) + 2\,O_2(g) \longrightarrow 4\,H_2O(l) & \Delta H^\circ = 4(-285.8\text{ kJ}) = -1143\text{ kJ}
\end{array}$$

Here is the overall change we have described: 3 mol C(graphite) and 4 mol $H_2(g)$ have been consumed, and 1 mol $C_3H_8(g)$ has been produced. This is exactly what is required in equation (7.18). We can now combine the three modified equations.

$$\begin{array}{lll}
-\textbf{(a)}: & \cancel{3\,CO_2(g)} + \cancel{4\,H_2O(l)} \longrightarrow C_3H_8(g) + \cancel{5\,O_2(g)} & \Delta H^\circ = +2219.9\text{ kJ} \\
3\times\textbf{(b)}: & 3\,C(\text{graphite}) + \cancel{3\,O_2(g)} \longrightarrow \cancel{3\,CO_2(g)} & \Delta H^\circ = -1181\text{ kJ} \\
4\times\textbf{(c)}: & 4\,H_2(g) + \cancel{2\,O_2(g)} \longrightarrow \cancel{4\,H_2O(l)} & \Delta H^\circ = -1143\text{ kJ} \\
\hline
 & 3\,C(\text{graphite}) + 4\,H_2(g) \longrightarrow C_3H_8(g) & \Delta H^\circ = -104\text{ kJ}
\end{array}$$

Assess

Hess's law is a powerful technique to determine the enthalpy of reaction by using a series of unrelated reactions, along with their enthalpies of reaction. In this example, we took three unrelated combustion reactions and were able to determine the enthalpy of reaction of another reaction.

PRACTICE EXAMPLE A: The standard heat of combustion of propene, $C_3H_6(g)$, is $-2058\text{ kJ/mol } C_3H_6(g)$. Use this value and other data from this example to determine ΔH° for the hydrogenation of propene to propane.

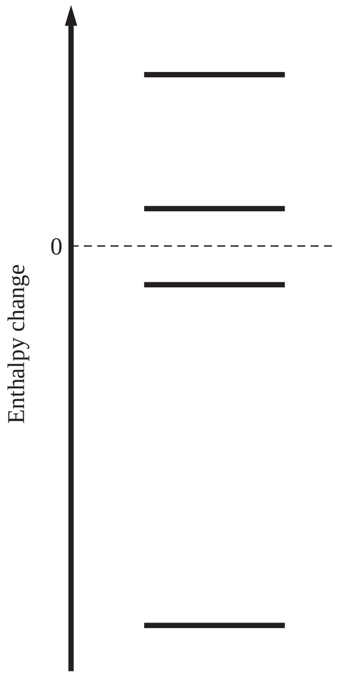
$$CH_3CH{=}CH_2(g) + H_2(g) \longrightarrow CH_3CH_2CH_3(g) \qquad \Delta H^\circ = ?$$

PRACTICE EXAMPLE B: From the data in Practice Example 7-9A and the following equation, determine the standard enthalpy of combustion of one mole of 2-propanol, $CH_3CHOHCH_3(l)$.

$$CH_3CH{=}CH_2(g) + H_2O(l) \longrightarrow CH_3CH(OH)CH_3(l) \qquad \Delta H^\circ = -52.3\text{ kJ}$$

we use the following standard heats of combustion $\Delta H^\circ_{\text{comb}}$ to calculate ΔH° for reaction (7.18).

$$\begin{aligned} \Delta H^\circ_{\text{comb}} \quad C_3H_8(g) &= -2219.9\ \text{kJ/mol}\ C_3H_8(g) \\ C(\text{graphite}) &= -393.5\ \text{kJ/mol}\ C(\text{graphite}) \\ H_2(g) &= -285.8\ \text{kJ/mol}\ H_2(g) \end{aligned}$$



7-9 CONCEPT ASSESSMENT

The heat of reaction between carbon (graphite) and the corresponding stoichiometric amounts of hydrogen gas to form $C_2H_2(g)$, $C_2H_4(g)$, and $C_2H_6(g)$ are 226.7, 52.3 and −84.7 kJmol^{-1}, respectively. Relate these values to the enthalpy diagram shown in the margin. Indicate on the diagram the standard enthalpy change for the reaction $C_2H_2(g) + 2\,H_2(g) \longrightarrow C_2H_6(g)$.

7-8 Standard Enthalpies of Formation

In the enthalpy diagrams we have drawn, we have not written any numerical values on the enthalpy axis. This is because we cannot determine *absolute* values of enthalpy, H. However, enthalpy *is* a function of state, so *changes* in enthalpy, ΔH, have unique values. We can deal just with these changes. Nevertheless, as with many other properties, it is still useful to have a starting point, a zero value.

Consider a map-making analogy: What do we list as the height of a mountain? Do we mean by this the vertical distance between the mountaintop and the center of Earth? Between the mountaintop and the deepest trench in the ocean? No. By agreement, we mean the vertical distance between the mountaintop and mean sea level. We *arbitrarily* assign to mean sea level an elevation of zero, and all other points on Earth are relative to this zero elevation. The elevation of Mt. Everest is +8848 m; that of Badwater, Death Valley, California, is −86 m. We do something similar with enthalpies. We relate our zero to the enthalpies of certain forms of the elements and determine the enthalpies of other substances relative to this zero.

KEEP IN MIND

that we use the expression "standard enthalpy of formation" even though what we are describing is actually a standard enthalpy *change*.

The **standard enthalpy of formation** (ΔH°_f) of a substance is the enthalpy *change* that occurs in the formation of one mole of the substance in the standard state from the *reference* forms of the elements in their standard states. The reference forms of the elements in all but a few cases are the most stable forms of the elements at one bar and the given temperature. The degree symbol denotes that the enthalpy change is a standard enthalpy change, and the subscript "f" signifies that the reaction is one in which a substance is formed from its elements. Because the formation of the most stable form of an element from itself is no change at all,

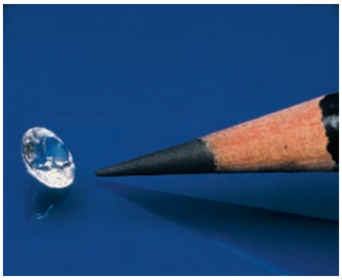
the standard enthalpy of formation of a pure element in its reference form is 0.

Listed here are the most stable forms of several elements at 298.15 K, the temperature at which thermochemical data are commonly tabulated.

$$Na(s) \quad H_2(g) \quad N_2(g) \quad O_2(g) \quad C(\text{graphite}) \quad Br_2(l)$$

The situation with carbon is an interesting one. In addition to graphite, carbon also exists naturally in the form of diamond. However, because there is a measurable enthalpy difference between them, they cannot both be assigned $\Delta H^\circ_f = 0$.

$$C(\text{graphite}) \longrightarrow C(\text{diamond}) \qquad \Delta H^\circ = 1.9\ \text{kJ}$$



▲ Diamond and graphite.

We choose as the reference form the more stable form, the one with the lower enthalpy. Thus, we assign $\Delta H^\circ_f(\text{graphite}) = 0$, and $\Delta H^\circ_f(\text{diamond}) =$

1.9 kJ/mol. Although we can obtain bromine in either the gaseous or liquid state at 298.15 K, $Br_2(l)$ is the most stable form. $Br_2(g)$, if obtained at 298.15 K and 1 bar pressure, immediately condenses to $Br_2(l)$.

$$Br_2(l) \longrightarrow Br_2(g) \qquad \Delta H_f^\circ = 30.91 \text{ kJ}$$

The enthalpies of formation are $\Delta H_f^\circ[Br_2(l)] = 0$ and $\Delta H_f^\circ[Br_2(g)] = 30.91$ kJ/mol.

A rare case in which the reference form is not the most stable form is the element phosphorus. Although over time it converts to solid red phosphorus, solid white phosphorus has been chosen as the reference form.

$$P(s, \text{white}) \longrightarrow P(s, \text{red}) \qquad \Delta H^\circ = -17.6 \text{ kJ}$$

The standard enthalpies of formation are $\Delta H_f^\circ[P(s, \text{white})] = 0$ and $\Delta H_f^\circ[P(s, \text{red})] = -17.6$ kJ/mol.

Standard enthalpies of formation of some common substances are presented in Table 7.2. Figure 7-18 emphasizes that both positive and negative standard enthalpies of formation are possible. It also suggests that standard enthalpies of formation are related to molecular structure.

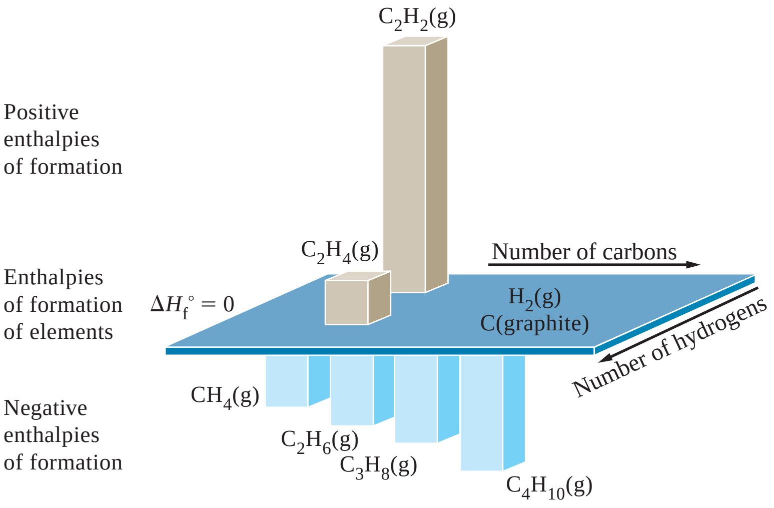
We will use standard enthalpies of formation in a variety of calculations. Often, the first thing we must do is write the chemical equation to which a ΔH_f° value applies, as in Example 7-10.

▲ Liquid bromine vaporizing.

TABLE 7.2 Some Standard Molar Enthalpies of Formation at 298.15 K, ΔH_f°

Substance	kJ/mol[a]	Substance	kJ/mol[a]
$CO(g)$	−110.5	$HBr(g)$	−36.40
$CO_2(g)$	−393.5	$HI(g)$	26.48
$CH_4(g)$	−74.81	$H_2O(g)$	−241.8
$C_2H_2(g)$	226.7	$H_2O(l)$	−285.8
$C_2H_4(g)$	52.26	$H_2S(g)$	−20.63
$C_2H_6(g)$	−84.68	$NH_3(g)$	−46.11
$C_3H_8(g)$	−103.8	$NO(g)$	90.25
$C_4H_{10}(g)$	−125.6	$N_2O(g)$	82.05
$CH_3OH(l)$	−238.7	$NO_2(g)$	33.18
$C_2H_5OH(l)$	−277.7	$N_2O_4(g)$	9.16
$HF(g)$	−271.1	$SO_2(g)$	−296.8
$HCl(g)$	−92.31	$SO_3(g)$	−395.7

[a] Values are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.



◀ FIGURE 7-18
Some standard enthalpies of formation at 298.15 K
Standard enthalpies of formation of elements are shown in the central plane, with $\Delta H_f^\circ = 0$. Substances with positive enthalpies of formation are above the plane, while those with negative enthalpies of formation are below the plane.

EXAMPLE 7-10 Relating a Standard Enthalpy of Formation to a Chemical Equation

The enthalpy of formation of formaldehyde is $\Delta H_f^\circ = \text{mol HCHO(g)}$ at 298 K. Write the chemical equation to which this value applies.

Analyze

The equation must be written for the formation of one mole of gaseous HCHO. The most stable forms of the elements at 298.15 K and 1 bar are gaseous H_2 and O_2 and solid carbon in the form of graphite (Fig. 7-19). Note that we need one fractional coefficient in this equation.

Solve

$$H_2(g) + \frac{1}{2}O_2(g) + C(\text{graphite}) \longrightarrow HCHO(g) \qquad \Delta H_f^\circ = -108.6\ \text{kJ}$$

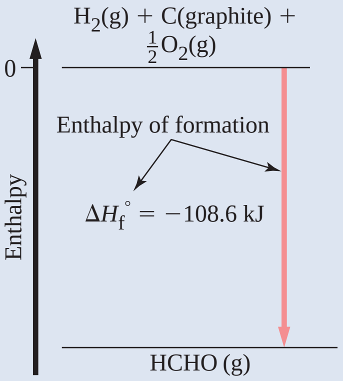
Assess

When answering these types of problems, we must remember to use the elements in their most stable form under the given conditions. In this example, the stated conditions were 298 K and 1 bar.

PRACTICE EXAMPLE A: The standard enthalpy of formation for the amino acid leucine is $-637.3\ \text{kJ/mol}\ C_6H_{13}O_2N(s)$. Write the chemical equation to which this value applies.

PRACTICE EXAMPLE B: How is ΔH° for the following reaction related to the standard enthalpy of formation of $NH_3(g)$ listed in Table 7.2? What is the value of $\Delta H^\circ = ?$

$$2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g) \qquad \Delta H^\circ = ?$$



▲ FIGURE 7-19 **Standard enthalpy of formation of formaldehyde, HCHO(g)** The formation of HCHO(g) from its elements in their standard states is an exothermic reaction. The heat evolved per mole of HCHO(g) formed is the standard enthalpy (heat) of formation.

7-2 ARE YOU WONDERING...

What is the significance of the sign of a ΔH_f° value?

A compound having a positive value of ΔH_f° is formed from its elements by an endothermic reaction. If the reaction is reversed, the compound decomposes into its elements in an exothermic reaction. We say that the compound is unstable with respect to its elements. This does not mean that the compound cannot be made, but it does suggest a tendency for the compound to enter into chemical reactions yielding products with lower enthalpies of formation.

When no other criteria are available, chemists sometimes use enthalpy change as a rough indicator of the likelihood of a chemical reaction occurring—exothermic reactions generally being more likely to occur unassisted than endothermic ones. We'll present much better criteria later in the text.

Standard Enthalpies of Reaction

We have learned that if the reactants and products of a reaction are in their standard states, the enthalpy change is a *standard* enthalpy change, which we can denote as ΔH° or $\Delta H^\circ_{\text{rxn}}$. One of the primary uses of standard enthalpies of formation is in calculating standard enthalpies of reaction.

Let us use Hess's law to calculate the standard enthalpy of reaction for the decomposition of sodium bicarbonate, a minor reaction that occurs when baking soda is used in baking.

$$2\,NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g) \qquad \Delta H^\circ = ? \qquad \textbf{(7.19)}$$

From Hess's law, we see that the following four equations yield equation (7.19) when added together.

$$\textbf{(a)}\quad 2\,\mathrm{NaHCO_3(s)} \longrightarrow 2\,\mathrm{Na(s)} + \mathrm{H_2(g)} + 2\,\mathrm{C\,(graphite)} + 3\,\mathrm{O_2(g)} \qquad \Delta H^\circ = -2 \times \Delta H_f^\circ[\mathrm{NaHCO_3(s)}]$$

$$\textbf{(b)}\quad 2\,\mathrm{Na(s)} + \mathrm{C(graphite)} + \frac{3}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{Na_2CO_3(s)} \qquad \Delta H^\circ = \Delta H_f^\circ[\mathrm{Na_2CO_3(s)}]$$

$$\textbf{(c)}\quad \mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{H_2O(l)} \qquad \Delta H^\circ = \Delta H_f^\circ[\mathrm{H_2O(l)}]$$

$$\textbf{(d)}\quad \mathrm{C(graphite)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \qquad \Delta H^\circ = \Delta H_f^\circ[\mathrm{CO_2(g)}]$$

$$2\,\mathrm{NaHCO_3(s)} \longrightarrow \mathrm{Na_2CO_3(s)} + \mathrm{H_2O(l)} + \mathrm{CO_2(g)} \qquad \Delta H^\circ = ?$$

Equation (a) is the *reverse* of the equation representing the formation of two moles of $[\mathrm{NaHCO_3(s)}]$ from its elements. This means that ΔH° for reaction (a) is the *negative* of twice $\Delta H_f^\circ[\mathrm{NaHCO_3(s)}]$. Equations (b), (c) and (d) represent the formation of *one* mole each of $\mathrm{Na_2CO_3(s)}$, $\mathrm{CO_2(g)}$ and $\mathrm{H_2O(l)}$. Thus, we can express the value of ΔH° for the decomposition reaction as

$$\Delta H^\circ = \Delta H_f^\circ[\mathrm{Na_2CO_3(s)}] + \Delta H_f^\circ[\mathrm{H_2O(l)}] + \Delta H_f^\circ[\mathrm{CO_2(g)}] - 2 \times \Delta H_f^\circ[\mathrm{NaHCO_3(s)}] \qquad \textbf{(7.20)}$$

We can use the enthalpy diagram in Figure 7-20 to visualize the Hess's law procedure and to show how the state function property of enthalpy enables us to arrive at equation (7.20). Imagine the decomposition of sodium bicarbonate taking place in two steps. In the first step, suppose a vessel contains 2 mol $\mathrm{NaHCO_3}$, which is allowed to decompose into 2 mol Na(s), 2 mol C(graphite), 1 mol $\mathrm{H_2(g)}$, and 3 mol $\mathrm{O_2(g)}$, as in equation (a) above. In the second step, recombine the 2 mol Na(s), 2 mol C(graphite), 1 mol $\mathrm{H_2(g)}$, and 3 mol $\mathrm{O_2(g)}$ to form the products according to equations (b), (c), and (d) above.

The pathway shown in Figure 7-20 *is not* how the reaction actually occurs. This does not matter, though, because enthalpy is a state function and the change of any state function is independent of the path chosen. The enthalpy change for the overall reaction is the sum of the standard enthalpy changes of the individual steps.

$$\Delta H^\circ = \Delta H^\circ_{\text{decomposition}} + \Delta H_{\text{recombination}}$$

$$\Delta H^\circ_{\text{decomposition}} = -2 \times \Delta H_f^\circ[\mathrm{NaHCO_3(s)}]$$

$$\Delta H^\circ_{\text{recombination}} = \Delta H_f^\circ[\mathrm{Na_2CO_3(s)}] + \Delta H_f^\circ[\mathrm{H_2O(l)}] + \Delta H_f^\circ[\mathrm{CO_2(g)}]$$

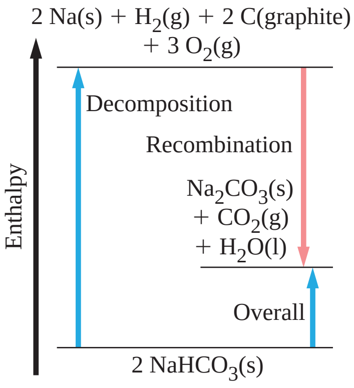
so that

$$\Delta H^\circ = \Delta H_f^\circ[\mathrm{Na_2CO_3(s)}] + \Delta H_f^\circ[\mathrm{H_2O(l)}] + \Delta H_f^\circ[\mathrm{CO_2(g)}] - 2 \times \Delta H_f^\circ[\mathrm{NaHCO_3(s)}]$$

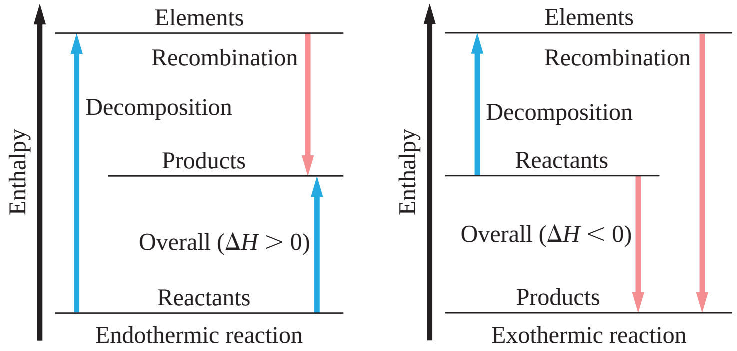
Equation (7.20) is a specific application of the following more general relationship for a standard enthalpy of reaction.

$$\Delta H^\circ = \sum v_p \Delta H_f^\circ(\text{products}) - \sum v_r \Delta H_f^\circ(\text{reactants}) \qquad \textbf{(7.21)}$$

The symbol Σ (Greek, sigma) means "the sum of." The terms that are added together are the products of the standard enthalpies of formation (ΔH_f°) and their stoichiometric coefficients, v. One sum is required for the reaction products (subscript p), and another for the initial reactants (subscript r). The enthalpy change of the reaction is the sum of terms for the products *minus* the sum of terms for the reactants. Equation (7.21) avoids the manipulation of a number of chemical equations. The state function basis for equation (7.21) is shown in Figure 7-21 and is applied in Example 7-11.



▲ FIGURE 7-20
Computing heats of reaction from standard enthalpies of formation
Enthalpy is a state function, hence ΔH° for the overall reaction $2\,\mathrm{NaHCO_3(s)} \longrightarrow \mathrm{Na_2CO_3(s)} + \mathrm{CO_2(g)} + \mathrm{H_2O(l)}$ is the sum of the enthalpy changes for the two steps shown.



▶ FIGURE 7-21
Diagrammatic representation of equation (7.21)

EXAMPLE 7-11 Calculating $\Delta H°$ from Tabulated Values of ΔH_f°

Let us apply equation (7.21) to calculate the standard enthalpy of combustion of ethane, $C_2H_6(g)$, a component of natural gas.

Analyze

This type of problem is a straightforward application of equation (7.21). Appendix D has a table of thermodynamic data which includes the standard enthalpy of formation for a number of compounds.

Solve

The reaction is

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$$

The relationship we need is equation (7.21). The data we substitute into the relationship are from Table 7.2.

$$\begin{aligned}\Delta H° &= \{2\text{ mol } CO_2 \times \Delta H_f^\circ[CO_2(g)] + 3\text{ mol } H_2O \times \Delta H_f^\circ[H_2O(l)]\}\\ &\qquad - \{1\text{ mol } C_2H_6 \times \Delta H_f^\circ[C_2H_6(g)] + \frac{7}{2}\text{mol } O_2 \times \Delta H_f^\circ[O_2(g)]\}\\ &= 2\text{ mol } CO_2 \times (-393.5\text{ kJ/mol } CO_2) + 3\text{ mol } H_2O \times (-285.8\text{ kJ/mol } H_2O)\\ &\qquad - 1\text{ mol } C_2H_6 \times (-84.7\text{ kJ/mol } C_2H_6) - \frac{7}{2}\text{mol } O_2 \times 0\text{ kJ/mol } O_2\\ &= -787.0\text{ kJ} - 857.4\text{ kJ} + 84.7\text{ kJ} = -1559.7\text{ kJ}\end{aligned}$$

Assess

In these types of problems, we must make sure to subtract the sum of the products' standard enthalpies of formation from the sum of the reactants' standard enthalpies of formation. We must also keep in mind that the standard enthalpy of formation of an element in its reference form is zero. Thus, we can drop the term involving $\Delta H_f^\circ[O_2(g)]$ at any time in the calculation.

PRACTICE EXAMPLE A: Use data from Table 7.2 to calculate the standard enthalpy of combustion of ethanol, $CH_3CH_2OH(l)$, at 298.15 K.

PRACTICE EXAMPLE B: Calculate the standard enthalpy of combustion at 298.15 K *per mole* of a gaseous fuel that contains C_3H_8 and C_4H_{10} in the mole fractions 0.62 and 0.38, respectively.

KEEP IN MIND

that the standard enthalpy of formation of an element in its reference form is zero. Thus, we can drop the term involving $\Delta H_f^\circ[O_2(g)]$ at any time in the calculation.

A type of calculation as important as the one illustrated in Example 7-11 is the determination of an unknown ΔH_f° value from a set of known ΔH_f° values and a known standard enthalpy of reaction, $\Delta H°$. As shown in Example 7-12, the essential step is to rearrange expression (7.21) to isolate the unknown ΔH_f° on one side of the equation. Also shown is a way of organizing the data that you may find helpful.

EXAMPLE 7-12 Calculating an Unknown ΔH_f° Value

Use the data here and in Table 7.2 to calculate ΔH_f° of benzene, $C_6H_6(l)$.

$$2\,C_6H_6(l) + 15\,O_2(g) \longrightarrow 12\,CO_2(g) + 6\,H_2O(l) \qquad \Delta H^\circ = -6535\ \text{kJ}$$

Analyze

We have a chemical equation and know the standard enthalpy of reaction. We are asked to determine a standard enthalpy of formation. Equation (7.21) relates a standard enthalpy of reaction to standard enthalpy of formations for reactants and products. To begin, we organize the data needed in the calculation by writing the chemical equation for the reaction with ΔH_f° data listed under the chemical formulas.

Solve

$$\begin{array}{lccccl} & 2\,C_6H_6(l) & + \ 15\,O_2(g) & \longrightarrow \ 12\,CO_2(g) & + \ 6\,H_2O(l) & \qquad \Delta H^\circ = -6535\ \text{kJ} \\ \Delta H_f^\circ,\ \text{kJ/mol} & ? & 0 & -393.5 & -285.8 & \end{array}$$

Now, we can substitute known data into expression (7.21) and rearrange the equation to obtain a lone term on the left: $\Delta H_f^\circ[C_6H_6(l)]$. The remainder of the problem simply involves numerical calculations.

$$\Delta H^\circ = \left\{12\ \text{mol}\ CO_2 \times -(393.5\ \text{kJ/mol}\ CO_2) + 6\ \text{mol}\ H_2O \times (-285.8\ \text{kJ/mol}\ H_2O)\right\}$$
$$- \ 2\ \text{mol}\ C_2H_6 \times \Delta H_f^\circ[C_6H_6(l)] = -6535\ \text{kJ}$$
$$\Delta H_f^\circ[C_6H_6(l)] = \frac{\left\{-4722\ \text{kJ} - 1715\ \text{kJ}\right\} + 6535\ \text{kJ}}{2\ \text{mol}\ C_6H_6} = 49\ \text{kJ/mol}\ C_6H_6(l)$$

Assess

By organizing the data as shown, we were able to identify what is unknown and see how to use equation (7.21). To obtain the correct answer, we also needed to use the correct states for the compounds. In combustion reactions, the water in the product is always liquid. If we had used the standard enthalpy of formation for gaseous water, we would have obtained the wrong answer.

PRACTICE EXAMPLE A: The overall reaction that occurs in photosynthesis in plants is

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g) \qquad \Delta H^\circ = 2803\ \text{kJ}$$

Determine the standard enthalpy of formation of glucose, $C_6H_{12}O_6(s)$, at 298 K.

PRACTICE EXAMPLE B: A handbook lists the standard enthalpy of combustion of gaseous dimethyl ether at 298 K as $-31.70\ \text{kJ/g}(CH_3)_2O(g)$. What is the standard molar enthalpy of formation of dimethyl ether at 298 K?

Ionic Reactions in Solutions

Many chemical reactions in aqueous solution are best thought of as reactions between ions and best represented by net ionic equations. Consider the neutralization of a strong acid by a strong base. Using a somewhat more accurate enthalpy of neutralization than we obtained in Example 7-4, we can write

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -55.8\ \text{kJ} \tag{7.22}$$

We should also be able to calculate this enthalpy of neutralization by using enthalpy of formation data in expression (7.21), but this requires us to have enthalpy of formation data for individual ions. And there is a slight problem in getting these. We cannot create ions of a single type in a chemical reaction. We always produce cations and anions simultaneously, as in the reaction of sodium and chlorine to produce Na^+ and Cl^- in NaCl. We must choose a particular ion to which we assign an enthalpy of formation of *zero* in its aqueous solutions. We then compare the enthalpies of formation of other ions to this reference ion. The ion we arbitrarily choose for our zero is $H^+(aq)$. Now let us see how we can use expression (7.21) and data from equation (7.22) to determine the enthalpy of formation of $OH^-(aq)$.

$$\Delta H^\circ = \{1\text{ mol H}_2\text{O} \times \Delta H_f^\circ[\text{H}_2\text{O(l)}] - 1\text{ mol H}^+ \times \Delta H_f^\circ[\text{H}^+\text{(aq)}]\} \\ -1\text{ mol OH}^- \times \Delta H_f^\circ[\text{OH}^-\text{(aq)}] = -55.8\text{ kJ}$$

$$\Delta H_f^\circ[\text{OH}^-\text{(aq)}] = \frac{55.8\text{ kJ} + (1\text{ mol H}_2\text{O} \times \Delta H_f^\circ[\text{H}_2\text{O(l)}]) - (1\text{ mol H}^+ \times \Delta H_f^\circ[\text{H}^+\text{(aq)}])}{1\text{ mol OH}^-}$$

$$\Delta H_f^\circ[\text{OH}^-\text{(aq)}] = \frac{55.8\text{ kJ} - 285.8\text{ kJ} - 0\text{ kJ}}{1\text{ mol OH}^-} = -230.0\text{ kJ/mol OH}^-$$

Table 7.3 lists data for several common ions in aqueous solution. Enthalpies of formation in solution depend on the solute concentration. These data are representative for *dilute* aqueous solutions (about 1 M), the type of solution that we normally deal with. Some of these data are used in Example 7-13.

TABLE 7.3 Some Standard Molar Enthalpies of Formation of Ions in Aqueous Solution at 298.15 K, ΔH_f°

Ion	kJ/mol	Ion	kJ/mol
H^+	0	OH^-	−230.0
Li^+	−278.5	Cl^-	−167.2
Na^+	−240.1	Br^-	−121.6
K^+	−252.4	I^-	−55.19
NH_4^+	−132.5	NO_3^-	−205.0
Ag^+	105.6	CO_3^{2-}	−677.1
Mg^{2+}	−466.9	S^{2-}	33.05
Ca^{2+}	−542.8	SO_4^{2-}	−909.3
Ba^{2+}	−537.6	$S_2O_3^{2-}$	−648.5
Cu^{2+}	64.77	PO_4^{3-}	−1277
Al^{3+}	−531		

EXAMPLE 7-13 Calculating the Enthalpy Change in an Ionic Reaction

Given that $\Delta H_f^\circ[\text{BaSO}_4\text{(s)}] = -1473$ kJ/mol, what is the standard enthalpy change for the precipitation of barium sulfate?

Analyze

First, write the net ionic equation for the reaction and introduce the relevant data. Then make use of equation (7.21).

Solve

Start by organizing the data in a table.

$$\begin{array}{llllll} & \text{Ba}^{2+}\text{(aq)} & + \ \text{SO}_4^{\,2-}\text{(aq)} & \longrightarrow & \text{BaSO}_4\text{(s)} & \Delta H^\circ = ? \\ \Delta H_f^\circ\text{, kJ/mol} & -537.6 & -909.3 & & -1473 & \end{array}$$

Then substitute data into equation (7.21).

$$\begin{aligned} \Delta H^\circ &= 1\text{ mol BaSO}_4 \times \Delta H_f^\circ[\text{BaSO}_4\text{(s)}] - 1\text{ mol Ba}^{2+} \times \Delta H_f^\circ[\text{Ba}^{2+}\text{(aq)}] - 1\text{ mol SO}_4^{\,2-} \times \Delta H_f^\circ[\text{SO}_4^{\,2-}\text{(aq)}] \\ &= 1\text{ mol BaSO}_4 \times (-1473\text{ kJ/mol BaSO}_4) - 1\text{ mol Ba}^{2+} \times (-537.6\text{ kJ/mol Ba}^{2+}) \\ &\quad - 1\text{ mol SO}_4^{\,2-} \times (-909.3\text{ kJ/mol SO}_4^{\,2-}) \\ &= -1473\text{ kJ} + 537.6\text{ kJ} + 909.3\text{ kJ} = -26\text{ kJ} \end{aligned}$$

Assess

The standard enthalpy of reaction determined here is the heat given off by the system (i.e., the ionic reaction).

PRACTICE EXAMPLE A: Given that $\Delta H_f^\circ[\text{AgI(s)}] = -61.84$ kJ/mol, what is the standard enthalpy change for the precipitation of silver iodide?

PRACTICE EXAMPLE B: The standard enthalpy change for the precipitation of Ag_2CO_3(s) is −39.9 kJ per mole of Ag_2CO_3(s) formed. What is $\Delta H_f^\circ[\text{Ag}_2\text{CO}_3\text{(s)}]$?

7-10 CONCEPT ASSESSMENT

Is it possible to calculate a heat of reaction at 373.15 K by using standard enthalpies of formation at 298.15 K? If so, explain how you would do this, and indicate any additional data you might need.

7-9 Fuels as Sources of Energy

One of the most important uses of thermochemical measurements and calculations is in assessing materials as energy sources. For the most part, these materials, called fuels, liberate heat through the process of combustion. We will briefly survey some common fuels, emphasizing matters that a thermochemical background helps us to understand.

Fossil Fuels

The bulk of current energy needs are met by petroleum, natural gas, and coal—so-called fossil fuels. These fuels are derived from plant and animal life of millions of years ago. The original source of the energy locked into these fuels is solar energy. In the process of *photosynthesis*, CO_2 and H_2O, in the presence of enzymes, the pigment chlorophyll, and sunlight, are converted to *carbohydrates*. These are compounds with formulas $C_m(H_2O)_n$, where m and n are integers. For example, in the sugar glucose $m = n = 6$, that is, $C_6(H_2O)_6 = C_6H_{12}O_6$. Its formation through photosynthesis is an *endothermic* process, represented as

◀ Although the formula $C_m(H_2O)_n$ suggests a "hydrate" of carbon, in carbohydrates, there are no H_2O units, as there are in hydrates, such as $CuSO_4 \cdot 5\,H_2O$. H and O atoms are simply found in the same numerical ratio as in H_2O.

$$6\,CO_2(g) + 6\,H_2O(l) \xrightarrow[\text{sunlight}]{\text{chlorophyll}} C_6H_{12}O_6(s) + 6\,O_2(g) \quad \Delta H° = +2.8 \times 10^3\ \text{kJ} \tag{7.23}$$

When reaction (7.23) is reversed, as in the combustion of glucose, heat is evolved. The combustion reaction is *exothermic*.

The complex carbohydrate cellulose, with molecular masses ranging up to 500,000 u, is the principal structural material of plants. When plant life decomposes in the presence of bacteria and out of contact with air, O and H atoms are removed and the approximate carbon content of the residue increases in the progression

$$\text{Peat} \longrightarrow \text{lignite (32\% C)} \longrightarrow \text{sub-bituminous coal (40\% C)} \longrightarrow$$
$$\text{bituminous coal (60\% C)} \longrightarrow \text{anthracite coal (80\% C)}$$

For this process to progress all the way to anthracite coal may take about 300 million years. Coal, then, is a combustible organic rock consisting of carbon, hydrogen, and oxygen, together with small quantities of nitrogen, sulfur, and mineral matter (ash). (One proposed formula for a "molecule" of bituminous coal is $C_{153}H_{115}N_3O_{13}S_2$.)

Petroleum and natural gas formed in a different way. The remains of plants and animals living in ancient seas fell to the ocean floor, where they were decomposed by bacteria and covered with sand and mud. Over time, the sand and mud were converted to sandstone by the weight of overlying layers of sand and mud. The high pressures and temperatures resulting from this overlying sandstone rock formation transformed the original organic matter into petroleum and natural gas. The ages of these deposits range from about 250 million to 500 million years.

A typical natural gas consists of about 85% methane (CH_4), 10% ethane (C_2H_6), 3% propane (C_3H_8), and small quantities of other combustible and noncombustible gases. A typical petroleum consists of several hundred different hydrocarbons that range in complexity from C_1 molecules (CH_4) to C_{40} or higher (such as $C_{40}H_{82}$).

TABLE 7.4 Approximate Heats of Combustion of Some Fuels

	Heat of Combustion
Fuel	kJ/g
Municipal waste	−12.7
Cellulose	−17.5
Pinewood	−21.2
Methanol	−22.7
Peat	−20.8
Bituminous coal	−28.3
Isooctane (a component of gasoline)	−47.8
Natural gas	−49.5

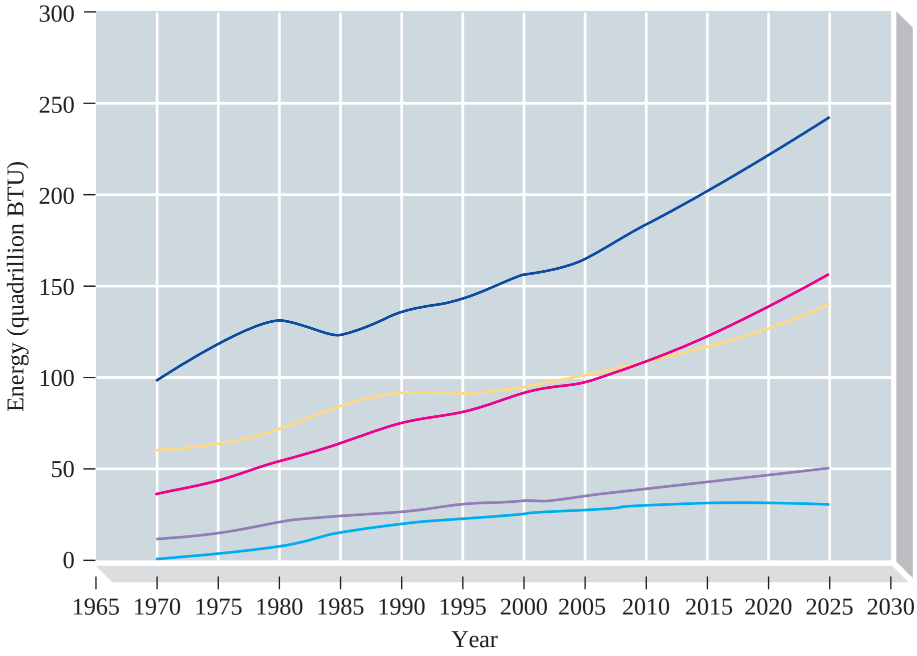
One way to compare different fuels is through their heats of combustion: In general, *the higher the heat of combustion, the better the fuel*. Table 7.4 lists approximate heats of combustion for the fossil fuels. These data show that *biomass* (living matter or materials derived from it—wood, alcohols, municipal waste) is a viable fuel, but that fossil fuels yield more energy per unit mass.

Problems Posed by Fossil Fuel Use There are two fundamental problems with the use of fossil fuels. First, fossil fuels are essentially *nonrenewable* energy sources. The world consumption of fossil fuels is expected to increase for the foreseeable future (Fig. 7-22), but when will Earth's supply of these fuels run out? There is currently a debate about whether oil production has peaked now and is about to decline, or whether it will peak more toward the middle of the this century. The second problem with fossil fuels is their environmental effect. Sulfur impurities in fuels produce oxides of sulfur. The high temperatures associated with combustion cause the reaction of N_2 and O_2 in air to form oxides of nitrogen. Oxides of sulfur and nitrogen are implicated in air pollution and are important contributors to the environmental problem known as acid rain. Another inevitable product of the combustion of fossil fuels is carbon dioxide, one of the "greenhouse" gases leading to *global warming* and potential changes in Earth's climate.

▶ Environmental issues associated with oxides of sulfur and nitrogen are discussed more fully in later chapters.

Global Warming—An Environmental Issue Involving Carbon Dioxide We do not normally think of CO_2 as an air pollutant because it is essentially nontoxic and is a natural and necessary component of air. Its ultimate effect on the environment, however, could be very significant. A buildup of $CO_2(g)$ in the atmosphere may disturb the energy balance on Earth.

Earth's atmosphere, discussed in Focus On 6 on the Mastering Chemistry website, is largely transparent to visible and UV radiation from the sun.

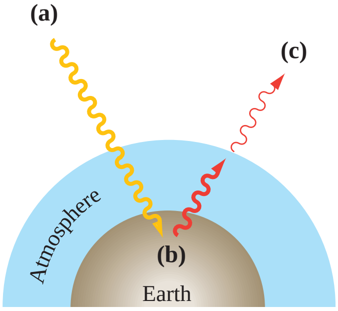


▲ FIGURE 7-22
World primary energy consumption by energy source
These graphs show the history of energy consumption since 1970, with predictions to 2025. Petroleum (dark blue line) is seen to be the major source of energy for the foreseeable future, followed by coal (yellow) and natural gas (pink), which are about the same. Other sources of energy included are wind power (purple) and nuclear power (light blue). The unit BTU is a measure of energy and stands for British thermal unit (see Exercise 95). [*Source: www.eia.doe.gov/oiaf/ieo/pdf/ieoreftab_2.pdf*]

This radiation is absorbed at Earth's surface, which is warmed by it. Some of this absorbed energy is reradiated as infrared radiation. Certain atmospheric gases, primarily CO_2, methane, and water vapor, absorb some of this infrared radiation, and the energy thus retained in the atmosphere produces a warming effect. This process, outlined in Figure 7-23, is often compared to the retention of thermal energy in a greenhouse and is called the "greenhouse effect."* The natural greenhouse effect is essential in maintaining the proper temperature for life on Earth. Without it, Earth would be permanently covered with ice.

Over the past 400,000 years, the atmospheric carbon dioxide concentration has varied from 180 to 300 parts per million with the preindustrial-age concentration at about 285 ppm. By 2005, the level had increased to about 376 ppm and is still rising (Fig. 7-24). Increasing atmospheric carbon dioxide concentrations result from the burning of carbon-containing fuels such as wood, coal, natural gas, and gasoline (Fig. 7-24) and from the deforestation of tropical regions (plants, through photosynthesis, consume CO_2 from the atmosphere). The expected effect of a CO_2 buildup is an increase in Earth's average temperature, a **global warming**. Some estimates are that a doubling of the CO_2 content over that of preindustrial times could occur before the end of the present century and that this doubling could produce an average global temperature increase of 1.5 to 4.5 °C.

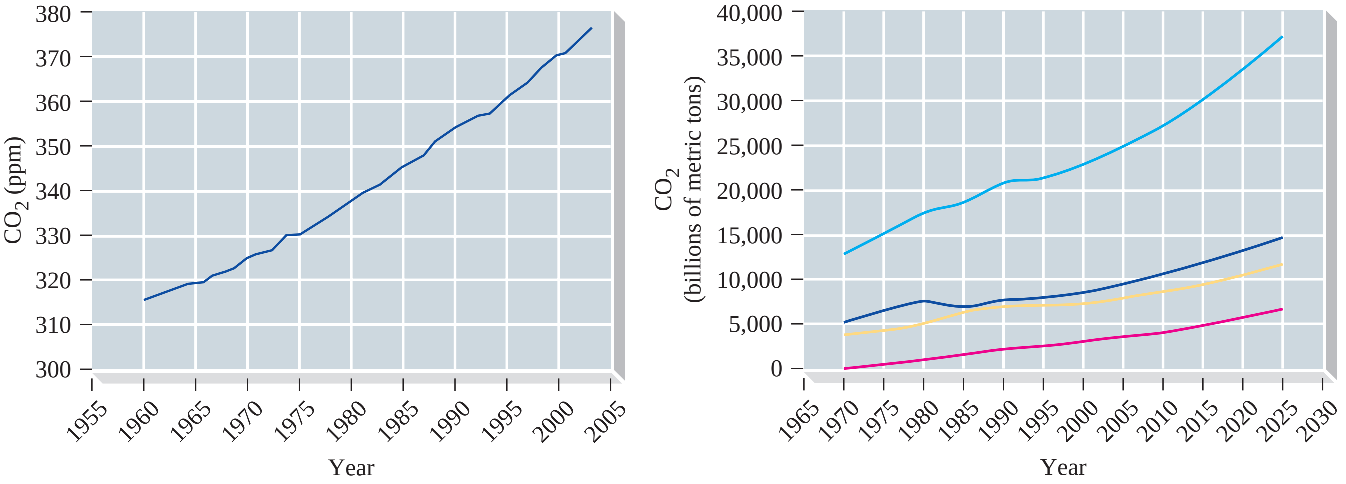
Predicting the probable effects of a CO_2 buildup in the atmosphere is done largely through computer models, and it is very difficult to know all the factors that should be included in these models and the relative importance of these factors. For example, global warming could lead to the increased evaporation of water and increased cloud formation. In turn, an increased cloud cover could reduce the amount of solar radiation reaching Earth's surface and, to some extent, offset global warming.



▲ FIGURE 7-23

The "greenhouse" effect

(a) Some incoming radiation from sunlight is reflected back into space by the atmosphere, and some, such as certain UV light, is absorbed by stratospheric ozone. Much of the radiation from sunlight, however, reaches Earth's surface. (b) Earth's surface re-emits some of this energy as infrared radiation. (c) Infrared radiation leaving Earth's atmosphere is less intense than that emitted by Earth's surface because some of this radiation is absorbed by CO_2 and other greenhouse gases and warms the atmosphere.



(a)

(b)

▲ FIGURE 7-24

Increasing carbon dioxide content of the atmosphere

(a) The global average atmospheric carbon dioxide level over a 50-year span, expressed in parts per million by volume, as measured by a worldwide cooperative sampling network. (b) The actual and predicted CO_2 emissions for a 55-year span due to the combustion of natural gas (pink line), coal (yellow), and petroleum (dark blue), together with the total of all CO_2 emissions (light blue). The CO_2 content of the atmosphere continues to increase, from approximately 375 ppm in 2003 to 385 ppm in 2008.

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*Glass, like CO_2, is transparent to visible and some UV light but absorbs infrared radiation. The glass in a greenhouse, though, acts primarily to prevent the bulk flow of warm air out of the greenhouse.

▲ An ice core from the ice sheet in Antarctica is cut into sections in a refrigerated clean room. The ice core is then analyzed to determine the amount and type of trapped gases and trace elements it contains. These data provide information regarding past changes in climate and current trends in the pollution of the atmosphere.

Some of the significant possible effects of global warming are

- local temperature changes. The average annual temperature for Alaska and Northern Canada has increased by 1.9 °C over the past 50 years. Alaskan winter temperatures have increased by an average of 3.5 °C over this same time period.
- a rise in sea level caused by the thermal expansion of seawater and increased melting of continental ice caps. A potential increase in sea level of up to 1 m by 2100 would displace tens of millions of inhabitants in Bangladesh alone.
- the migration of plant and animal species. Vegetation now characteristic of certain areas of the globe could migrate into regions several hundred kilometers closer to the poles. The areas in which diseases, such as malaria, are endemic could also expand.

Although some of the current thinking involves speculation, a growing body of evidence supports the likelihood of global warming, also called climate change. For example, analyses of tiny air bubbles trapped in the Antarctic ice cap show a strong correlation between the atmospheric CO_2 content and temperature for the past 160,000 years—low temperatures during periods of low CO_2 levels and higher temperatures with higher levels of CO_2.

CO_2 is not the only greenhouse gas. Several gases are even stronger infrared absorbers—specifically, methane (CH_4), ozone (O_3), nitrous oxide (N_2O), and chlorofluorocarbons (CFCs). Furthermore, atmospheric concentrations of some of these gases have been growing at a faster rate than that of CO_2. No strategies beyond curtailing the use of chlorofluorocarbons and fossil fuels have emerged for countering a possible global warming. Like several other major environmental issues, some aspects of climate change are not well understood, and research, debate, and action are all likely to occur simultaneously for a long time to come.

Coal and Other Energy Sources

In the United States, reserves of coal far exceed those of petroleum and natural gas. Despite this relative abundance, however, the use of coal has not increased significantly in recent years. In addition to the environmental effects cited above, the expense and hazards involved in the deep mining of coal are considerable. Surface mining, which is less hazardous and expensive than deep mining, is also more damaging to the environment. One promising possibility for using coal reserves is to convert coal to gaseous or liquid fuels, either in surface installations or while the coal is still underground.

Gasification of Coal

Before cheap natural gas became available in the 1940s, gas produced from coal (variously called producer gas, town gas, or city gas) was widely used in the United States. This gas was manufactured by passing steam and air through heated coal and involved such reactions as

$$\text{C(graphite)} + \text{H}_2\text{O(g)} \longrightarrow \text{CO(g)} + \text{H}_2\text{(g)} \qquad \Delta H^\circ = +131.3\ \text{kJ} \qquad \textbf{(7.24)}$$

$$\text{CO(g)} + \text{H}_2\text{O(g)} \longrightarrow \text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \qquad \Delta H^\circ = -41.2\ \text{kJ} \qquad \textbf{(7.25)}$$

$$2\text{C(graphite)} + \text{O}_2\text{(g)} \longrightarrow 2\,\text{CO(g)} \qquad \Delta H^\circ = -221.0\ \text{kJ} \qquad \textbf{(7.26)}$$

$$\text{C(graphite)} + 2\,\text{H}_2\text{(g)} \longrightarrow \text{CH}_4\text{(g)} \qquad \Delta H^\circ = -74.8\ \text{kJ} \qquad \textbf{(7.27)}$$

The principal gasification reaction (7.24) is highly endothermic. The heat requirements for this reaction are met by the carefully controlled partial burning of coal (reaction 7.26).

A typical producer gas consists of about 23% CO, 18% H_2, 8% CO_2, and 1% CH_4 by volume. It also contains about 50% N_2 because air is used in its production. Because the N_2 and CO_2 are noncombustible, producer gas has only about 10% to 15% of the heat value of natural gas. Modern gasification processes include several features:

1. They use $O_2(g)$ instead of air, thereby eliminating $N_2(g)$ in the product.
2. They provide for the removal of noncombustible $CO_2(g)$ and sulfur impurities. For example,

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$$
$$2\,H_2S(g) + SO_2(g) \longrightarrow 3\,S(s) + 2\,H_2O(g)$$

3. They include a step (called *methanation*) to convert CO and H_2, in the presence of a catalyst, to CH_4.

$$CO(g) + 3\,H_2(g) \xrightarrow{\text{catalyst}} CH_4(g) + H_2O(l)$$

The product is called *substitute natural gas* (SNG), a gaseous mixture with composition and heat value similar to that of natural gas.

Liquefaction of Coal The first step in obtaining liquid fuels from coal generally involves gasification of coal, as in reaction (7.24). This step is followed by catalytic reactions in which liquid hydrocarbons are formed.

$$n\,CO + (2n + 1)H_2 \longrightarrow C_nH_{2n+2} + n\,H_2O$$

In still another process, liquid methanol is formed.

$$CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(l) \qquad \textbf{(7.28)}$$

In 1942, some 32 million gallons of aviation fuel were made from coal in Germany. In South Africa, the Sasol process for coal liquefaction has been a major source of gasoline and a variety of other petroleum products and chemicals for more than 50 years.

Methanol

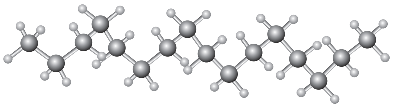
Methanol, CH_3OH, can be obtained from coal by reaction (7.28). It can also be produced by thermal decomposition (pyrolysis) of wood, manure, sewage, or municipal waste. The heat of combustion of methanol is only about one-half that of a typical gasoline on a mass basis, but methanol has a high octane number—106—compared with 100 for the gasoline hydrocarbon isooctane and about 92 for premium gasoline. Methanol has been tested and used as a fuel in internal combustion engines and is cleaner burning than gasoline. Methanol can also be used for space heating, electric power generation, fuel cells, and as a reactant to make a variety of other organic compounds.

Ethanol

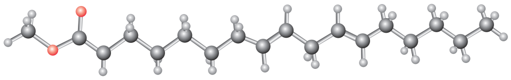
Ethanol, C_2H_5OH, is produced mostly from ethylene, C_2H_4, which in turn is derived from petroleum. Current interest centers on the production of ethanol by the fermentation of organic matter, a process known throughout recorded history. Ethanol production by fermentation is probably most advanced in Brazil, where sugarcane and cassava (manioc) are the plant matter (biomass) used. In the United States, corn-based ethanol is used chiefly as an additive to gasoline to improve its octane rating and reduce air pollution. Also, a 90% gasoline–10% ethanol mixture is used as an automotive fuel under the name *gasohol*.

Biofuels

Biofuels are renewable energy sources that are similar to fossil fuels. Biofuels are fuels derived from dead biological material, most commonly plants. Fossil fuels are derived from biological material that has been dead for a very long time. The use of biofuels is not new; several car inventors had envisioned their vehicles running on such fuels as peanut oil, hemp-derived fuel, and ethanol. Reacting vegetable oil with a base–alcohol mixture produces a compound commonly called a biodiesel. A typical petro–diesel compound is the hydrocarbon cetane ($C_{16}H_{34}$), and the typical biodiesel compound contains oxygen atoms, as illustrated in the figure below. The standard enthalpies of combustion of the petro–diesel and the biodiesel are very similar.



Cetane (liquid)
$\Delta H_f^\circ = -456.3 \text{ kJ mol}^{-1}$
$\Delta H_{comb}^\circ = -10699.1 \text{ kJ mol}^{-1}$



Linoleic acid methyl ester (liquid)
$\Delta H_f^\circ = -604.88 \text{ kJ mol}^{-1}$
$\Delta H_{comb}^\circ = -11690.1 \text{ kJ mol}^{-1}$

Although biofuels are appealing replacements for fossil fuels, their widespread adoption has several potential drawbacks. One major concern is the food-versus-fuel issue. Typical plants used for food (e.g., sugar cane) are sources of biofuels, which drives up the cost of food. A positive aspect of biofuels is that they are carbon neutral; that is, the $CO_2(g)$ produced by the burning of a biofuel is then used by plants for new growth, resulting in no net gain of carbon in the atmosphere. Biofuels and their use have many other advantages and disadvantages. Importantly, chemical knowledge of these compounds is needed to address these issues.

Hydrogen

Another fuel with great potential is hydrogen. Its most attractive features are that

- on a per gram basis, its heat of combustion is more than twice that of methane and about three times that of gasoline;
- the product of its combustion is H_2O, not CO and CO_2 as with gasoline.

Currently, the bulk of hydrogen used commercially is made from petroleum and natural gas, but for hydrogen to be a significant fuel of the future, efficient methods must be perfected for obtaining hydrogen from other sources, especially water. Alternative methods of producing hydrogen and the prospects of developing an economy based on hydrogen are discussed later in the text.

Alternative Energy Sources

Combustion reactions are only one means of extracting useful energy from materials. An alternative, for example, is to carry out reactions that yield the same products as combustion reactions in electrochemical cells called *fuel cells*. The energy is released as electricity rather than as heat (see Section 20-5). Solar energy can be used directly, without recourse to photosynthesis. Nuclear processes can be used in place of chemical reactions (Chapter 25). Other alternative sources in various stages of development and use include hydroelectric energy, geothermal energy, and tidal and wind power.

MasteringCHEMISTRY www.masteringchemistry.com.

For a discussion of Fats, Carbohydrates, and Energy Storage, go to Focus On 7-1 on the MasteringChemistry site.

Summary

7-1 Getting Started: Some Terminology—The subject of a thermochemical study is broken down into the **system** of interest and the portions of the universe with which the system may interact, the **surroundings**. An **open system** can exchange both energy and matter with its surroundings. A **closed system** can exchange only energy and not matter. An **isolated system** can exchange neither energy nor matter with its surroundings (Fig. 7-1). **Energy** is the capacity to do work, and **work** is performed when a force acts through a distance. Energy can be further characterized (Fig. 7-2) as **kinetic energy** (energy associated with matter in motion) or **potential energy** (energy resulting from the position or composition of matter). Kinetic energy associated with random molecular motion is sometimes called **thermal energy**.

7-2 Heat—**Heat** is energy transferred between a system and its surroundings as a result of a temperature difference between the two. In some cases, heat can be transferred at constant temperature, as in a change in state of matter in the system. A quantity of heat is the product of the heat capacity of the system and the temperature change (equation 7.5). In turn, **heat capacity** is the product of mass and **specific heat**, the amount of heat required to change the temperature of one gram of substance by one degree Celsius. Historically, the unit for measuring heat has been the **calorie** (**cal**), but the SI unit of heat is the joule, the same as for other forms of energy (equation 7.2). Energy transfers between a system and its surroundings must conform to the **law of conservation of energy**, meaning that all heat lost by a system is gained by its surroundings (equation 7.6).

7-3 Heats of Reaction and Calorimetry—In a chemical reaction, a change in the **chemical energy** associated with the reactants and products may appear as heat. The **heat of reaction** is the quantity of heat exchanged between a system and its surroundings when the reaction occurs at a constant temperature. In an **exothermic reaction**, heat is given off by the system; in an **endothermic reaction** the system absorbs heat. Heats of reaction are determined in a **calorimeter**, a device for measuring quantities of heat (equation 7.10). Exothermic combustion reactions are usually studied in a **bomb calorimeter** (Fig. 7-5). A common type of calorimeter used in the general chemistry laboratory is constructed from ordinary Styrofoam cups (Fig. 7-6).

7-4 Work—In some reactions an energy transfer between a system and its surroundings occurs as work. This is commonly the work involved in the expansion or compression of gases (Fig. 7-8) and is called **pressure–volume work** (equation 7.11).

7-5 The First Law of Thermodynamics—**Internal energy** (U) is the total energy (both kinetic and potential) in a system. The **first law of thermodynamics** relates changes in the internal energy of a system (ΔU) to the quantities of heat (q) and work (w) exchanged between the system and its surroundings. The relationship is $\Delta U = q + w$ (equation 7.12) and requires that a set of sign conventions be consistently followed. A **function of state** (**state function**) has a value that depends only on the exact condition or state in which a system is found and not on how that state was reached. Internal energy is a state function. A path-dependent function, such as heat or work, depends on how a change in a system is achieved. A change that is accomplished through an infinite number of infinitesimal steps is a **reversible process** (Fig. 7-12), whereas a change accomplished in one step or a series of finite steps is **irreversible**.

7-6 Heats of Reaction: Δ*U* and Δ*H*—In a chemical reaction with work limited to pressure–volume work and conducted at constant volume, the heat of reaction is equal to the change in internal energy (equation 7.13). For reactions at constant pressure a more useful function is **enthalpy** (H), defined as the internal energy (U) of a system plus the pressure–volume product $(P - V)$. The **enthalpy change** (ΔH) in a reaction proves to be the heat of reaction at constant pressure (equation 7.14). Most heats of reaction are reported as ΔH values. A substance under a pressure of 1 bar $(10^5\ \text{Pa})$ and at the temperature of interest is said to be in its **standard state**. If the reactants and products of a reaction are in their standard states, the enthalpy change in a reaction is called the **standard enthalpy of reaction** and designated as $\Delta H°$. Enthalpy changes can be represented schematically through **enthalpy diagrams** (Fig. 7-15).

7-7 Indirect Determination of Δ*H*: Hess's Law—Often an unknown ΔH value can be established indirectly through **Hess's law**, which states that an overall enthalpy change is the sum of the enthalpy changes of the individual steps leading to the overall process (Fig. 7-17).

7-8 Standard Enthalpies of Formation—By arbitrarily assigning an enthalpy of zero to the reference forms of the elements in their standard states, the enthalpy change in the formation of a compound from its elements becomes a **standard enthalpy of formation** (ΔH_f°). Using tabulated standard enthalpies of formation (Table 7.2), it is possible to calculate standard enthalpies of reactions without having to perform additional experiments (equation 7.21).

7-9 Fuels as Sources of Energy—One of the chief applications of thermochemistry is in the study of the combustion of fuels as energy sources. Currently, the principal fuels are the fossil fuels, but potential alternative fuels are also mentioned in this chapter and discussed in more depth later in the text. One of the problems with the use of fossil fuels is the potential for **global warming**.

Integrative Example

When charcoal is burned in a limited supply of oxygen in the presence of H_2O, a mixture of CO, H_2, and other noncombustible gases (mostly CO_2) is obtained. Such a mixture is called *synthesis gas*. This gas can be used to synthesize organic compounds, or it can be burned as a fuel. A typical synthesis gas consists of 55.0% CO(g), 33.0% H_2(g), and 12.0% noncombustible gases (mostly CO_2), *by volume*. To what temperature can 25.0 kg water at 25.0 °C be heated with the heat liberated by the combustion of 0.205 m^3 of this typical synthesis gas, measured at 25.0 °C and 102.6 kPa pressure?

Analyze

First, use the ideal gas equation to calculate the total number of moles of gas, and then use equation (6.17) to establish the number of moles of each combustible gas. Next, write an equation for the combustion of each gas. Use these equations and enthalpy of formation data to calculate the total amount of heat released by the combustion. Finally, use equation (7.5) to calculate the temperature increase when this quantity of heat is absorbed by the 25.0 kg of water. The final water temperature is then easily established.

Solve

Substitute the applicable data into the ideal gas equation using SI units, with $R = 8.3145\ \mathrm{m^3\ Pa\ mol^{-1}\ K^{-1}}$. Solve for n.

$$n = \frac{PV}{RT} = \frac{102.6\ \mathrm{kPa} \times 1000\ \mathrm{Pa}/1\ \mathrm{kPa} \times 0.205\ \mathrm{m^3}}{8.3145\ \mathrm{m^3\ Pa\ mol^{-1}\ K^{-1}} \times 298.2\ \mathrm{K}}$$
$$= 8.48\ \text{mol gas}$$

Now, apportion the 8.48 moles among the three gases present, converting the volume percents to mole fractions and using equation (6.17).

$$n_{CO} = n_{tot} \times x_{CO} = 8.48\ \mathrm{mol} \times 0.550 = 4.66\ \mathrm{mol\ CO}$$
$$n_{H_2} = n_{tot} \times x_{H_2} = 8.48\ \mathrm{mol} \times 0.330 = 2.80\ \mathrm{mol\ H_2}$$

(remaining gas noncombustible)

Write an equation for the combustion of CO(g), list ΔH_f° data beneath the equation, and determine ΔH°_{comb} per mole of CO(g).

$$\mathrm{CO(g)} + \frac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)}$$

ΔH_f°: −110.5 kJ/mol −393.5 kJ/mol

$$\Delta H^\circ_{comb} = 1\ \mathrm{mol\ CO_2} \times (-393.5\ \mathrm{kJ/mol\ CO_2}) - 1\ \mathrm{mol\ CO} \times (-110.5\ \mathrm{kJ/mol\ CO})$$
$$= -283.0\ \mathrm{kJ}$$

Write another equation for the combustion of H_2(g), again listing ΔH_f° data beneath the equation, and determining ΔH°_{comb} per mole of H_2(g).

$$\mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{H_2O(l)}$$

ΔH_f°: 0 kJ/mol −285.8 kJ/mol

$$\Delta H^\circ_{comb} = 1\ \mathrm{mol\ H_2O} \times (-285.8\ \mathrm{kJ/mol\ H_2O}) = -285.8\ \mathrm{kJ}$$

Determine the total heat released in the combustion of the amounts of CO and H_2 in the 0.205 m^3 of gas.

$$4.66\ \mathrm{mol\ CO} \times (-283.0\ \mathrm{kJ/mol\ CO}) + 2.80\ \mathrm{mol\ H_2} \times (-285.8\ \mathrm{kJ/mol\ H_2})$$
$$= -2.12 \times 10^3\ \mathrm{kJ}$$

The quantity of heat absorbed by the 25.0 kg of water is

$$q_{water} = -q_{comb}$$
$$= -\left(-2.12 \times 10^3\ \mathrm{kJ} \times \frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}}\right) = 2.12 \times 10^6\ \mathrm{J}$$

Rearrange equation (7.6) to solve for the temperature change in the 2.50×10^4 g (25.0 kg) of water.

$$\Delta T = \frac{q_{water}}{\text{mass water} \times \text{sp ht water}}$$

$$\Delta T = \frac{2.12 \times 10^6\ \mathrm{J}}{\left(2.50 \times 10^4\ \mathrm{g\ H_2O} \times \dfrac{4.18\ \mathrm{J}}{\mathrm{g\ H_2O\,^\circ C}}\right)} = 20.3\ ^\circ\mathrm{C}$$

From the initial temperature and the temperature change, determine the final temperature.

$$T_f = T_i + \Delta T = 25.0\ ^\circ\mathrm{C} + 20.3\ ^\circ\mathrm{C} = 45.3\ ^\circ\mathrm{C}$$

Assess

The assumption that the gas sample obeys the ideal gas law is probably valid since the temperature of the gas (25.0 °C) is not particularly low and the gas pressure, about 1 atm, is not particularly high. However, the implicit assumption that all the heat of combustion could be transferred to the water was probably not valid. If the transfer were to occur in an ordinary gas-fired water heater, some of the heat would undoubtedly be lost through the exhaust vent. Thus, our calculation was of the highest temperature that could possibly be attained. Note that in using the ideal gas equation the simplest approach was to work with SI units because those were the units of the data that were given.

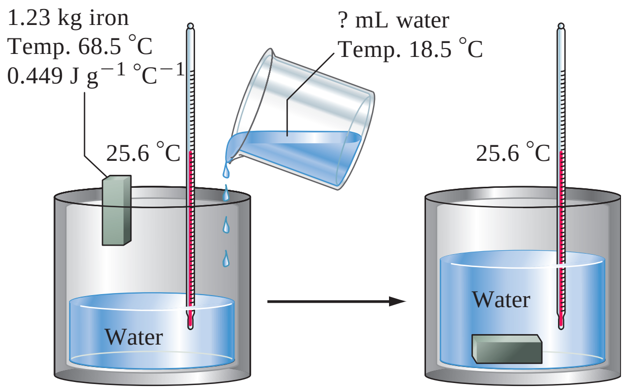
PRACTICE EXAMPLE A: The enthalpy of combustion for 1-hexadecene, $C_{16}H_{32}$, is $-10539.0\ \text{kJ mol}^{-1}$, and that of hexadecane, $C_{16}H_{34}$, is $-10699.1\ \text{kJ mol}^{-1}$. What is the enthalpy of hydrogenation of 1-hexadecene to hexadecane?

PRACTICE EXAMPLE B: A chemist mixes 56 grams of CaO, powdered lime, with 100 mL of water at 20 °C. After the completion of the reaction, $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$, what are the contents of the reaction vessel? [*Hint:* Assume that the heat released by the reaction is absorbed by the water.]

Exercises

Heat Capacity (Specific Heat)

1. Calculate the quantity of heat, in kilojoules, **(a)** required to raise the temperature of 9.25 L of water from 22.0 to 29.4 °C; **(b)** associated with a 33.5 °C decrease in temperature in a 5.85 kg aluminum bar (specific heat of aluminum $= 0.903\ \text{J g}^{-1}\,^{\circ}\text{C}^{-1}$).
2. Calculate the final temperature that results when **(a)** a 12.6 g sample of water at 22.9 °C absorbs 875 J of heat; **(b)** a 1.59 kg sample of platinum at 78.2 °C gives off 1.05 kcal of heat (sp ht of Pt $= 0.032\ \text{cal g}^{-1}\,^{\circ}\text{C}^{-1}$).
3. Refer to Example 7-2. The experiment is repeated with several different metals substituting for the lead. The masses of metal and water and the initial temperatures of the metal and water are the same as in Figure 7-3. The final temperatures are **(a)** Zn, 38.9 °C; **(b)** Pt, 28.8 °C; **(c)** Al, 52.7 °C. What is the specific heat of each metal, expressed in $\text{J g}^{-1}\,^{\circ}\text{C}^{-1}$?
4. A 75.0 g piece of Ag metal is heated to 80.0 °C and dropped into 50.0 g of water at 23.2 °C. The final temperature of the $Ag{-}H_2O$ mixture is 27.6 °C. What is the specific heat of silver?
5. A 465 g chunk of iron is removed from an oven and plunged into 375 g water in an insulated container. The temperature of the water increases from 26 to 87 °C. If the specific heat of iron is $0.449\ \text{J g}^{-1}\,^{\circ}\text{C}^{-1}$, what must have been the original temperature of the iron?
6. A piece of stainless steel (sp ht $= 0.50\ \text{J g}^{-1}\,^{\circ}\text{C}^{-1}$) is transferred from an oven at 183 °C into 125 mL of water at 23.2 °C. The water temperature rises to 51.5 °C. What is the mass of the steel? How precise is this method of mass determination? Explain.
7. A 1.00 kg sample of magnesium at 40.0 °C is added to 1.00 L of water maintained at 20.0 °C in an insulated container. What will be the final temperature of the $Mg{-}H_2O$ mixture (specific heat of Mg $= 1.024\ \text{J g}^{-1}\,^{\circ}\text{C}^{-1}$)?
8. Brass has a density of $8.40\ \text{g/cm}^3$ and a specific heat of $0.385\ \text{J g}^{-1}\,^{\circ}\text{C}^{-1}$. A $15.2\ \text{cm}^3$ piece of brass at an initial temperature of 163 °C is dropped into an insulated container with 150.0 g water initially at 22.4 °C. What will be the final temperature of the brass–water mixture?
9. A 74.8 g sample of copper at 143.2 °C is added to an insulated vessel containing 165 mL of glycerol, $C_3H_8O_3(l)$ ($d = 1.26\ \text{g/mL}$), at 24.8 °C. The final temperature is 31.1°C. The specific heat of copper is $0.385\ \text{J g}^{-1}\,^{\circ}\text{C}^{-1}$. What is the heat capacity of glycerol in $\text{J mol}^{-1}\,^{\circ}\text{C}^{-1}$?
10. What volume of 18.5 °C water must be added, together with a 1.23 kg piece of iron at 68.5 °C, so that the temperature of the water in the insulated container shown in the figure remains constant at 25.6 °C?



11. In the form of heat, 6.052 J of energy is transferred to a 1.0 L sample of air ($d = 1.204\ \text{mg/cm}^3$) at 20.0 °C. The final temperature of the air is 25.0 °C. What is the heat capacity of air in J/K?

12. What is the final temperature (in °C) of 1.24 g of water with an initial temperature of 20.0 °C after 6.052 J of heat is added to it?

Heats of Reaction

13. How much heat, in kilojoules, is associated with the production of 283 kg of slaked lime, $Ca(OH)_2$?

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) \qquad \Delta H^\circ = -65.2\ \text{kJ}$$

14. The standard enthalpy change in the combustion of the hydrocarbon octane is $\Delta H^\circ = -5.48 \times 10^3\ \text{kJ/mol}$ $C_8H_{18}(l)$. How much heat, in kilojoules, is liberated *per gallon* of octane burned? (Density of octane = 0.703 g/mL; 1 gal = 3.785 L.)

15. How much heat, in kilojoules, is evolved in the complete combustion of **(a)** 1.325 g $C_4H_{10}(g)$ at 25 °C and 1 atm; **(b)** 28.4 L $C_4H_{10}(g)$ at STP; **(c)** 12.6 L $C_4H_{10}(g)$ at 23.6 °C and 738 mmHg? Assume that the enthalpy change for the reaction does not change significantly with temperature or pressure. The complete combustion of butane, $C_4H_{10}(g)$, is represented by the equation

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4\,CO_2(g) + 5\,H_2O(l) \qquad \Delta H^\circ = -2877\ \text{kJ}$$

16. Upon complete combustion, the indicated substances evolve the given quantities of heat. Write a balanced equation for the combustion of 1.00 mol of each substance, including the enthalpy change, ΔH, for the reaction.
(a) 0.584 g of propane, $C_3H_8(g)$, yields 29.4 kJ
(b) 0.136 g of camphor, $C_{10}H_{16}O(s)$, yields 5.27 kJ
(c) 2.35 mL of acetone, $(CH_3)_2CO(l)$ ($d = 0.791$ g/mL), yields 58.3 kJ

17. The combustion of methane gas, the principal constituent of natural gas, is represented by the equation

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H^\circ = -890.3\ \text{kJ}$$

(a) What mass of methane, in kilograms, must be burned to liberate 2.80×10^7 kJ of heat?
(b) What quantity of heat, in kilojoules, is liberated in the complete combustion of 1.65×10^4 L of $CH_4(g)$, measured at 18.6 °C and 768 mmHg?
(c) If the quantity of heat calculated in part **(b)** could be transferred with 100% efficiency to water, what volume of water, in liters, could be heated from 8.8 to 60.0 °C as a result?

18. Refer to the Integrative Example. What volume of the synthesis gas, measured at STP and burned in an open flame (constant-pressure process), is required to heat 40.0 gal of water from 15.2 to 65.0 °C? (1 gal = 3.785 L.)

19. The combustion of hydrogen–oxygen mixtures is used to produce very high temperatures (approximately 2500 °C) needed for certain types of welding operations. Consider the reaction to be

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H^\circ = -241.8\ \text{kJ}$$

What is the quantity of heat evolved, in kilojoules, when a 180 g mixture containing equal parts of H_2 and O_2 by mass is burned?

20. Thermite mixtures are used for certain types of welding, and the thermite reaction is highly exothermic.

$$Fe_2O_3(s) + 2\,Al(s) \longrightarrow Al_2O_3(s) + 2\,Fe(s) \qquad \Delta H^\circ = -852\ \text{kJ}$$

1.00 mol of granular Fe_2O_3 and 2.00 mol of granular Al are mixed at room temperature (25 °C), and a reaction is initiated. The liberated heat is retained within the products, whose combined specific heat over a broad temperature range is about $0.8\ \text{J g}^{-1}\,{}^\circ\text{C}^{-1}$. (The melting point of iron is 1530 °C.) Show that the quantity of heat liberated is more than sufficient to raise the temperature of the products to the melting point of iron.

21. A 0.205 g pellet of potassium hydroxide, KOH, is added to 55.9 g water in a Styrofoam coffee cup. The water temperature rises from 23.5 to 24.4 °C. [Assume that the specific heat of dilute KOH(aq) is the same as that of water.]
(a) What is the approximate heat of solution of KOH, expressed as kilojoules per mole of KOH?
(b) How could the precision of this measurement be improved *without* modifying the apparatus?

22. The heat of solution of KI(s) in water is +20.3 kJ/mol KI. If a quantity of KI is added to sufficient water at 23.5 °C in a Styrofoam cup to produce 150.0 mL of 2.50 M KI, what will be the final temperature? (Assume a density of 1.30 g/mL and a specific heat of $2.7\ \text{J g}^{-1}\,{}^\circ\text{C}^{-1}$ for 2.50 M KI.)

23. You are planning a lecture demonstration to illustrate an endothermic process. You want to lower the temperature of 1400 mL water in an insulated container from 25 to 10 °C. Approximately what mass of $NH_4Cl(s)$ should you dissolve in the water to achieve this result? The heat of solution of NH_4Cl is +14.7 kJ/mol NH_4Cl.

24. Care must be taken in preparing solutions of solutes that liberate heat on dissolving. The heat of solution of NaOH is −44.5 kJ/mol NaOH. To what maximum temperature may a sample of water, originally at 21 °C, be raised in the preparation of 500 mL of 7.0 M NaOH? Assume the solution has a density of 1.08 g/mL and specific heat of $4.00\ \text{J g}^{-1}\,{}^\circ\text{C}^{-1}$.

25. Refer to Example 7-4. The product of the neutralization is 0.500 M NaCl. For this solution, assume a density of 1.02 g/mL and a specific heat of $4.02\ \text{J g}^{-1}\,{}^\circ\text{C}^{-1}$. Also, assume a heat capacity for the Styrofoam cup of 10 J/°C, and recalculate the heat of neutralization.

26. The heat of neutralization of HCl(aq) by NaOH(aq) is −55.84 kJ/mol H_2O produced. If 50.00 mL of 1.05 M NaOH is added to 25.00 mL of 1.86 M HCl, with both solutions originally at 24.72 °C, what will be the final solution temperature? (Assume that no heat is lost to the surrounding air and that the solution produced in the neutralization reaction has a density of 1.02 g/mL and a specific heat of $3.98\ \text{J g}^{-1}\,{}^\circ\text{C}^{-1}$.)

27. Acetylene (C_2H_2) torches are used in welding. How much heat (in kJ) evolves when 5.0 L of C_2H_2 ($d = 1.0967\ \mathrm{kg/m^3}$) is mixed with a stoichiometric amount of oxygen gas? The combustion reaction is

$$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l) \qquad \Delta H° = -1299.5\ \mathrm{kJ}$$

28. Propane (C_3H_8) gas ($d = 1.83\ \mathrm{kg/m^3}$) is used in most gas grills. What volume (in liters) of propane is needed to generate 273.8 kJ of heat?

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H° = -2219.9\ \mathrm{kJ}$$

Enthalpy Changes and States of Matter

29. What mass of ice can be melted with the same quantity of heat as required to raise the temperature of 3.50 mol $H_2O(l)$ by 50.0 °C? [$\Delta H°_{\mathrm{fusion}} = 6.01\ \mathrm{kJ/mol}\ H_2O(s)$]

30. What will be the final temperature of the water in an insulated container as the result of passing 5.00 g of steam [$H_2O(g)$] at 100.0 °C into 100.0 g of water at 25.0 °C? ($\Delta H°_{\mathrm{vap}} = 40.6\ \mathrm{kJ/mol}\ H_2O$)

31. A 125-g stainless steel ball bearing (sp ht = $0.50\ \mathrm{J\,g^{-1}\,°C^{-1}}$) at 525 °C is dropped into 75.0 mL of water at 28.5 °C in an open Styrofoam cup. As a result, the water is brought to a boil when the temperature reaches 100.0 °C. What mass of water vaporizes while the boiling continues? ($\Delta H°_{\mathrm{vap}} = 40.6\ \mathrm{kJ/mol}\ H_2O$)

32. If the ball bearing described in Exercise 27 is dropped onto a large block of ice at 0 °C, what mass of liquid water will form? ($\Delta H°_{\mathrm{fusion}} = 6.01\ \mathrm{kJ/mol}\ H_2O(s)$)

33. The enthalpy of sublimation (solid → gas) for dry ice (i.e., CO_2) is $\Delta H°_{\mathrm{sub}} = 571\ \mathrm{kJ/kg}$ at −78.5 °C. If 125.0 J of heat is transferred to a block of dry ice that is −78.5°C, what volume of CO_2 gas ($d = 1.98\ \mathrm{g/L}$) will be generated?

34. Enthalpy of vaporization for $N_2(l)$ is 5.56 kJ/mol. How much heat (in J) is required to vaporize 1.0 L of $N_2(l)$ at 77.36 K and 1.0 atm?

Calorimetry

35. A sample gives off 5228 cal when burned in a bomb calorimeter. The temperature of the calorimeter assembly increases by 4.39 °C. Calculate the heat capacity of the calorimeter, in kilojoules per degree Celsius.

36. The following substances undergo complete combustion in a bomb calorimeter. The calorimeter assembly has a heat capacity of 5.136 kJ/°C. In each case, what is the final temperature if the initial water temperature is 22.43 °C?
(a) 0.3268 g caffeine, $C_8H_{10}O_2N_4$ (heat of combustion = −1014.2 kcal/mol caffeine);
(b) 1.35 ml of methyl ethyl ketone, $C_4H_8O(l)$, $d = 0.805\ \mathrm{g/mL}$ (heat of combustion = −2444 kJ/mol methyl ethyl ketone).

37. A bomb calorimetry experiment is performed with xylose, $C_5H_{10}O_5(s)$, as the combustible substance. The data obtained are

mass of xylose burned:	1.183 g
heat capacity of calorimeter:	4.728 kJ/°C
initial calorimeter temperature:	23.29 °C
final calorimeter temperature:	27.19 °C

(a) What is the heat of combustion of xylose, in kilojoules per mole? **(b)** Write the chemical equation for the complete combustion of xylose, and represent the value of ΔH in this equation. (Assume for this reaction that $\Delta U \approx \Delta H$.)

38. A coffee-cup calorimeter contains 100.0 mL of 0.300 M HCl at 20.3 °C. When 1.82 g Zn(s) is added, the temperature rises to 30.5 °C. What is the heat of reaction per mol Zn? Make the same assumptions as in Example 7-4, and also assume that there is no heat lost with the $H_2(g)$ that escapes.

$$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

39. A 0.75 g sample of KCl is added to 35.0 g H_2O in a Styrofoam cup and stirred until it dissolves. The temperature of the solution drops from 24.8 to 23.6 °C. **(a)** Is the process endothermic or exothermic? **(b)** What is the heat of solution of KCl expressed in kilojoules per mole of KCl?

40. The heat of solution of potassium acetate in water is $-15.3\ \mathrm{kJ/mol}\ KC_2H_3O_2$. What will be the final temperature when 0.136 mol $KC_2H_3O_2$ is dissolved in 525 mL water that is initially at 25.1 °C?

41. A 1.620 g sample of naphthalene, $C_{10}H_8(s)$, is completely burned in a bomb calorimeter assembly and a temperature increase of 8.44 °C is noted. If the heat of combustion of naphthalene is $-5156\ \mathrm{kJ/mol}\ C_{10}H_8$, what is the heat capacity of the bomb calorimeter?

42. Salicylic acid, $C_7H_6O_3$, has been suggested as a calorimetric standard. Its heat of combustion is $-3.023 \times 10^3\ \mathrm{kJ/mol}\ C_7H_6O_3$. From the following data determine the heat capacity of a bomb calorimeter assembly (that is, the bomb, water, stirrer, thermometer, wires, and so forth).

mass of salicylic acid burned:	1.201 g
initial calorimeter temperature:	23.68°C
final calorimeter temperature:	29.82°C

43. Refer to Example 7-3. Based on the heat of combustion of sucrose established in the example, what should be the temperature change (ΔT) produced by the combustion of 1.227 g $C_{12}H_{22}O_{11}$ in a bomb calorimeter assembly with a heat capacity of 3.87 kJ/°C?

44. A 1.397 g sample of thymol, $C_{10}H_{14}O(s)$ (a preservative and a mold and mildew preventative), is burned in a bomb calorimeter assembly. The temperature increase is 11.23 °C, and the heat capacity of the bomb calorimeter is 4.68 kJ/°C. What is the heat of combustion of thymol, expressed in kilojoules per mole of $C_{10}H_{14}O$?

45. A 5.0 g sample of NaCl is added to a Styrofoam cup of water, and the change in water temperature is 5.0 °C. The heat of solution of NaCl is 3.76 kJ/mol. What is the mass (in g) of water in the Styrofoam cup?

46. We can determine the purity of solid materials by using calorimetry. A gold ring (for pure gold, specific heat $= 0.1291\ \mathrm{J\ g^{-1}\ K^{-1}}$) with mass of 10.5 g is heated to 78.3 °C and immersed in 50.0 g of 23.7 °C water in a constant-pressure calorimeter. The final temperature of the water is 31.0 °C. Is this a pure sample of gold?

Pressure–Volume Work

47. Calculate the quantity of work associated with a 3.5 L expansion of a gas (ΔV) against a pressure of 748 mmHg in the units **(a)** liter atmospheres (L atm); **(b)** joules (J); **(c)** calories (cal).

48. Calculate the quantity of work, in joules, associated with the compression of a gas from 5.62 L to 3.37 L by a constant pressure of 1.23 atm.

49. A 1.00 g sample of Ne(g) at 1 atm pressure and 27 °C is allowed to expand into an *evacuated* vessel of 2.50 L volume. Does the gas do work? Explain.

50. Compressed air in aerosol cans is used to free electronic equipment of dust. Does the air do any work as it escapes from the can?

51. In each of the following processes, is any work done when the reaction is carried out at constant pressure in a vessel open to the atmosphere? If so, is work done by the reacting system or on it? **(a)** Neutralization of $Ba(OH)_2(aq)$ by HCl(aq); **(b)** conversion of gaseous nitrogen dioxide to gaseous dinitrogen tetroxide; **(c)** decomposition of calcium carbonate to calcium oxide and carbon dioxide gas.

52. In each of the following processes, is any work done when the reaction is carried out at constant pressure in a vessel open to the atmosphere? If so, is work done by the reacting system or on it? **(a)** Reaction of nitrogen monoxide and oxygen gases to form gaseous nitrogen dioxide; **(b)** precipitation of magnesium hydroxide by the reaction of aqueous solutions of NaOH and $MgCl_2$; **(c)** reaction of copper(II) sulfate and water vapor to form copper(II) sulfate pentahydrate.

53. If 325 J of work is done by a system at a pressure of 1.0 atm and 298 K, what is the change in the volume of the system?

54. A movable cylinder containing 5.0 L of nitrogen gas is used to lift a 1.23 kg object to a height of 4.5 meters. How much work (in J) was done by the gas?

First Law of Thermodynamics

55. What is the change in internal energy of a system if the system **(a)** absorbs 58 J of heat and does 58 J of work; **(b)** absorbs 125 J of heat and does 687 J of work; **(c)** evolves 280 cal of heat and has 1.25 kJ of work done on it?

56. What is the change in internal energy of a system if the *surroundings* **(a)** transfer 235 J of heat and 128 J of work to the system; **(b)** absorb 145 J of heat from the system while doing 98 J of work on the system; **(c)** exchange no heat, but receive 1.07 kJ of work from the system?

57. The internal energy of a fixed quantity of an ideal gas depends only on its temperature. A sample of an ideal gas is allowed to expand at a constant temperature (isothermal expansion). **(a)** Does the gas do work? **(b)** Does the gas exchange heat with its surroundings? **(c)** What happens to the temperature of the gas? **(d)** What is ΔU for the gas?

58. In an *adiabatic* process, a system is thermally insulated—there is no exchange of heat between system and surroundings. For the adiabatic expansion of an ideal gas **(a)** does the gas do work? **(b)** Does the internal energy of the gas increase, decrease, or remain constant? **(c)** What happens to the temperature of the gas? [*Hint*: Refer to Exercise 57.]

59. Do you think the following observation is in any way possible? An ideal gas is expanded isothermally and is observed to do twice as much work as the heat absorbed from its surroundings. Explain your answer. [*Hint:* Refer to Exercises 57 and 58.]

60. Do you think the following observation is any way possible? A gas absorbs heat from its surroundings while being compressed. Explain your answer. [*Hint:* Refer to Exercises 55 and 56.]

61. There are other forms of work besides P–V work. For example, electrical work is defined as the potential × change in charge, $w = \phi\, dq$. If a charge in a system is changed from 10 C to 5 C in a potential of 100 V and 45 J of heat is liberated, what is the change in the internal energy?

62. Another form of work is extension, defined as the tension × change in length, $w = f\,\Delta l$. A piece of DNA has an approximate tension of $f = 10$ pN. What is the change in the internal energy of the adiabatic stretching of DNA by 10 pm?

Relating ΔH and ΔU

63. Only one of the following expressions holds true for the heat of a chemical reaction, *regardless of how the reaction is carried out.* Which is the correct expression and why? **(a)** q_V; **(b)** q_P; **(c)** $\Delta U - w$; **(d)** ΔU; **(e)** ΔH.

64. Determine whether ΔH is equal to, greater than, or less than ΔU for the following reactions. Keep in mind that "greater than" means more positive or less negative, and "less than" means less positive or more negative. Assume that the only significant change in volume during a reaction at constant pressure is that associated with changes in the amounts of gases.

(a) The complete combustion of one mole of 1-butanol(l).

(b) The complete combustion of one mole of glucose, $C_6H_{12}O_6(s)$.

(c) The decomposition of solid ammonium nitrate to produce liquid water and gaseous dinitrogen monoxide.

65. The heat of combustion of 2-propanol at 298.15 K, determined in a bomb calorimeter, is −33.41 kJ/g. For the combustion of one mole of 2-propanol, determine **(a)** ΔU, and **(b)** ΔH.

66. Write an equation to represent the combustion of thymol referred to in Exercise 44. Include in this equation the values for ΔU and ΔH.

Hess's Law

67. The standard enthalpy of formation of $NH_3(g)$ is −46.11 kJ/mol NH_3. What is $\Delta H°$ for the following reaction?

$$\frac{2}{3}NH_3(g) \longrightarrow \frac{1}{3}N_2(g) + H_2(g) \qquad \Delta H° =$$

68. Use Hess's law to determine $\Delta H°$ for the reaction $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$, given that

$$C(\text{graphite}) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H° = -110.54\text{ kJ}$$

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -393.51\text{ kJ}$$

69. Use Hess's law to determine $\Delta H°$ for the reaction $C_3H_4(g) + 2\,H_2(g) \longrightarrow C_3H_8(g)$, given that

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H° = -285.8\text{ kJ}$$

$$C_3H_4(g) + 4\,O_2(g) \longrightarrow 3\,CO_2(g) + 2\,H_2O(l) \qquad \Delta H° = -1937\text{ kJ}$$

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H° = -2219.1\text{ kJ}$$

70. Given the following information:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H_1°$$

$$NH_3(g) + \frac{5}{4}O_2(g) \longrightarrow NO(g) + \frac{3}{2}H_2O(l) \qquad \Delta H_2°$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_3°$$

Determine $\Delta H°$ for the following reaction, expressed in terms of $\Delta H_1°$, $\Delta H_2°$, and $\Delta H_3°$.

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \qquad \Delta H° = ?$$

71. For the reaction $C_2H_4(g) + Cl_2(g) \longrightarrow C_2H_4Cl_2(l)$, determine $\Delta H°$, given that

$$4\,HCl(g) + O_2(g) \longrightarrow 2\,Cl_2(g) + 2\,H_2O(l) \qquad \Delta H° = -202.4\text{ kJ}$$

$$2\,HCl(g) + C_2H_4(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_4Cl_2(l) + H_2O(l) \qquad \Delta H° = -318.7\text{ kJ}$$

72. Determine $\Delta H°$ for this reaction from the data below.

$$N_2H_4(l) + 2\,H_2O_2(l) \longrightarrow N_2(g) + 4\,H_2O(l)$$

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2\,H_2O(l) \qquad \Delta H° = -622.2\text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H° = -285.8\text{ kJ}$$

$$H_2(g) + O_2(g) \longrightarrow H_2O_2(l) \qquad \Delta H° = -187.8\text{ kJ}$$

73. Substitute natural gas (SNG) is a gaseous mixture containing $CH_4(g)$ that can be used as a fuel. One reaction for the production of SNG is

$$4\,CO(g) + 8\,H_2(g) \longrightarrow 3\,CH_4(g) + CO_2(g) + 2\,H_2O(l) \qquad \Delta H° = ?$$

Use appropriate data from the following list to determine $\Delta H°$ for this SNG reaction.

$$C(\text{graphite}) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H° = -110.5\text{ kJ}$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -283.0\text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H° = -285.8\text{ kJ}$$

$$C(\text{graphite}) + 2\,H_2(g) \longrightarrow CH_4(g) \qquad \Delta H° = -74.81\text{ kJ}$$

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H° = -890.3\text{ kJ}$$

74. CCl_4, an important commercial solvent, is prepared by the reaction of $Cl_2(g)$ with a carbon compound. Determine $\Delta H°$ for the reaction

$$CS_2(l) + 3\,Cl_2(g) \longrightarrow CCl_4(l) + S_2Cl_2(l).$$

Use appropriate data from the following listing.

$$CS_2(l) + 3\,O_2(g) \longrightarrow CO_2(g) + 2\,SO_2(g) \qquad \Delta H° = -1077\text{ kJ}$$

$$2\,S(s) + Cl_2(g) \longrightarrow S_2Cl_2(l) \qquad \Delta H° = -58.2\text{ kJ}$$

$$C(s) + 2\,Cl_2(g) \longrightarrow CCl_4(l) \qquad \Delta H° = -135.4\text{ kJ}$$

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H° = -296.8\text{ kJ}$$

$$SO_2(g) + Cl_2(g) \longrightarrow SO_2Cl_2(l) \qquad \Delta H° = +97.3\text{ kJ}$$

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

$$CCl_4(l) + O_2(g) \longrightarrow COCl_2(g) + Cl_2O(g) \qquad \Delta H° = -5.2\text{ kJ}$$

75. Use Hess's law and the following data

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad \Delta H° = -802\text{ kJ}$$

$$CH_4(g) + CO_2(g) \longrightarrow 2\,CO(g) + 2\,H_2(g) \qquad \Delta H° = +247\text{ kJ}$$

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3\,H_2(g) \qquad \Delta H° = +206\text{ kJ}$$

to determine $\Delta H°$ for the following reaction, an important source of hydrogen gas

$$CH_4(g) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + 2\,H_2(g)$$

76. The standard heats of combustion ($\Delta H°$) per mole of 1,3-butadiene, $C_4H_6(g)$; butane, $C_4H_{10}(g)$; and $H_2(g)$ are −2540.2, −2877.6, and −285.8 kJ, respectively. Use these data to calculate the heat of hydrogenation of 1,3-butadiene to butane.

$$C_4H_6(g) + 2\,H_2(g) \longrightarrow C_4H_{10}(g) \qquad \Delta H° = ?$$

[*Hint:* Write equations for the combustion reactions. In each combustion, the products are $CO_2(g)$ and $H_2O(l)$.]

77. One glucose molecule, $C_6H_{12}O_6(s)$, is converted to two lactic acid molecules, $CH_3CH\ (OH)COOH(s)$ during glycolysis. Given the combustion reactions of glucose and lactic acid, determine the standard enthalpy for glycolysis.

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l) \qquad \Delta H° = -2808\text{ kJ}$$

$$CH_3CH(OH)COOH(s) + 3\,O_2(g) \longrightarrow 3\,CO_2(g) + 3\,H_2O(l) \qquad \Delta H° = -1344\text{ kJ}$$

78. The standard enthalpy of fermentation of glucose to ethanol is

$$C_6H_{12}O_6(s) \rightarrow 2\,CH_3CH_2OH(l) + 2\,CO_2(g) \qquad \Delta H° = -72\text{ kJ}$$

Use the standard enthalpy of combustion for glucose to calculate the enthalpy of combustion for ethanol.

Standard Enthalpies of Formation

79. Use standard enthalpies of formation from Table 7.2 and equation (7.21) to determine the standard enthalpy changes in the following reactions.
(a) $C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$;
(b) $2\,H_2S(g) + 3\,O_2(g) \longrightarrow 2\,SO_2(g) + 2\,H_2O(l)$.

80. Use standard enthalpies of formation from Tables 7.2 and 7.3 and equation (7.21) to determine the standard enthalpy change in the following reaction.

$$NH_4^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + NH_3(g).$$

81. Use the information given here, data from Appendix D, and equation (7.21) to calculate the standard enthalpy of formation per mole of ZnS(s).

$$2\,ZnS(s) + 3\,O_2(g) \longrightarrow 2\,ZnO(s) + 2\,SO_2(g) \qquad \Delta H° = -878.2\text{ kJ}$$

82. Use the data in Figure 7-18 and information from Section 3-7 to establish possible relationships between the molecular structure of the hydrocarbons and their standard enthalpies of formation.

83. Use standard enthalpies of formation from Table 7.2 to determine the enthalpy change at 25 °C for the following reaction.

$$2\,Cl_2(g) + 2\,H_2O(l) \longrightarrow 4\,HCl(g) + O_2(g) \qquad \Delta H° = ?$$

84. Use data from Appendix D to calculate the standard enthalpy change for the following reaction at 25 °C.

$$Fe_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Fe(s) + 3\,CO_2(g) \qquad \Delta H° = ?$$

85. Use data from Table 7.2 to determine the standard heat of combustion of $C_2H_5OH(l)$, if reactants and products are maintained at 25 °C and 1 atm.

86. Use data from Table 7.2, together with the fact that $\Delta H° = -3509$ kJ for the complete combustion of one mole of pentane, $C_5H_{12}(l)$, to calculate $\Delta H°$ for the synthesis of 1 mol $C_5H_{12}(l)$ from CO(g) and $H_2(g)$.

$$5\,CO(g) + 11\,H_2(g) \longrightarrow C_5H_{12}(l) + 5\,H_2O(l) \qquad \Delta H° = ?$$

87. Use data from Table 7.2 and $\Delta H°$ for the following reaction to determine the standard enthalpy of formation of $CCl_4(g)$ at 25 °C and 1 atm.

$$CH_4(g) + 4\,Cl_2(g) \longrightarrow CCl_4(g) + 4\,HCl(g) \qquad \Delta H° = -397.3\text{ kJ}$$

88. Use data from Table 7.2 and $\Delta H°$ for the following reaction to determine the standard enthalpy of formation of hexane, $C_6H_{14}(l)$, at 25 °C and 1 atm.

$$2\,C_6H_{14}(l) + 19\,O_2(g) \longrightarrow 12\,CO_2(g) + 14\,H_2O(l) \qquad \Delta H° = -8326\text{ kJ}$$

89. Use data from Table 7.3 and Appendix D to determine the standard enthalpy change in the following reaction.

$$Al^{3+}(aq) + 3\,OH^-(aq) \longrightarrow Al(OH)_3(s) \qquad \Delta H° = ?$$

90. Use data from Table 7.3 and Appendix D to determine the standard enthalpy change in the following reaction.

$$Mg(OH)_2(s) + 2\,NH_4^+(aq) \longrightarrow Mg^{2+}(aq) + 2\,H_2O(l) + 2\,NH_3(g) \qquad \Delta H° = ?$$

91. The decomposition of limestone, $CaCO_3(s)$, into quicklime, CaO(s), and $CO_2(g)$ is carried out in a gas-fired kiln. Use data from Appendix D to determine how much heat is required to decompose 1.35×10^3 kg $CaCO_3(s)$. (Assume that heats of reaction are the same as at 25 °C and 1 atm.)

92. Use data from Table 7.2 to calculate the volume of butane, $C_4H_{10}(g)$, measured at 24.6 °C and 756 mmHg, that must be burned to liberate 5.00×10^4 kJ of heat.

93. Ants release formic acid (HCOOH) when they bite. Use the data in Table 7.2 and the standard enthalpy of combustion for formic acid ($\Delta H° = -255$ kJ/mol) to calculate the standard enthalpy of formation for formic acid.

94. Calculate the enthalpy of combustion for lactic acid by using the data in Table 7.2 and the standard enthalpy of formation for lactic acid: $\Delta H_f^\circ = -694.0$ kJ/mol.

Integrative and Advanced Exercises

95. A British thermal unit (Btu) is defined as the quantity of heat required to change the temperature of 1 lb of water by 1 °F. Assume the specific heat of water to be independent of temperature. How much heat is required to raise the temperature of the water in a 40 gal water heater from 48 to 145 °F in **(a)** Btu; **(b)** kcal; **(c)** kJ?

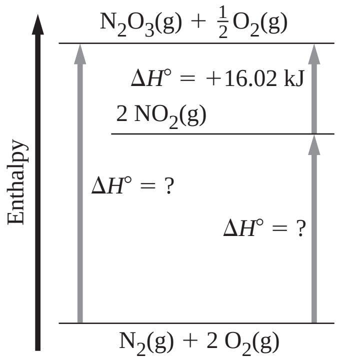
96. A 7.26 kg shot (as used in the sporting event, the shot put) is dropped from the top of a building 168 m high. What is the maximum temperature increase that could occur in the shot? Assume a specific heat of $0.47\ \mathrm{J\ g^{-1}\ {}^\circ C^{-1}}$ for the shot. Why would the actual measured temperature increase likely be less than the calculated value?

97. An alternative approach to bomb calorimetry is to establish the heat capacity of the calorimeter, *exclusive* of the water it contains. The heat absorbed by the water and by the rest of the calorimeter must be calculated separately and then added together. A bomb calorimeter assembly containing 983.5 g water is calibrated by the combustion of 1.354 g anthracene. The temperature of the calorimeter rises from 24.87 to 35.63 °C. When 1.053 g citric acid is burned in the same assembly, but with 968.6 g water, the temperature increases from 25.01 to 27.19 °C. The heat of combustion of anthracene, $C_{14}H_{10}(s)$, is −7067 kJ/mol $C_{14}H_{10}$. What is the heat of combustion of citric acid, $C_6H_8O_7$, expressed in kJ/mol?

98. The method of Exercise 97 is used in some bomb calorimetry experiments. A 1.148 g sample of benzoic acid is burned in excess $O_2(g)$ in a bomb immersed in 1181 g of water. The temperature of the water rises from 24.96 to 30.25 °C. The heat of combustion of benzoic acid is −26.42 kJ/g. In a second experiment, a 0.895 g powdered coal sample is burned in the same calorimeter assembly. The temperature of 1162 g of water rises from 24.98 to 29.81 °C. How many metric tons (1 metric ton = 1000 kg) of this coal would have to be burned to release 2.15×10^9 kJ of heat?

99. A handbook lists two different values for the heat of combustion of hydrogen: 33.88 kcal/g H_2 if $H_2O(l)$ is formed, and 28.67 kcal/g H_2 if $H_2O(g)$ is formed. Explain why these two values are different, and indicate what property this difference represents. Devise a means of verifying your conclusions.

100. Determine the missing values of ΔH° in the diagram shown below.



101. A particular natural gas consists, in mole percents, of 83.0% CH_4, 11.2% C_2H_6, and 5.8% C_3H_8. A 385 L sample of this gas, measured at 22.6 °C and 739 mmHg, is burned at constant pressure in an excess of oxygen gas. How much heat, in kilojoules, is evolved in the combustion reaction?

102. An overall reaction for a coal gasification process is

$$2\,C(\text{graphite}) + 2\,H_2O(g) \longrightarrow CH_4(g) + CO_2(g)$$

Show that this overall equation can be established by an appropriate combination of equations from Section 7-9.

103. Which of the following gases has the greater fuel value on a per liter (STP) basis? That is, which has the greater heat of combustion? [*Hint:* The only combustible gases are CH_4, C_3H_8, CO, and H_2.]
(a) coal gas: 49.7% H_2, 29.9% CH_4, 8.2% N_2, 6.9% CO, 3.1% C_3H_8, 1.7% CO_2, and 0.5% O_2, by volume.
(b) sewage gas: 66.0% CH_4, 30.0% CO_2, and 4.0% N_2, by volume.

104. A calorimeter that measures an exothermic heat of reaction by the quantity of ice that can be melted is called an ice calorimeter. Now consider that 0.100 L of methane gas, $CH_4(g)$, at 25.0 °C and 744 mmHg is burned at constant pressure in air. The heat liberated is captured and used to melt 9.53 g ice at 0 °C (ΔH_{fusion} of ice = 6.01 kJ/mol).
(a) Write an equation for the complete combustion of CH_4, and show that combustion is incomplete in this case.
(b) Assume that CO(g) is produced in the incomplete combustion of CH_4, and represent the combustion as best you can through a single equation with small whole numbers as coefficients. ($H_2O(l)$ is another product of the combustion.)

105. For the reaction

$$C_2H_4(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(l) \qquad \Delta H^\circ = -1410.9\ \text{kJ}$$

if the H_2O were obtained as a gas rather than a liquid, **(a)** would the heat of reaction be greater (more negative) or smaller (less negative) than that indicated in the equation? **(b)** Explain your answer. **(c)** Calculate the value of ΔH° in this case.

106. Some of the butane, $C_4H_{10}(g)$, in a 200.0 L cylinder at 26.0 °C is withdrawn and burned at a constant pressure in an excess of air. As a result, the pressure of the gas in the cylinder falls from 2.35 atm to 1.10 atm. The liberated heat is used to raise the temperature of 132.5 L of water in a heater from 26.0 to 62.2 °C. Assume that the combustion products are $CO_2(g)$ and $H_2O(l)$ exclusively, and determine the efficiency of the water heater. (That is, what percent of the heat of combustion was absorbed by the water?)

107. The metabolism of glucose, $C_6H_{12}O_6$, yields $CO_2(g)$ and $H_2O(l)$ as products. Heat released in the process is converted to useful work with about 70% efficiency. Calculate the mass of glucose metabolized by a 58.0 kg person in climbing a mountain with an elevation gain of 1450 m. Assume that the work performed in the climb is about four times that required to simply lift 58.0 kg by 1450 m. (ΔH_f° of $C_6H_{12}O_6(s)$ is −1273.3 kJ/mol.)

108. An alkane hydrocarbon has the formula C_nH_{2n+2}. The enthalpies of formation of the alkanes decrease (become more negative) as the number of C atoms increases. Starting with butane, $C_4H_{10}(g)$, for each additional CH_2 group in the formula, the enthalpy of formation, ΔH_f°, changes by about −21 kJ/mol. Use this fact and data from Table 7.2 to estimate the heat of combustion of heptane, $C_7H_{16}(l)$.

109. Upon complete combustion, a 1.00-L sample (at STP) of a natural gas gives off 43.6 kJ of heat. If the gas is a mixture of $CH_4(g)$ and $C_2H_6(g)$, what is its percent composition, *by volume*?

110. Under the entry H_2SO_4, a reference source lists many values for the standard enthalpy of formation. For example, for pure $H_2SO_4(l)$, $\Delta H_f^\circ = -814.0$ kJ/mol; for a solution with 1 mol H_2O per mole of H_2SO_4, −841.8; with 10 mol H_2O, −880.5; with 50 mol H_2O; −886.8; with 100 mol H_2O, −887.7; with 500 mol H_2O, −890.5; with 1000 mol H_2O, −892.3; with 10,000 mol H_2O, −900.8; and with 100,000 mol H_2O, −907.3. **(a)** Explain why these values are not all the same. **(b)** The value of $\Delta H_f^\circ[H_2SO_4(aq)]$ in an infinitely dilute solution is −909.3 kJ/mol. What data from this chapter can you cite to confirm this value? Explain. **(c)** If 500.0 mL of 1.00 M $H_2SO_4(aq)$ is prepared from pure $H_2SO_4(l)$, what is the approximate change in temperature that should be observed? Assume that the $H_2SO_4(l)$ and $H_2O(l)$ are at the same temperature initially and that the specific heat of the $H_2SO_4(aq)$ is about 4.2 J g^{-1} °C^{-1}.

111. Refer to the discussion of the gasification of coal (page 278), and show that some of the heat required in the gasification reaction (equation 7.24) can be supplied by the *methanation* reaction. This fact contributes to the success of modern processes that produce *synthetic natural gas* (SNG).

112. A 1.103 g sample of a gaseous carbon–hydrogen–oxygen compound that occupies a volume of 582 mL at 765.5 Torr and 25.00 °C is burned in an excess of $O_2(g)$ in a bomb calorimeter. The products of the combustion are 2.108 g $CO_2(g)$, 1.294 g $H_2O(l)$, and enough heat to raise the temperature of the calorimeter assembly from 25.00 to 31.94 °C. The heat capacity of the calorimeter is 5.015 kJ/°C. Write an equation for the combustion reaction, and indicate ΔH° for this reaction at 25.00 °C.

113. Several factors are involved in determining the cooking times required for foods in a microwave oven. One of these factors is specific heat. Determine the approximate time required to warm 250 mL of chicken broth from 4 °C (a typical refrigerator temperature) to 50 °C in a 700 W microwave oven. Assume that the density of chicken broth is about 1 g/mL and that its specific heat is approximately 4.2 J g^{-1} °C^{-1}.

114. Suppose you have a setup similar to the one depicted in Figure 7-8 except that there are two different weights rather than two equal weights. One weight is a steel cylinder 10.00 cm in diameter and 25 cm long, the other weight produces a pressure of 745 Torr. The temperature of the gas in the cylinder in which the expansion takes place is 25.0 °C. The piston restraining the gas has a diameter of 12.00 cm, and the height of the piston above the base of the gas expansion cylinder is 8.10 cm. The density of the steel is 7.75 g/cm^3. How much work is done when the steel cylinder is suddenly removed from the piston?

115. When one mole of sodium carbonate decahydrate (washing soda) is gently warmed, 155.3 kJ of heat is absorbed, water vapor is formed, and sodium carbonate heptahydrate remains. On more vigorous heating, the heptahydrate absorbs 320.1 kJ of heat and loses more water vapor to give the monohydrate. Continued heating gives the anhydrous salt (soda ash) while 57.3 kJ of heat is absorbed. Calculate ΔH for the conversion of one mole of washing soda into soda ash. Estimate ΔU for this process. Why is the value of ΔU only an estimate?

116. The oxidation of $NH_3(g)$ to $NO(g)$ in the Ostwald process must be very carefully controlled in terms of temperature, pressure, and contact time with the catalyst. This is because the oxidation of $NH_3(g)$ can yield any one of the products $N_2(g)$, $N_2O(g)$, $NO(g)$, and $NO_2(g)$, depending on conditions. Show that oxidation of $NH_3(g)$ to $N_2(g)$ is the most exothermic of the four possible reactions.

117. In the Are You Wondering 7-1 box, the temperature variation of enthalpy is discussed, and the equation q_P = heat capacity × temperature change = $C_P \times \Delta T$ was introduced to show how enthalpy changes with temperature for a constant-pressure process. Strictly speaking, the heat capacity of a substance at constant pressure is the slope of the line representing the variation of enthalpy (H) with temperature, that is

$$C_P = \frac{dH}{dT} \qquad \text{(at constant pressure)}$$

where C_P is the heat capacity of the substance in question. Heat capacity is an extensive quantity and heat capacities are usually quoted as molar heat capacities $C_{P,\mathrm{m}}$, the heat capacity of one mole of substance; an intensive property. The heat capacity at constant pressure is used to estimate the change in enthalpy due to a change in temperature. For infinitesimal changes in temperature,

$$dH = C_P dT \qquad \text{(at constant pressure)}$$

To evaluate the change in enthalpy for a particular temperature change, from T_1 to T_2, we write

$$\int_{H(T_1)}^{H(T_2)} dH = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_P dT$$

If we assume that C_P is independent of temperature, then we recover equation (7.5)

$$\Delta H = C_P \times \Delta T$$

On the other hand, we often find that the heat capacity is a function of temperature; a convenient empirical expression is

$$C_{P,\mathrm{m}} = a + bT + \frac{c}{T^2}$$

What is the change in molar enthalpy of N_2 when it is heated from 25.0 °C to 100.0 °C? The molar heat capacity of nitrogen is given by

$$C_{P,\mathrm{m}} = 28.58 + 3.77 \times 10^{-3}\,T - \frac{0.5 \times 10^{5}}{T^{2}}\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

118. How much heat is required to vaporize 10.0 g of ice at −5.0 °C? The temperature-dependent constant-pressure specific heat of ice is $C_p(T)/(\mathrm{kJ\,kg^{-1}\,K^{-1}}) = 1.0187T - 1.49 \times 10^{-2}$. The temperature-dependent constant-pressure specific heat for water is $C_p(T)/(\mathrm{kJ\,kg^{-1}\,K^{-1}}) = -1.0 \times 10^{-7}T^3 + 1.0 \times 10^{-4}T^2 - 3.92 \times 10^{-2}T + 8.7854$.

119. The standard enthalpy of formation of gaseous H_2O at 298.15 K is $-241.82\,\mathrm{kJ\,mol^{-1}}$. Using the ideas contained in Figure 7-16, estimate its value at 100.0 °C given the following values of the molar heat capacities at constant pressure: $H_2O(g)$: $33.58\,\mathrm{J\,K^{-1}\,mol^{-1}}$; $H_2(g)$: $28.84\,\mathrm{J\,K^{-1}\,mol^{-1}}$; $O_2(g)$: $29.37\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Assume the heat capacities are independent of temperature.

Feature Problems

120. James Joule published his definitive work related to the first law of thermodynamics in 1850. He stated that “the quantity of heat capable of increasing the temperature of one pound of water by 1 °F requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lb through the space of one foot.” Validate this statement by relating it to information given in this text.

121. Based on specific heat measurements, Pierre Dulong and Alexis Petit proposed in 1818 that the specific heat of an element is inversely related to its atomic weight (atomic mass). Thus, by measuring the specific heat of a new element, its atomic weight could be readily established.

(a) Use data from Table 7.1 and inside the front cover to plot a *straight-line* graph relating atomic mass and specific heat. Write the equation for this straight line.

(b) Use the measured specific heat of $0.23\,\mathrm{J\,g^{-1}\,°C^{-1}}$ and the equation derived in part **(a)** to obtain an approximate value of the atomic mass of cadmium, an element discovered in 1817.

(c) To raise the temperature of 75.0 g of a particular metal by 15 °C requires 450 J of heat. What might this metal be?

122. We can use the heat liberated by a neutralization reaction as a means of establishing the stoichiometry of the reaction. The data in the table are for the reaction of 1.00 M NaOH with 1.00 M citric acid, $C_6H_8O_7$, in a total solution volume of 60.0 mL.

mL 1.00 M NaOH Used	mL 1.00 M Citric Acid Used	ΔT, °C
20.0	40.0	4.7
30.0	30.0	6.3
40.0	20.0	8.2
50.0	10.0	6.7
55.0	5.0	2.7

(a) Plot ΔT versus mL 1.00 M NaOH, and identify the exact stoichiometric proportions of NaOH and citric acid at the equivalence point of the neutralization reaction.

(b) Why is the temperature change in the neutralization greatest when the reactants are in their exact stoichiometric proportions? That is, why not use an excess of one of the reactants to ensure that the neutralization has gone to completion to achieve the maximum temperature increase?

(c) Rewrite the formula of citric acid to reflect more precisely its acidic properties. Then write a balanced net ionic equation for the neutralization reaction.

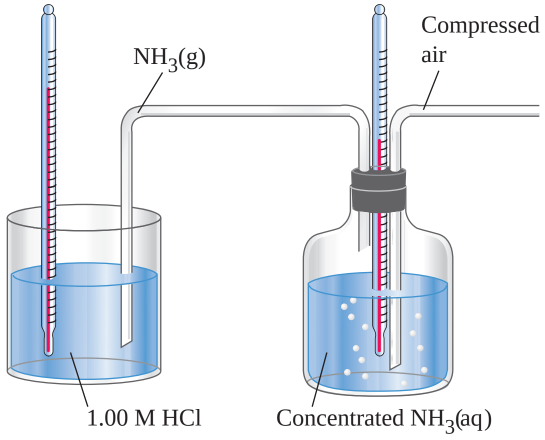
123. In a student experiment to confirm Hess’s law, the reaction

$$NH_3(\text{concd aq}) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

was carried out in two different ways. First, 8.00 mL of concentrated $NH_3(aq)$ was added to 100.0 mL of 1.00 M HCl in a calorimeter. [The $NH_3(aq)$ was slightly in excess.] The reactants were initially at 23.8 °C, and the final temperature after neutralization was 35.8 °C. In the second experiment, air was bubbled through 100.0 mL of concentrated $NH_3(aq)$, sweeping out $NH_3(g)$ (see sketch). The $NH_3(g)$ was neutralized in 100.0 mL of 1.00 M HCl. The temperature of the concentrated $NH_3(aq)$ fell from 19.3 to 13.2 °C. At the same time, the temperature of the 1.00 M HCl rose from 23.8 to 42.9 °C as it was neutralized by $NH_3(g)$. Assume that all solutions have densities of 1.00 g/mL and specific heats of $4.18\,\mathrm{J\,g^{-1}\,°C^{-1}}$.

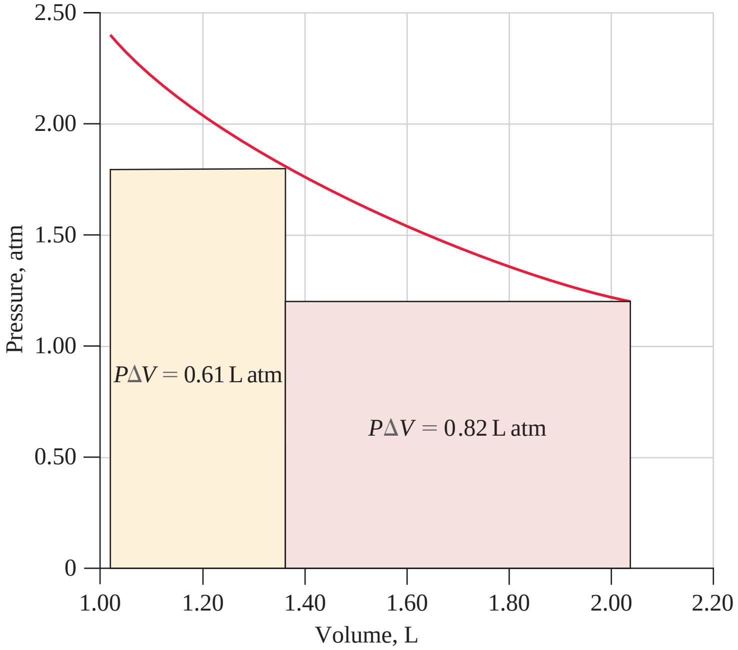
(a) Write the two equations and ΔH values for the processes occurring in the second experiment. Show that the sum of these two equations is the same as the equation for the reaction in the first experiment.

(b) Show that, within the limits of experimental error, ΔH for the overall reaction is the same in the two experiments, thereby confirming Hess’s law.



124. When an ideal gas is heated, the change in internal energy is limited to increasing the average translational kinetic energy of the gas molecules. Thus, there is a simple relationship between ΔU of the gas and the change in temperature that occurs. Derive this relationship with the help of ideas about the kinetic-molecular theory of gases developed in Chapter 6. After doing so, obtain numerical values (in $\text{J mol}^{-1}\,\text{K}^{-1}$) for the following molar heat capacities.
(a) The heat capacity, C_V, for one mole of gas under constant-volume conditions
(b) The heat capacity, C_P, for one mole of gas under constant-pressure conditions

125. Refer to Example 7-5 dealing with the work done by 0.100 mol He at 298 K in expanding in a single step from 2.40 to 1.20 atm. Review also the two-step expansion $(2.40\text{ atm} \longrightarrow 1.80\text{ atm} \longrightarrow 1.20\text{ atm})$ described on page (257) (see Figure 7-11).
(a) Determine the total work that would be done if the He expanded in a series of steps, at 0.10 atm intervals, from 2.40 to 1.20 atm.
(b) Represent this total work on the graph below, in which the quantity of work done in the two-step expansion is represented by the sum of the colored rectangles.
(c) Show that the maximum amount of work would occur if the expansion occurred in an infinite number of steps. To do this, express each infinitesimal quantity of work as $dw = P\,dV$ and use the methods of integral calculus (integration) to sum these quantities. Assume ideal behavior for the gas.
(d) Imagine reversing the process, that is, compressing the He from 1.20 to 2.40 atm. What are the maximum and minimum amounts of work required to produce this compression? Explain.
(e) In the isothermal compression described in part (d), what is the change in internal energy assuming ideal gas behavior? What is the value of q?
(f) Using the formula for the work derived in part (c), obtain an expression for q/T. Is this new function a state function? Explain.



126. Look up the specific heat of several elements, and plot the products of the specific heats and atomic masses as a function of the atomic masses. Based on the plot, develop a hypothesis to explain the data. How could you test your hypothesis?

Self-Assessment Exercises

127. In your own words, define or explain the following terms or symbols: **(a)** ΔH; **(b)** $P\Delta V$; **(c)** ΔH_f°; **(d)** standard state; **(e)** fossil fuel.

128. Briefly describe each of the following ideas or methods: **(a)** law of conservation of energy; **(b)** bomb calorimetry; **(c)** function of state; **(d)** enthalpy diagram; **(e)** Hess's law.

129. Explain the important distinctions between each pair of terms: **(a)** system and surroundings; **(b)** heat and work; **(c)** specific heat and heat capacity; **(d)** endothermic and exothermic; **(e)** constant-volume process and constant-pressure process.

130. The temperature increase of 225 mL of water at 25 °C contained in a Styrofoam cup is noted when a 125 g sample of a metal at 75 °C is added. With reference to Table 7.1, the greatest temperature increase will be noted if the metal is **(a)** lead; **(b)** aluminum; **(c)** iron; **(d)** copper.

131. A plausible final temperature when 75.0 mL of water at 80.0 °C is added to 100.0 mL of water at 20 °C is **(a)** 28 °C; **(b)** 40 °C; **(c)** 46 °C; **(d)** 50 °C.

132. $\Delta U = 100$ J for a system that gives off 100 J of heat and **(a)** does no work; **(b)** does 200 J of work; **(c)** has 100 J of work done on it; **(d)** has 200 J of work done on it.

133. The heat of solution of NaOH(s) in water is −41.6 kJ/mol NaOH. When NaOH(s) is dissolved in water the solution temperature **(a)** increases; **(b)** decreases; **(c)** remains constant; **(d)** either increases or decreases, depending on how much NaOH is dissolved.

134. The standard molar enthalpy of formation of $CO_2(g)$ is equal to **(a)** 0; **(b)** the standard molar heat of combustion of graphite; **(c)** the sum of the standard molar enthalpies of formation of CO(g) and $O_2(g)$; **(d)** the standard molar heat of combustion of CO(g).

135. Which two of the following statements are false? **(a)** $q_V = q_P$ for the reaction $N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$; **(b)** $\Delta H > 0$ for an endothermic reaction; **(c)** By convention, the most stable form of an element must always be chosen as the reference form and assigned the value $\Delta H_f^\circ = 0$; **(d)** ΔU and ΔH for a reaction can never have the same value; **(e)** $\Delta H < 0$ for the neutralization of a strong acid by a strong base.

136. A 1.22 kg piece of iron at 126.5 °C is dropped into 981 g water at 22.1 °C. The temperature rises to 34.4 °C. What will be the final temperature if this same piece of iron at 99.8 °C is dropped into 325 mL of glycerol, $CH_2OHCHOHCH_2OH(l)$ at 26.2 °C? For glycerol, $d = 1.26$ g/mL; $C_p = 219\ \text{J K}^{-1}\ \text{mol}^{-1}$.

137. Write the balanced chemical equations for reactions that have the following as their standard enthalpy changes.

(a) $\Delta H_f^\circ = +82.05$ kJ/mol $N_2O(g)$

(b) $\Delta H_f^\circ = -394.1$ kJ/mol $SO_2Cl_2(l)$

(c) $\Delta H^\circ_{\text{combustion}} = -1527$ kJ/mol $CH_3CH_2COOH(l)$

138. The standard molar heats of combustion of C(graphite) and CO(g) are −393.5 and −283 kJ/mol, respectively. Use those data and that for the following reaction

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g) \qquad \Delta H^\circ = -108\ \text{kJ}$$

to calculate the standard molar enthalpy of formation of $COCl_2(g)$.

139. Can a chemical compound have a standard enthalpy of formation of zero? If so, how likely is this to occur? Explain.

140. Is it possible for a chemical reaction to have $\Delta U < 0$ and $\Delta H > 0$? Explain.

141. Use principles from this chapter to explain the observation that professional chefs prefer to cook with a gas stove rather than an electric stove.

142. Hot water and a piece of cold metal come into contact in an isolated container. When the final temperature of the metal and water are identical, is the total energy change in this process **(a)** zero; **(b)** negative; **(c)** positive; **(d)** not enough information.

143. A clay pot containing water at 25 °C is placed in the shade on a day in which the temperature is 30 °C. The outside of the clay pot is kept moist. Will the temperature of the water inside the clay pot **(a)** increase; **(b)** decrease; **(c)** remain the same?

144. Construct a concept map encompassing the ideas behind the first law of thermodynamics.

145. Construct a concept map to show the use of enthalpy for chemical reactions.

146. Construct a concept map to show the interrelationships between path-dependent and path-independent quantities in thermodynamics.