6 Thermochemistry

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Hot lava flowing into the ocean in Hawaii Volcanoes National Park creates clouds of steam.

Energy is the essence of our very existence as individuals and as a society. The food that we eat furnishes the energy to live, work, and play, just as the coal and oil consumed by manufacturing and transportation systems power our modern industrialized civilization.

In the past, huge quantities of carbon-based fossil fuels have been available for the taking. This abundance of fuels has led to a world society with a voracious appetite for energy, consuming millions of barrels of petroleum every day. We are now dangerously dependent on the dwindling supplies of oil, and this dependence is an important source of tension among nations in today's world. In an incredibly short time we have moved from a period of ample and cheap supplies of petroleum to one of high prices and uncertain supplies. If our present standard of living is to be maintained, we must find alternatives to petroleum. To do this, we need to know the relationship between chemistry and energy, which we explore in this chapter.

There are additional problems with fossil fuels. The waste products from burning fossil fuels significantly affect our environment. For example, when a carbon-based fuel is burned, the carbon reacts with oxygen to form carbon dioxide, which is released into the atmosphere. Although much of this carbon dioxide is consumed in various natural processes such as photosynthesis and the formation of carbonate materials, the amount of carbon dioxide in the atmosphere is steadily increasing. This increase is significant because atmospheric carbon dioxide absorbs heat radiated from the earth's surface and radiates it back toward the earth. Since this is an important mechanism for controlling the earth's temperature, many scientists fear that an increase in the concentration of carbon dioxide will warm the earth, causing significant changes in climate. In addition, impurities in the fossil fuels react with components of the air to produce air pollution. We discussed some aspects of this problem in Chapter 5.

Just as energy is important to our society on a macroscopic scale, it is critically important to each living organism on a microscopic scale. The living cell is a miniature chemical factory powered by energy from chemical reactions. The process of cellular respiration extracts the energy stored in sugars and other nutrients to drive the various tasks of the cell. Although the extraction process is more complex and more subtle, the energy obtained from "fuel" molecules by the cell is the same as would be obtained from burning the fuel to power an internal combustion engine.

Whether it is an engine or a cell that is converting energy from one form to another, the processes are all governed by the same principles, which we will begin to explore in this chapter. Additional aspects of energy transformation will be covered in Chapter 16.

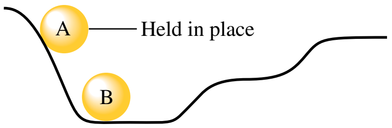
6.1 The Nature of Energy

One interesting definition of energy is that which is needed to oppose natural attractions (for example, gravity and electrostatic attractions).

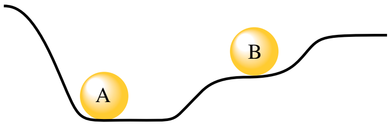
The total energy content of the universe is constant.

Although the concept of energy is quite familiar, energy itself is rather difficult to define precisely. We will define **energy** as the *capacity to do work or to produce heat.* In this chapter we will concentrate specifically on the heat transfer that accompanies chemical processes.

One of the most important characteristics of energy is that it is conserved. The **law of conservation of energy** states that *energy can be converted from one form to another but can be neither created nor destroyed.* That is, the energy of the universe is constant. Energy can be classified as either potential or kinetic energy. **Potential energy** is energy due to position or composition. For example, water behind a dam has potential energy that can be converted to work when the water flows down through turbines, thereby creating electricity. Attractive and repulsive forces also lead to potential energy. The energy released when gasoline is burned results from differences in attractive forces between the nuclei and electrons in the reactants and products. The **kinetic energy** of an object is energy due to the motion of the object and depends on the mass of the object *m* and its velocity *v*: $KE = \frac{1}{2}mv^2$.



(a) Initial



(b) Final

FIGURE 6.1
(a) In the initial positions, ball A has a higher potential energy than ball B. (b) After A has rolled down the hill, the potential energy lost by A has been converted to random motions of the components of the hill (frictional heating) and to the increase in the potential energy of B.

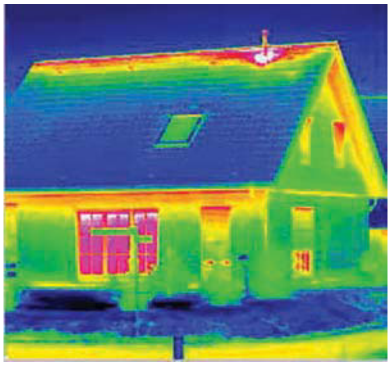
Energy can be converted from one form to another. For example, consider the two balls in Fig. 6.1(a). Ball A, because of its higher position initially, has more potential energy than ball B. When A is released, it moves down the hill and strikes B. Eventually, the arrangement shown in Fig. 6.1(b) is achieved. What has happened in going from the initial to the final arrangement? The potential energy of A has decreased, but since energy is conserved, all the energy lost by A must be accounted for. How is this energy distributed?

Initially, the potential energy of A is changed to kinetic energy as the ball rolls down the hill. Part of this kinetic energy is then transferred to B, causing it to be raised to a higher final position. Thus the potential energy of B has been increased. However, since the final position of B is lower than the original position of A, some of the energy is still unaccounted for. Both balls in their final positions are at rest, so the missing energy cannot be due to their motions. What has happened to the remaining energy?

The answer lies in the interaction between the hill's surface and the ball. As ball A rolls down the hill, some of its kinetic energy is transferred to the surface of the hill as heat. This transfer of energy is called *frictional heating*. The temperature of the hill increases very slightly as the ball rolls down.

Heat involves a transfer of energy.

Before we proceed further, it is important to recognize that heat and temperature are decidedly different. As we saw in Chapter 5, *temperature* is a property that reflects the random motions of the particles in a particular substance. **Heat,** on the other hand, involves the *transfer* of energy between two objects due to a temperature difference. Heat is not a substance contained by an object, although we often talk of heat as if this were true.



This infrared photo of a house shows where energy leaks occur. The more red the color, the more energy (heat) is leaving the house.

Note that in going from the initial to the final arrangements in Fig. 6.1, ball B gains potential energy because work was done by ball A on B. **Work** is defined as force acting over a distance. Work is required to raise B from its original position to its final one. Part of the original energy stored as potential energy in A has been transferred through work to B, thereby increasing B's potential energy. Thus there are two ways to transfer energy: through work and through heat.

In rolling to the bottom of the hill shown in Fig. 6.1, ball A will always lose the same amount of potential energy. However, the way that this energy transfer is divided between work and heat depends on the specific conditions—the **pathway.** For example, the surface of the hill might be so rough that the energy of A is expended completely through frictional heating; A is moving so slowly when it hits B that it cannot move B to the next level. In this case, no work is done. Regardless of the condition of the hill's surface, the *total energy* transferred will be constant. However, the amounts of heat and work will differ. Energy change is independent of the pathway; however, work and heat are both dependent on the pathway.

This brings us to a very important concept: the **state function** or **state property.** A state function refers to a property of the system that depends only on its *present state.* A state function (property) does not depend in any way on the system's past (or future). In other words, the value of a state function does not depend on how the system arrived at the present state; it depends only on the characteristics of the present state. This leads to a very important characteristic of a state function: A change in this function (property) in going from one state to another state is independent of the particular pathway taken between the two states.

Visualization: Coffee Creamer Flammability

A nonscientific analogy that illustrates the difference between a state function and a nonstate function is elevation on the earth's surface and distance between two points. In traveling from Chicago (elevation 674 ft) to Denver (elevation 5280 ft), the change in elevation is always 5280 − 674 = 4606 ft regardless of the route taken between the two cities. The distance traveled, however, depends on how you make the trip. Thus elevation is a function that does not depend on the route (pathway) but distance is pathway dependent. Elevation is a state function and distance is not.

Energy is a state function; work and heat are not.

Of the functions considered in our present example, energy is a state function, but work and heat are not state functions.

Chemical Energy

The ideas we have just illustrated using mechanical examples also apply to chemical systems. The combustion of methane, for example, is used to heat many homes in the United States:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{energy (heat)}$$

To discuss this reaction, we divide the universe into two parts: the system and the surroundings. The **system** is the part of the universe on which we wish to focus attention; the **surroundings** include everything else in the universe. In this case we define the system as the reactants and products of the reaction. The surroundings consist of the reaction container (a furnace, for example), the room, and anything else other than the reactants and products.

Visualization: Sugar and Potassium Chlorate

When a reaction results in the evolution of heat, it is said to be **exothermic** (*exo-* is a prefix meaning "out of"); that is, energy flows *out of the system.* For example, in the combustion of methane, energy flows out of the system as heat. Reactions that absorb energy from the surroundings are said to be **endothermic.** When the heat flow is *into a system,* the process is endothermic. For example, the formation of nitric oxide from nitrogen and oxygen is endothermic:

$$N_2(g) + O_2(g) + \text{energy (heat)} \longrightarrow 2NO(g)$$

Where does the energy, released as heat, come from in an exothermic reaction? The answer lies in the difference in potential energies between the products and the reactants. Which has lower potential energy, the reactants or the products? We know that total energy is conserved and that energy flows from the system into the surroundings in an exothermic reaction. This means that *the energy gained by the surroundings must be equal to the energy lost by the system.* In the combustion of methane, the energy content of the system decreases, which means that 1 mole of CO_2 and 2 moles of H_2O molecules (the products) possess less potential energy than do 1 mole of CH_4 and 2 moles of O_2 molecules (the reactants). The heat flow into the surroundings results from a lowering of the potential energy of the reaction system. This always holds true. *In any exothermic reaction, some of the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat.*

The energy diagram for the combustion of methane is shown in Fig. 6.2, where $\Delta(PE)$ represents the *change* in potential energy stored in the bonds of the products as compared with the bonds of the reactants. In other words, this quantity represents the difference between

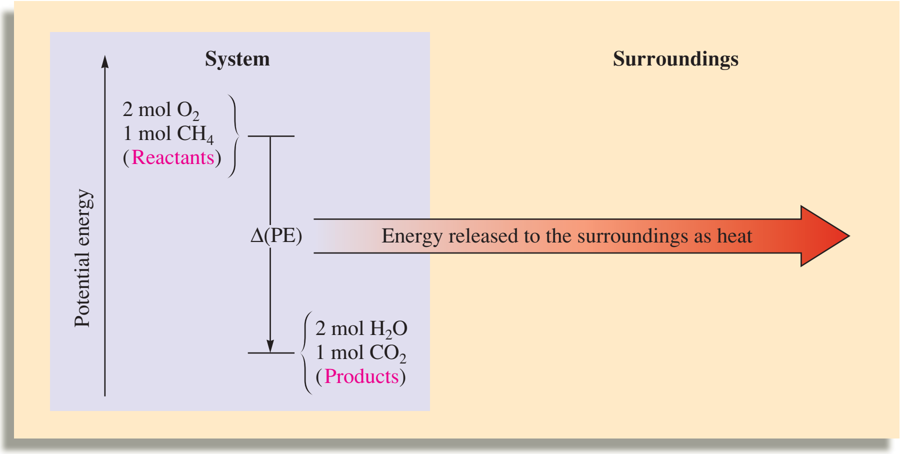


FIGURE 6.2
The combustion of methane releases the quantity of energy Δ(PE) to the surroundings via heat flow. This is an exothermic process.

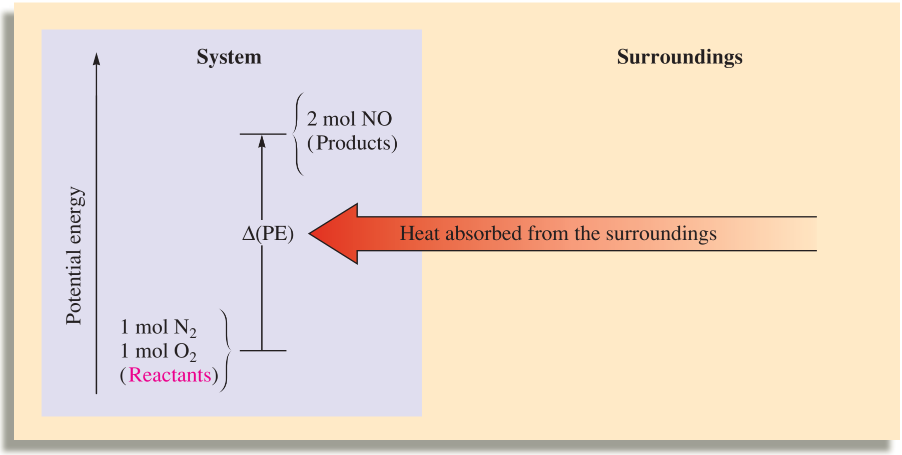


FIGURE 6.3
The energy diagram for the reaction of nitrogen and oxygen to form nitric oxide. This is an endothermic process: Heat [equal in magnitude to Δ(PE)] flows into the system from the surroundings.

the energy required to break the bonds in the reactants and the energy released when the bonds in the products are formed. In an exothermic process, the bonds in the products are stronger (on average) than those of the reactants. That is, more energy is released by forming the new bonds in the products than is consumed to break the bonds in the reactants. The net result is that the quantity of energy Δ(PE) is transferred to the surroundings through heat.

For an endothermic reaction, the situation is reversed, as shown in Fig. 6.3. Energy that flows into the system as heat is used to increase the potential energy of the system. In this case the products have higher potential energy (weaker bonds on average) than the reactants.

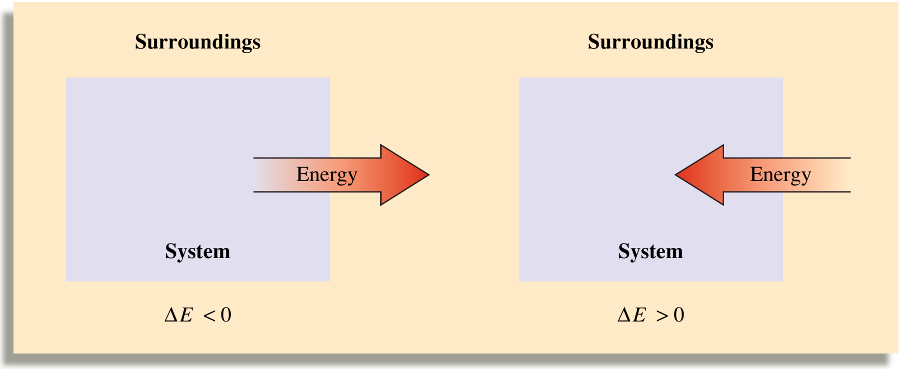
The study of energy and its interconversions is called **thermodynamics.** The law of conservation of energy is often called the **first law of thermodynamics** and is stated as follows: *The energy of the universe is constant.*

The **internal energy** E of a system can be defined most precisely as the sum of the kinetic and potential energies of all the "particles" in the system. The internal energy of a system can be changed by a flow of work, heat, or both. That is,

$$\Delta E = q + w$$

where ΔE represents the change in the system's internal energy, q represents heat, and w represents work.

Thermodynamic quantities always consist of two parts: a *number*, giving the magnitude of the change, and a *sign,* indicating the direction of the flow. *The sign reflects the system's point of view.* For example, if a quantity of energy flows *into* the system via heat (an endothermic process), q is equal to $+x$, where the *positive* sign indicates that the *system's energy is increasing.* On the other hand, when energy flows *out of* the system via heat (an exothermic process), q is equal to $-x$, where the *negative* sign indicates that the *system's energy is decreasing.*



In this text the same conventions also apply to the flow of work. If the system does work on the surroundings (energy flows out of the system), w is negative. If the surroundings do work on the system (energy flows into the system), w is positive. We define work from the system's point of view to be consistent for all thermodynamic quantities. That is, in this convention the signs of both q and w reflect what happens to the system; thus we use $\Delta E = q + w$.

The convention in this text is to take the system's point of view; $q = -x$ denotes an exothermic process, and $q = +x$ denotes an endothermic one.

In this text we *always* take the system's point of view. This convention is not followed in every area of science. For example, engineers are in the business of designing machines to do work, that is, to make the system (the machine) transfer energy to its surroundings through work. Consequently, engineers define work from the surroundings' point of view. In their convention, work that flows out of the system is treated as positive because the energy of the surroundings has increased. The first law of thermodynamics is then written $\Delta E = q - w'$, where w' signifies work from the surroundings' point of view.

Sample Exercise 6.1

Internal Energy

Calculate ΔE for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system.

The joule (J) is the fundamental SI unit for energy:

$$\mathrm{J} = \frac{\mathrm{kg \cdot m^2}}{\mathrm{s^2}}$$

One kilojoule (kJ) $= 10^3$ J.

Solution

We use the equation

$$\Delta E = q + w$$

where $q = +15.6$ kJ, since the process is endothermic, and $w = +1.4$ kJ, since work is done on the system. Thus

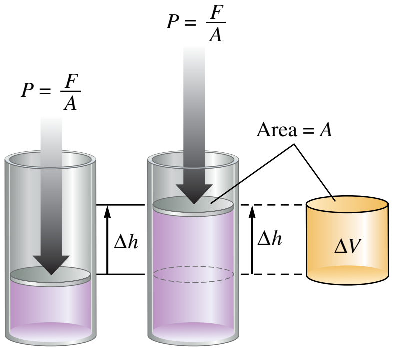
$$\Delta E = 15.6 \text{ kJ} + 1.4 \text{ kJ} = 17.0 \text{ kJ}$$

The system has gained 17.0 kJ of energy.

See Exercises 6.21 and 6.22.

Visualization: Work versus Energy Flow

A common type of work associated with chemical processes is work done by a gas (through *expansion*) or work done to a gas (through *compression*). For example, in an automobile engine, the heat from the combustion of the gasoline expands the gases in the cylinder to push back the piston, and this motion is then translated into the motion of the car.



(a) Initial state (b) Final state

FIGURE 6.4
(a) The piston, moving a distance Δh against a pressure P, does work on the surroundings. (b) Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas is given by $\Delta h \times A = \Delta V$.

Suppose we have a gas confined to a cylindrical container with a movable piston as shown in Fig. 6.4, where F is the force acting on a piston of area A. Since pressure is defined as force per unit area, the pressure of the gas is

$$P = \frac{F}{A}$$

Work is defined as force applied over a distance, so if the piston moves a distance Δh, as shown in Fig. 6.4, then the work done is

$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h$$

Since $P = F/A$ or $F = P \times A$, then

$$\text{Work} = F \times \Delta h = P \times A \times \Delta h$$

Since the volume of a cylinder equals the area of the piston times the height of the cylinder (Fig. 6.4), the change in volume ΔV resulting from the piston moving a distance Δh is

$$\Delta V = \text{final volume} - \text{initial volume} = A \times \Delta h$$

Substituting $\Delta V = A \times \Delta h$ into the expression for work gives

$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

This gives us the *magnitude* (size) of the work required to expand a gas ΔV against a pressure P.

What about the sign of the work? The gas (the system) is expanding, moving the piston against the pressure. Thus the system is doing work on the surroundings, so from the system's point of view the sign of the work should be negative.

For an *expanding* gas, ΔV is a positive quantity because the volume is increasing. Thus ΔV and w must have opposite signs, which leads to the equation

w and $P\Delta V$ have opposite signs because when the gas expands (ΔV is positive), work flows into the surroundings (w is negative).

$$w = -P\Delta V$$

Note that for a gas expanding against an external pressure P, w is a negative quantity as required, since work flows out of the system. When a gas is *compressed,* ΔV is a negative quantity (the volume decreases), which makes w a positive quantity (work flows into the system).

Sample Exercise 6.2 *PV* Work

Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm.

Solution

For a gas at constant pressure,

$$w = -P\Delta V$$

In this case $P = 15$ atm and $\Delta V = 64 - 46 = 18$ L. Hence

$$w = -15 \text{ atm} \times 18 \text{ L} = -270 \text{ L} \cdot \text{atm}$$

For an ideal gas, work can occur only when its volume changes. Thus, if a gas is heated at constant volume, the pressure increases but no work occurs.

Note that since the gas expands, it does work on its surroundings.

Reality Check: Energy flows out of the gas, so w is a negative quantity.

See Exercises 6.25 through 6.27.

In dealing with "*PV* work," keep in mind that the P in $P\Delta V$ always refers to the external pressure—the pressure that causes a compression or that resists an expansion.

Sample Exercise 6.3 Internal Energy, Heat, and Work

A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6 L to 4.50×10^6 L by the addition of 1.3×10^8 J of energy as heat. Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process. (To convert between L · atm and J, use 1 L · atm = 101.3 J.)

Solution

To calculate ΔE, we use the equation

$$\Delta E = q + w$$

Since the problem states that 1.3×10^8 J of energy is *added* as heat,

$$q = +1.3 \times 10^8 \text{ J}$$

A propane burner is used to heat the air in a hot-air balloon.

The work done can be calculated from the expression

$$w = -P\Delta V$$

In this case $P = 1.0$ atm and

$$\begin{aligned}\Delta V &= V_{\text{final}} - V_{\text{initial}}\\ &= 4.50 \times 10^6 \text{ L} - 4.00 \times 10^6 \text{ L} = 0.50 \times 10^6 \text{ L} = 5.0 \times 10^5 \text{ L}\end{aligned}$$

Thus

$$w = -1.0 \text{ atm} \times 5.0 \times 10^5 \text{ L} = -5.0 \times 10^5 \text{ L} \cdot \text{atm}$$

Note that the negative sign for w makes sense, since the gas is expanding and thus doing work on the surroundings.

To calculate ΔE, we must sum q and w. However, since q is given in units of J and w is given in units of L · atm, we must change the work to units of joules:

$$w = -5.0 \times 10^5 \cancel{\text{L} \cdot \text{atm}} \times \frac{101.3 \text{ J}}{\cancel{\text{L} \cdot \text{atm}}} = -5.1 \times 10^7 \text{ J}$$

Then

$$\Delta E = q + w = (+1.3 \times 10^8 \text{ J}) + (-5.1 \times 10^7 \text{ J}) = 8 \times 10^7 \text{ J}$$

Reality Check: Since more energy is added through heating than the gas expends doing work, there is a net increase in the internal energy of the gas in the balloon. Hence ΔE is positive.

See Exercises 6.28 through 6.30.

6.2 Enthalpy and Calorimetry

Enthalpy

So far we have discussed the internal energy of a system. A less familiar property of a system is its **enthalpy,** H, which is defined as

$$H = E + PV$$

where E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system.

Enthalpy is a state function. A change in enthalpy does not depend on the pathway between two states.

Since internal energy, pressure, and volume are all state functions, *enthalpy is also a state function.* But what exactly is enthalpy? To help answer this question, consider a process carried out at constant pressure and where the only work allowed is pressure–volume work ($w = -P\Delta V$). Under these conditions, the expression

$$\Delta E = q_P + w$$

becomes

$$\Delta E = q_P - P\Delta V$$

or

$$q_P = \Delta E + P\Delta V$$

Recall from the previous section that w and $P\Delta V$ have opposite signs:

$$w = -P\Delta V$$

where q_P is the heat at constant pressure.

We will now relate q_P to a change in enthalpy. The definition of enthalpy is $H = E + PV$. Therefore, we can say

$$\text{Change in } H = (\text{change in } E) + (\text{change in } PV)$$

or

$$\Delta H = \Delta E + \Delta(PV)$$

Since P is constant, the change in PV is due only to a change in volume. Thus

$$\Delta(PV) = P\Delta V$$

and

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

This expression is identical to the one we obtained for q_P:

$$q_P = \Delta E + P\Delta V$$

Thus, for a process carried out at constant pressure and where the only work allowed is that from a volume change, we have

$$\Delta H = q_P$$

$\Delta H = q$ *only* at constant pressure.

The change in enthalpy of a system has no easily interpreted meaning except at constant pressure, where $\Delta H =$ heat.

At constant pressure (where only PV work is allowed), the change in enthalpy ΔH of the system is equal to the energy flow as heat. This means that for a reaction studied at constant pressure, the flow of heat is a measure of the change in enthalpy for the system. For this reason, the terms *heat of reaction* and *change in enthalpy* are used interchangeably for reactions studied at constant pressure.

For a chemical reaction, the enthalpy change is given by the equation

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

At constant pressure, exothermic means ΔH is negative; endothermic means ΔH is positive.

In a case in which the products of a reaction have a greater enthalpy than the reactants, ΔH will be positive. Thus heat will be absorbed by the system, and the reaction is endothermic. On the other hand, if the enthalpy of the products is less than that of the reactants, ΔH will be negative. In this case the overall decrease in enthalpy is achieved by the generation of heat, and the reaction is exothermic.

Sample Exercise 6.4

Enthalpy

When 1 mole of methane (CH_4) is burned at constant pressure, 890 kJ of energy is released as heat. Calculate ΔH for a process in which a 5.8-g sample of methane is burned at constant pressure.

Solution

At constant pressure, 890 kJ of energy per mole of CH_4 is produced as heat:

$$q_P = \Delta H = -890 \text{ kJ/mol CH}_4$$

Note that the minus sign indicates an exothermic process. In this case, a 5.8-g sample of CH_4 (molar mass = 16.0 g/mol) is burned. Since this amount is smaller than 1 mole, less than 890 kJ will be released as heat. The actual value can be calculated as follows:

$$5.8 \cancel{\text{g CH}_4} \times \frac{1 \text{ mol CH}_4}{16.0 \cancel{\text{g CH}_4}} = 0.36 \text{ mol CH}_4$$

and

$$0.36 \cancel{\text{mol CH}_4} \times \frac{-890 \text{ kJ}}{\cancel{\text{mol CH}_4}} = -320 \text{ kJ}$$

Thus, when a 5.8-g sample of CH_4 is burned at constant pressure,

$$\Delta H = \text{heat flow} = -320 \text{ kJ}$$

See Exercises 6.35 through 6.38.

TABLE 6.1 The Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity (J/°C · g)
$H_2O(l)$	4.18
$H_2O(s)$	2.03
$Al(s)$	0.89
$Fe(s)$	0.45
$Hg(l)$	0.14
$C(s)$	0.71

Calorimetry

The device used experimentally to determine the heat associated with a chemical reaction is called a **calorimeter. Calorimetry,** the science of measuring heat, is based on observing the temperature change when a body absorbs or discharges energy as heat. Substances respond differently to being heated. One substance might require a great deal of heat energy to raise its temperature by one degree, whereas another will exhibit the same temperature change after absorbing relatively little heat. The **heat capacity** *C* of a substance, which is a measure of this property, is defined as

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$

When an element or a compound is heated, the energy required will depend on the amount of the substance present (for example, it takes twice as much energy to raise the temperature of two grams of water by one degree than it takes to raise the temperature of one gram of water by one degree). Thus, in defining the heat capacity of a substance, the amount of substance must be specified. If the heat capacity is given *per gram* of substance, it is called the **specific heat capacity,** and its units are J/°C · g or J/K · g. If the heat capacity is given *per mole* of the substance, it is called the **molar heat capacity,** and it has the units J/°C · mol or J/K · mol. The specific heat capacities of some common substances are given in Table 6.1. Note from this table that the heat capacities of metals are very different from that of water. It takes much less energy to change the temperature of a gram of a metal by 1°C than for a gram of water.

Specific heat capacity: the energy required to raise the temperature of one gram of a substance by one degree Celsius.

Molar heat capacity: the energy required to raise the temperature of one mole of a substance by one degree Celsius.

Although the calorimeters used for highly accurate work are precision instruments, a very simple calorimeter can be used to examine the fundamentals of calorimetry. All we need are two nested Styrofoam cups with a cover through which a stirrer and thermometer can be inserted, as shown in Fig. 6.5. This device is called a "coffee-cup calorimeter." The outer cup is used to provide extra insulation. The inner cup holds the solution in which the reaction occurs.

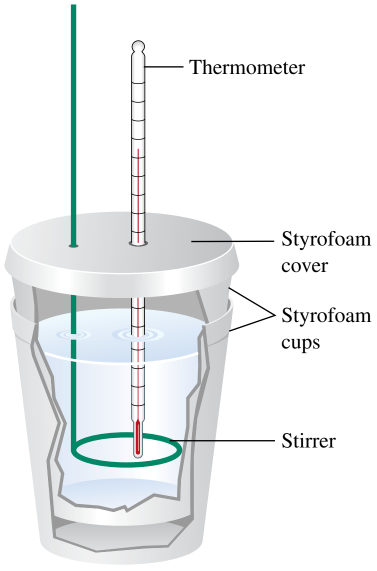


FIGURE 6.5
A coffee-cup calorimeter made of two Styrofoam cups.

The measurement of heat using a simple calorimeter such as that shown in Fig. 6.5 is an example of **constant-pressure calorimetry,** since the pressure (atmospheric pressure) remains constant during the process. Constant-pressure calorimetry is used in determining the changes in enthalpy (heats of reactions) for reactions occurring in solution. Recall that under these conditions, the change in enthalpy equals the heat.

For example, suppose we mix 50.0 mL of 1.0 *M* HCl at 25.0°C with 50.0 mL of 1.0 *M* NaOH also at 25°C in a calorimeter. After the reactants are mixed by stirring, the temperature is observed to increase to 31.9°C. As we saw in Section 4.8, the net ionic equation for this reaction is

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

When these reactants (each originally at the same temperature) are mixed, the temperature of the mixed solution is observed to increase. Therefore, the chemical reaction must be releasing energy as heat. This released energy increases the random motions of the solution components, which in turn increases the temperature. The quantity of energy released can be determined from the temperature increase, the mass of solution, and the specific heat capacity of the solution. For an approximate result, we will assume that the calorimeter does not absorb or leak any heat and that the solution can be treated as if it were pure water with a density of 1.0 g/mL.

We also need to know the heat required to raise the temperature of a given amount of water by 1°C. Table 6.1 lists the specific heat capacity of water as 4.18 J/°C · g. This means that 4.18 J of energy is required to raise the temperature of 1 gram of water by 1°C.

CHEMICAL IMPACT

Nature Has Hot Plants

The voodoo lily is a beautiful, seductive—and foul-smelling—plant. The exotic-looking lily features an elaborate reproductive mechanism—a purple spike that can reach nearly 3 feet in length and is cloaked by a hoodlike leaf. But approach to the plant reveals bad news—it smells terrible!

Despite its antisocial odor, this putrid plant has fascinated biologists for many years because of its ability to generate heat. At the peak of its metabolic activity, the plant's blossom can be as much as 15°C above its ambient temperature. To generate this much heat, the metabolic rate of the plant must be close to that of a flying hummingbird!

What's the purpose of this intense heat production? For a plant faced with limited food supplies in the very competitive tropical climate where it grows, heat production seems like a great waste of energy. The answer to this mystery is that the voodoo lily is pollinated mainly by carrion-loving insects. Thus the lily prepares a malodorous mixture of chemicals characteristic of rotting meat, which it then "cooks" off into the surrounding air to attract flesh-feeding beetles and flies. Then, once the insects enter the pollination chamber, the high temperatures there (as high as 110°F) cause the insects to remain very active to better carry out their pollination duties.

The voodoo lily is only one of many such thermogenic (heat-producing) plants. Another interesting example is the eastern skunk cabbage, which produces enough heat to bloom inside of a snow bank by creating its own ice caves. These plants are of special interest to biologists because they provide opportunities to study metabolic reactions that are quite subtle in "normal" plants. For example, recent studies have shown that salicylic acid, the active form of aspirin, is probably very important in producing the metabolic bursts in thermogenic plants.

Besides studying the dramatic heat effects in thermogenic plants, biologists are also interested in calorimetric

If two reactants at the same temperature are mixed and the resulting solution gets warmer, this means the reaction taking place is exothermic. An endothermic reaction cools the solution.

From these assumptions and definitions, we can calculate the heat (change in enthalpy) for the neutralization reaction:

Energy released by the reaction

$$\begin{aligned} &= \text{energy absorbed by the solution} \\ &= \text{specific heat capacity} \times \text{mass of solution} \times \text{increase in temperature} \\ &= s \times m \times \Delta T \end{aligned}$$

In this case the increase in temperature $(\Delta T) = 31.9°\text{C} - 25.0°\text{C} = 6.9°\text{C}$, and the mass of solution $(m) = 100.0\text{ mL} \times 1.0\text{ g/mL} = 1.0 \times 10^2\text{ g}$. Thus

$$\begin{aligned} \text{Energy released} &= s \times m \times \Delta T \\ &= \left(4.18 \frac{\text{J}}{°\cancel{\text{C}} \cdot \cancel{\text{g}}}\right)(1.0 \times 10^2\ \cancel{\text{g}})(6.9°\cancel{\text{C}}) \\ &= 2.9 \times 10^3\text{ J} \end{aligned}$$

How much energy would have been released if twice these amounts of solutions had been mixed? The answer is that twice as much energy would have been produced. The heat of a reaction is an *extensive property;* it depends directly on the amount of substance, in this case on the amounts of reactants. In contrast, an *intensive property* is not related to the amount of a substance. For example, temperature is an intensive property.

Enthalpies of reaction are often expressed in terms of moles of reacting substances. The number of moles of H^+ ions consumed in the preceding experiment is

$$50.0\ \cancel{\text{mL}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{1.0\text{ mol}}{\cancel{\text{L}}}\text{H}^+ = 5.0 \times 10^{-2}\text{ mol H}^+$$

Thus 2.9×10^3 J heat was released when 5.0×10^{-2} mol H^+ ions reacted, or

$$\frac{2.9 \times 10^3\text{ J}}{5.0 \times 10^{-2}\text{ mol H}^+} = 5.8 \times 10^4\text{ J/mol}$$

studies of regular plants. For example, very precise calorimeters have been designed that can be used to study the heat produced, and thus the metabolic activities, of clumps of cells no larger than a bread crumb. Several scientists have suggested that a single calorimetric measurement taking just a few minutes on a tiny plant might be useful in predicting the growth rate of the mature plant throughout its lifetime. If true, this would provide a very efficient method for selecting the plants most likely to thrive as adults.

Because the study of the heat production by plants is an excellent way to learn about plant metabolism, this continues to be a "hot" area of research.

The voodoo lily attracts pollinating insects with its foul odor.

Notice that in this example we mentally keep track of the direction of the energy flow and assign the correct sign at the end of the calculation.

of heat released per 1.0 mol H^+ ions neutralized. Thus the *magnitude* of the enthalpy change per mole for the reaction

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

is 58 kJ/mol. Since heat is *evolved,* $\Delta H = -58$ kJ/mol.

Sample Exercise 6.5 Constant-Pressure Calorimetry

When 1.00 L of 1.00 *M* $Ba(NO_3)_2$ solution at 25.0°C is mixed with 1.00 L of 1.00 *M* Na_2SO_4 solution at 25°C in a calorimeter, the white solid $BaSO_4$ forms and the temperature of the mixture increases to 28.1°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the specific heat capacity of the solution is 4.18 J/°C · g, and that the density of the final solution is 1.0 g/mL, calculate the enthalpy change per mole of $BaSO_4$ formed.

Solution

The ions present before any reaction occurs are Ba^{2+}, NO_3^-, Na^+, and SO_4^{2-}. The Na^+ and NO_3^- ions are spectator ions, since $NaNO_3$ is very soluble in water and will not precipitate under these conditions. The net ionic equation for the reaction is therefore

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

Since the temperature increases, formation of the solid $BaSO_4$ must be exothermic; ΔH will be negative.

Heat evolved by reaction

= heat absorbed by solution

= specific heat capacity × mass of solution × increase in temperature

Since 1.00 L of each solution is used, the total solution volume is 2.00 L, and

$$\text{Mass of solution} = 2.00\ \cancel{\text{L}} \times \frac{1000\ \cancel{\text{mL}}}{1\ \cancel{\text{L}}} \times \frac{1.0\ \text{g}}{\cancel{\text{mL}}} = 2.0 \times 10^3\ \text{g}$$

$$\text{Temperature increase} = 28.1^\circ\text{C} - 25.0^\circ\text{C} = 3.1^\circ\text{C}$$

$$\text{Heat evolved} = (4.18\ \text{J}/^\circ\cancel{\text{C}} \cdot \cancel{\text{g}})(2.0 \times 10^3\ \cancel{\text{g}})(3.1^\circ\cancel{\text{C}}) = 2.6 \times 10^4\ \text{J}$$

Thus

$$q = q_P = \Delta H = -2.6 \times 10^4\ \text{J}$$

Since 1.0 L of 1.0 M $Ba(NO_3)_2$ contains 1 mol Ba^{2+} ions and 1.0 L of 1.0 M Na_2SO_4 contains 1.0 mol $SO_4{}^{2-}$ ions, 1.0 mol solid $BaSO_4$ is formed in this experiment. Thus the enthalpy change per mole of $BaSO_4$ formed is

$$\Delta H = -2.6 \times 10^4\ \text{J/mol} = -26\ \text{kJ/mol}$$

See Exercises 6.51 through 6.54.

Calorimetry experiments also can be performed at **constant volume.** For example, when a photographic flashbulb flashes, the bulb becomes very hot, because the reaction of the zirconium or magnesium wire with the oxygen inside the bulb is exothermic. The reaction occurs inside the flashbulb, which is rigid and does not change volume. Under these conditions, no work is done (because the volume must change for pressure–volume work to be performed). To study the energy changes in reactions under conditions of constant volume, a "bomb calorimeter" (Fig. 6.6) is used. Weighed reactants are placed inside a rigid steel container (the "bomb") and ignited. The energy change is determined by measuring the increase in the temperature of the water and other calorimeter parts. For a constant-volume process, the change in volume ΔV is equal to zero, so work (which is $-P\Delta V$) is also equal to zero. Therefore,

$$\Delta E = q + w = q = q_V \qquad \text{(constant volume)}$$

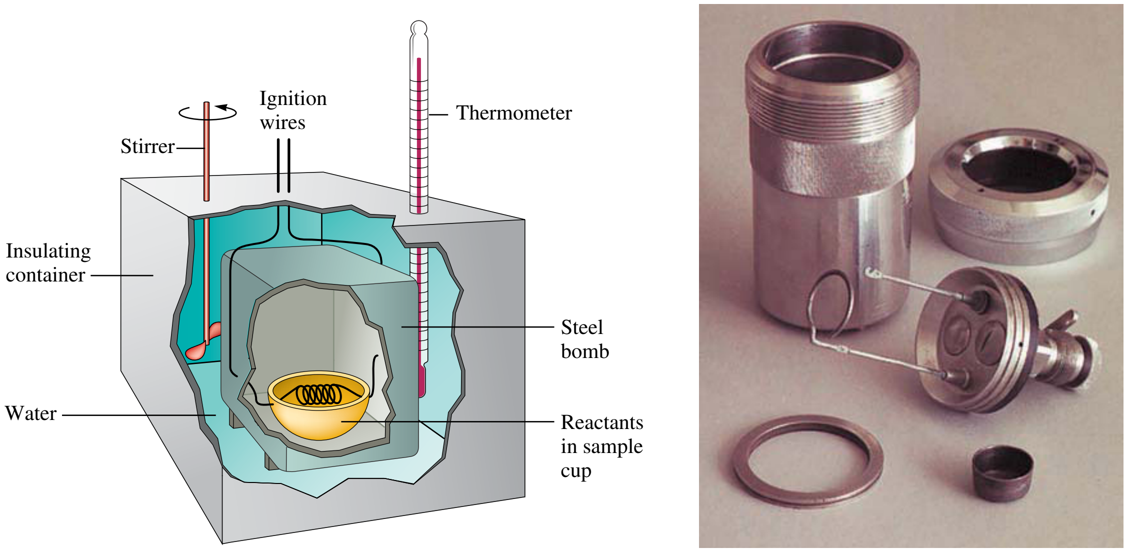


FIGURE 6.6
A bomb calorimeter. The reaction is carried out inside a rigid steel "bomb" (photo of actual disassembled "bomb" shown on right), and the heat evolved is absorbed by the surrounding water and other calorimeter parts. The quantity of energy produced by the reaction can be calculated from the temperature increase.

CHEMICAL IMPACT

Firewalking: Magic or Science?

A group of firewalkers in Japan.

For millennia people have been amazed at the ability of Eastern mystics to walk across beds of glowing coals without any apparent discomfort. Even in the United States, thousands of people have performed feats of firewalking as part of motivational seminars. How is this possible? Do firewalkers have supernatural powers?

Actually, there are good scientific explanations, based on the concepts covered in this chapter, of why firewalking is possible. The first important factor concerns the heat capacity of feet. Because human tissue is mainly composed of water, it has a relatively large specific heat capacity. This means that a large amount of energy must be transferred from the coals to significantly change the temperature of the feet. During the brief contact between feet and coals, there is relatively little time for energy flow so the feet do not reach a high enough temperature to cause damage.

Second, although the surface of the coals has a very high temperature, the red hot layer is very thin. Therefore, the quantity of energy available to heat the feet is smaller than might be expected. This factor points to the difference between temperature and heat. Temperature reflects the *intensity* of the random kinetic energy in a given sample of matter. The amount of energy available for heat flow, on the other hand, depends on the quantity of matter at a given temperature—10 grams of matter at a given temperature contains 10 times as much thermal energy as 1 gram of the same matter. This is why the tiny spark from a sparkler does not hurt when it hits your hand. The spark has a very high temperature but has so little mass that no significant energy transfer occurs to your hand. This same argument applies to the very thin hot layer on the coals.

Thus, although firewalking is an impressive feat, there are several sound scientific reasons why it is possible (with the proper training and a properly prepared bed of coals).

Suppose we wish to measure the energy of combustion of octane (C_8H_{18}), a component of gasoline. A 0.5269-g sample of octane is placed in a bomb calorimeter known to have a heat capacity of 11.3 kJ/°C. This means that 11.3 kJ of energy is required to raise the temperature of the water and other parts of the calorimeter by 1°C. The octane is ignited in the presence of excess oxygen, and the temperature increase of the calorimeter is 2.25°C. The amount of energy released is calculated as follows:

Energy released by the reaction

$$= \text{temperature increase} \times \text{energy required to change the temperature by } 1^\circ\text{C}$$

$$= \Delta T \times \text{heat capacity of calorimeter}$$

$$= 2.25\cancel{^\circ\text{C}} \times 11.3 \text{ kJ}/\cancel{^\circ\text{C}} = 25.4 \text{ kJ}$$

This means that 25.4 kJ of energy was released by the combustion of 0.5269 g octane.

The number of moles of octane is

$$0.5269 \cancel{\text{g octane}} \times \frac{1 \text{ mol octane}}{114.2 \cancel{\text{g octane}}} = 4.614 \times 10^{-3} \text{ mol octane}$$

Since 25.4 kJ of energy was released for 4.614×10^{-3} mol octane, the energy released per mole is

$$\frac{25.4 \text{ kJ}}{4.614 \times 10^{-3} \text{ mol}} = 5.50 \times 10^{3} \text{ kJ/mol}$$

Since the reaction is exothermic, ΔE is negative:

$$\Delta E_{\text{combustion}} = -5.50 \times 10^{3} \text{ kJ/mol}$$

Note that since no work is done in this case, ΔE is equal to the heat.

$$\Delta E = q + w = q \qquad \text{since } w = 0$$

Thus $q = -5.50 \times 10^{3}$ kJ/mol.

Sample Exercise 6.6

Constant-Volume Calorimetry

Hydrogen's potential as a fuel is discussed in Section 6.6.

It has been suggested that hydrogen gas obtained by the decomposition of water might be a substitute for natural gas (principally methane). To compare the energies of combustion of these fuels, the following experiment was carried out using a bomb calorimeter with a heat capacity of 11.3 kJ/°C. When a 1.50-g sample of methane gas was burned with excess oxygen in the calorimeter, the temperature increased by 7.3°C. When a 1.15-g sample of hydrogen gas was burned with excess oxygen, the temperature increase was 14.3°C. Calculate the energy of combustion (per gram) for hydrogen and methane.

Solution

We calculate the energy of combustion for methane using the heat capacity of the calorimeter (11.3 kJ/°C) and the observed temperature increase of 7.3°C:

$$\begin{aligned}\text{Energy } \textit{released} \text{ in the combustion of 1.5 g } CH_4 &= (11.3 \text{ kJ/°C})(7.3\text{°C}) \\ &= 83 \text{ kJ}\\ \text{Energy } \textit{released} \text{ in the combustion of 1 g } CH_4 &= \frac{83 \text{ kJ}}{1.5 \text{ g}} = 55 \text{ kJ/g}\end{aligned}$$

The direction of energy flow is indicated by words in this example. Using signs to designate the direction of energy flow:

$$\Delta E_{\text{combustion}} = -55 \text{ kJ/g}$$

for methane and

$$\Delta E_{\text{combustion}} = -141 \text{ kJ/g}$$

for hydrogen.

Similarly, for hydrogen

$$\begin{aligned}\text{Energy } \textit{released} \text{ in the combustion of 1.15 g } H_2 &= (11.3 \text{ kJ/°C})(14.3\text{°C}) \\ &= 162 \text{ kJ}\\ \text{Energy } \textit{released} \text{ in the combustion of 1 g } H_2 &= \frac{162 \text{ kJ}}{1.15 \text{ g}} = 141 \text{ kJ/g}\end{aligned}$$

The energy released in the combustion of 1 g hydrogen is approximately 2.5 times that for 1 g methane, indicating that hydrogen gas is a potentially useful fuel.

See Exercises 6.55 and 6.56.

6.3 Hess's Law

ΔH is not dependent on the reaction pathway.

Since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is independent of the pathway. This means that *in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.* This principle is known as **Hess's law** and can be illustrated by examining the oxidation of nitrogen to produce nitrogen dioxide. The overall reaction can be written in one step, where the enthalpy change is represented by ΔH_1.

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H_1 = 68 \text{ kJ}$$

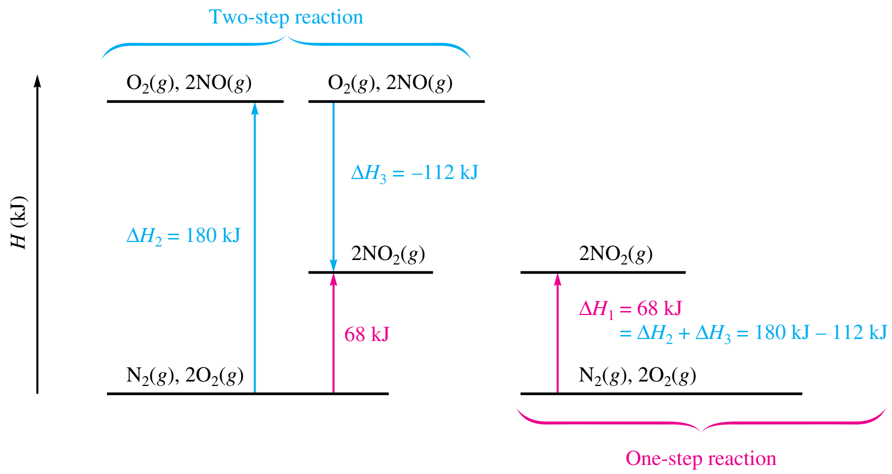


FIGURE 6.7
The principle of Hess's law. The same change in enthalpy occurs when nitrogen and oxygen react to form nitrogen dioxide, regardless of whether the reaction occurs in one (red) or two (blue) steps.

Visualization: Hess's Law

This reaction also can be carried out in two distinct steps, with enthalpy changes designated by ΔH_2 and ΔH_3:

$$\begin{array}{llll} & N_2(g) + O_2(g) \longrightarrow 2NO(g) & & \Delta H_2 = 180 \text{ kJ} \\ & 2NO(g) + O_2(g) \longrightarrow 2NO_2(g) & & \Delta H_3 = -112 \text{ kJ} \\ \hline \text{Net reaction:} & N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) & \Delta H_2 + \Delta H_3 = 68 \text{ kJ} & \end{array}$$

Note that the sum of the two steps gives the net, or overall, reaction and that

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = 68 \text{ kJ}$$

The principle of Hess's law is shown schematically in Fig. 6.7.

Characteristics of Enthalpy Changes

Reversing the direction of a reaction changes the sign of ΔH.

To use Hess's law to compute enthalpy changes for reactions, it is important to understand two characteristics of ΔH for a reaction:

1. If a reaction is reversed, the sign of ΔH is also reversed.
2. The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

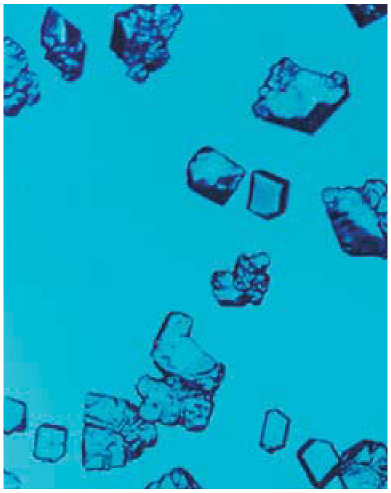
Both these rules follow in a straightforward way from the properties of enthalpy changes. The first rule can be explained by recalling that the *sign* of ΔH indicates the *direction* of the heat flow at constant pressure. If the direction of the reaction is reversed, the direction of the heat flow also will be reversed. To see this, consider the preparation of xenon tetrafluoride, which was the first binary compound made from a noble gas:

$$Xe(g) + 2F_2(g) \longrightarrow XeF_4(s) \qquad \Delta H = -251 \text{ kJ}$$

This reaction is exothermic, and 251 kJ of energy flows into the surroundings as heat. On the other hand, if the colorless XeF_4 crystals are decomposed into the elements, according to the equation

$$XeF_4(s) \longrightarrow Xe(g) + 2F_2(g)$$

the opposite energy flow occurs because 251 kJ of energy must be added to the system to produce this endothermic reaction. Thus, for this reaction, $\Delta H = +251$ kJ.


Crystals of xenon tetrafluoride, the first reported binary compound containing a noble gas element.

The second rule comes from the fact that ΔH is an extensive property, depending on the amount of substances reacting. For example, since 251 kJ of energy is evolved for the reaction

$$Xe(g) + 2F_2(g) \longrightarrow XeF_4(s)$$

then for a preparation involving twice the quantities of reactants and products, or

$$2\text{Xe}(g) + 4\text{F}_2(g) \longrightarrow 2\text{XeF}_4(s)$$

twice as much heat would be evolved:

$$\Delta H = 2(-251 \text{ kJ}) = -502 \text{ kJ}$$

Sample Exercise 6.7 Hess's Law I

Two forms of carbon are *graphite,* the soft, black, slippery material used in "lead" pencils and as a lubricant for locks, and *diamond,* the brilliant, hard gemstone. Using the enthalpies of combustion for graphite (-394 kJ/mol) and diamond (-396 kJ/mol), calculate ΔH for the conversion of graphite to diamond:

$$\text{C}_{\text{graphite}}(s) \longrightarrow \text{C}_{\text{diamond}}(s)$$

Solution

The combustion reactions are

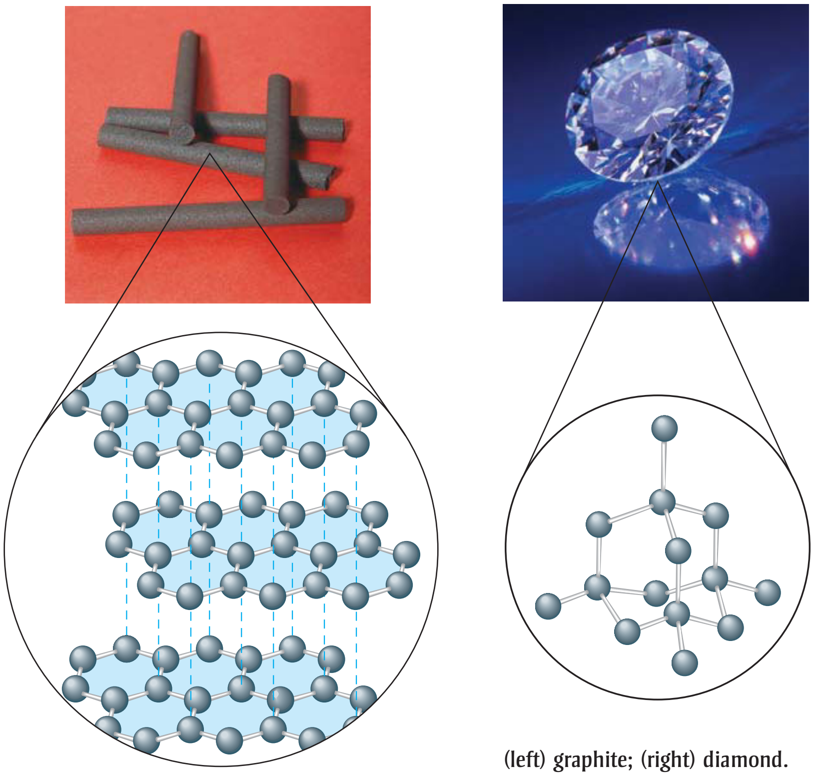
$$\begin{array}{llll} \text{C}_{\text{graphite}}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) & & \Delta H = -394 \text{ kJ} \\ \text{C}_{\text{diamond}}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) & & \Delta H = -396 \text{ kJ} \end{array}$$

Note that if we reverse the second reaction (which means we must change the sign of ΔH) and sum the two reactions, we obtain the desired reaction:

$$\begin{array}{rll} \text{C}_{\text{graphite}}(s) + \text{O}_2(g) \longrightarrow & \text{CO}_2(g) & \Delta H = -394 \text{ kJ} \\ \text{CO}_2(g) \longrightarrow & \text{C}_{\text{diamond}}(s) + \text{O}_2(g) & \Delta H = -(-396 \text{ kJ}) \\ \hline \text{C}_{\text{graphite}}(s) \longrightarrow & \text{C}_{\text{diamond}}(s) & \Delta H = 2 \text{ kJ} \end{array}$$

Thus 2 kJ of energy is required to change 1 mol graphite to diamond. This process is endothermic.

See Exercises 6.57 and 6.58.



(left) graphite; (right) diamond.

Sample Exercise 6.8

Hess's Law II

Diborane (B_2H_6) is a highly reactive boron hydride that was once considered as a possible rocket fuel for the U.S. space program. Calculate ΔH for the synthesis of diborane from its elements, according to the equation

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$$

using the following data:

Reaction	ΔH
(a) $2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)$	-1273 kJ
(b) $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$	-2035 kJ
(c) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	-286 kJ
(d) $H_2O(l) \longrightarrow H_2O(g)$	44 kJ

Solution

To obtain ΔH for the required reaction, we must somehow combine equations (a), (b), (c), and (d) to produce that reaction and add the corresponding ΔH values. This can best be done by focusing on the reactants and products of the required reaction. The reactants are $B(s)$ and $H_2(g)$, and the product is $B_2H_6(g)$. How can we obtain the correct equation? Reaction (a) has $B(s)$ as a reactant, as needed in the required equation. Thus reaction (a) will be used as it is. Reaction (b) has $B_2H_6(g)$ as a reactant, but this substance is needed as a product. Thus reaction (b) must be reversed, and the sign of ΔH must be changed accordingly. Up to this point we have

$$\begin{array}{llcll}
\text{(a)} & 2B(s) + \tfrac{3}{2}O_2(g) & \longrightarrow & B_2O_3(s) & \Delta H = -1273 \text{ kJ} \\
-\text{(b)} & B_2O_3(s) + 3H_2O(g) & \longrightarrow & B_2H_6(g) + 3O_2(g) & \Delta H = -(-2035 \text{ kJ}) \\
\hline
\text{Sum:} & B_2O_3(s) + 2B(s) + \tfrac{3}{2}O_2(g) + 3H_2O(g) & \longrightarrow & B_2O_3(s) + B_2H_6(g) + 3O_2(g) & \Delta H = 762 \text{ kJ}
\end{array}$$

Deleting the species that occur on both sides gives

$$2B(s) + 3H_2O(g) \longrightarrow B_2H_6(g) + \tfrac{3}{2}O_2(g) \qquad \Delta H = 762 \text{ kJ}$$

We are closer to the required reaction, but we still need to remove $H_2O(g)$ and $O_2(g)$ and introduce $H_2(g)$ as a reactant. We can do this using reactions (c) and (d). If we multiply reaction (c) and its ΔH value by 3 and add the result to the preceding equation, we have

$$\begin{array}{llcll}
 & 2B(s) + 3H_2O(g) & \longrightarrow & B_2H_6(g) + \tfrac{3}{2}O_2(g) & \Delta H = 762 \text{ kJ} \\
3 \times \text{(c)} & 3[H_2(g) + \tfrac{1}{2}O_2(g) & \longrightarrow & H_2O(l)] & \Delta H = 3(-286 \text{ kJ}) \\
\hline
\text{Sum:} & 2B(s) + 3H_2(g) + \tfrac{3}{2}O_2(g) + 3H_2O(g) & \longrightarrow & B_2H_6(g) + \tfrac{3}{2}O_2(g) + 3H_2O(l) & \Delta H = -96 \text{ kJ}
\end{array}$$

We can cancel the $\frac{3}{2}O_2(g)$ on both sides, but we cannot cancel the H_2O because it is gaseous on one side and liquid on the other. This can be solved by adding reaction (d), multiplied by 3:

$$\begin{array}{llcll}
 & 2B(s) + 3H_2(g) + 3H_2O(g) & \longrightarrow & B_2H_6(g) + 3H_2O(l) & \Delta H = -96 \text{ kJ} \\
3 \times \text{(d)} & 3[H_2O(l) & \longrightarrow & H_2O(g)] & \Delta H = 3(44 \text{ kJ}) \\
\hline
 & 2B(s) + 3H_2(g) + 3H_2O(g) + 3H_2O(l) & \longrightarrow & B_2H_6(g) + 3H_2O(l) + 3H_2O(g) & \Delta H = +36 \text{ kJ}
\end{array}$$

This gives the reaction required by the problem:

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g) \qquad \Delta H = +36 \text{ kJ}$$

Thus ΔH for the synthesis of 1 mol diborane from the elements is +36 kJ.

See Exercises 6.59 through 6.64.

Hints for Using Hess's Law

Calculations involving Hess's law typically require that several reactions be manipulated and combined to finally give the reaction of interest. In doing this procedure you should

- Work *backward* from the required reaction, using the reactants and products to decide how to manipulate the other given reactions at your disposal
- Reverse any reactions as needed to give the required reactants and products
- Multiply reactions to give the correct numbers of reactants and products

This process involves some trial and error, but it can be very systematic if you always allow the final reaction to guide you.

6.4 Standard Enthalpies of Formation

For a reaction studied under conditions of constant pressure, we can obtain the enthalpy change using a calorimeter. However, this process can be very difficult. In fact, in some cases it is impossible, since certain reactions do not lend themselves to such study. An example is the conversion of solid carbon from its graphite form to its diamond form:

$$C_{\text{graphite}}(s) \longrightarrow C_{\text{diamond}}(s)$$

The value of ΔH for this process cannot be obtained by direct measurement in a calorimeter because the process is much too slow under normal conditions. However, as we saw in Sample Exercise 6.7, ΔH for this process can be calculated from heats of combustion. This is only one example of how useful it is to be able to *calculate* ΔH values for chemical reactions. We will next show how to do this using standard enthalpies of formation.

The **standard enthalpy of formation** (ΔH_f°) of a compound is defined as the *change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.*

A *degree symbol* on a thermodynamic function, for example, ΔH°, indicates that the corresponding process has been carried out under standard conditions. The **standard state** for a substance is a precisely defined reference state. Because thermodynamic functions often depend on the concentrations (or pressures) of the substances involved, we must use a common reference state to properly compare the thermodynamic properties of two substances. This is especially important because, for most thermodynamic properties, we can measure only *changes* in the property. For example, we have no method for determining absolute values of enthalpy. We can measure enthalpy changes (ΔH values) only by performing heat-flow experiments.

Recently, the International Union of Pure and Applied Chemists (IUPAC) has adopted 1 bar (100,000 Pa) as the standard pressure instead of 1 atm (101,305 Pa). Both standards are now in wide use.

Standard state is *not* the same as the standard temperature and pressure (STP) for a gas (discussed in Section 5.4).

Conventional Definitions of Standard States

For a Compound

- The standard state of a gaseous substance is a pressure of exactly 1 atmosphere.
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
- For a substance present in a solution, the standard state is a concentration of exactly 1 *M*.

For an Element

- The standard state of an element is the form in which the element exists under conditions of 1 atmosphere and 25°C. (The standard state for oxygen is $O_2(g)$ at a pressure of 1 atmosphere; the standard state for sodium is Na(*s*); the standard state for mercury is Hg(*l*); and so on.)

Several important characteristics of the definition of the enthalpy of formation will become clearer if we again consider the formation of nitrogen dioxide from the elements in their standard states:

$$\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^\circ = 34 \text{ kJ/mol}$$

Note that the reaction is written so that both elements are in their standard states, and 1 mole of product is formed. Enthalpies of formation are *always* given per mole of product with the product in its standard state.

The formation reaction for methanol is written as

$$C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3OH(l) \qquad \Delta H_f^\circ = -239 \text{ kJ/mol}$$

The standard state of carbon is graphite, the standard states for oxygen and hydrogen are the diatomic gases, and the standard state for methanol is the liquid.

The ΔH_f° values for some common substances are shown in Table 6.2. More values are found in Appendix 4. The importance of the tabulated ΔH_f° values is that enthalpies for many reactions can be calculated using these numbers. To see how this is done, we will calculate the standard enthalpy change for the combustion of methane:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Enthalpy is a state function, so we can invoke Hess's law and choose *any* convenient pathway from reactants to products and then sum the enthalpy changes along the chosen pathway. A convenient pathway, shown in Fig. 6.8, involves taking the reactants apart to the respective elements in their standard states in reactions (a) and (b) and then forming the products from these elements in reactions (c) and (d). This general pathway will work for any reaction, since atoms are conserved in a chemical reaction.

Note from Fig. 6.8 that reaction (a), where methane is taken apart into its elements,

$$CH_4(g) \longrightarrow C(s) + 2H_2(g)$$

is just the reverse of the formation reaction for methane:

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H_f^\circ = -75 \text{ kJ/mol}$$

Since reversing a reaction means changing the sign of ΔH but keeping the magnitude the same, ΔH for reaction (a) is $-\Delta H_f^\circ$, or 75 kJ. Thus $\Delta H^\circ_{(a)} = 75$ kJ.

Next we consider reaction (b). Here oxygen is already an element in its standard state, so no change is needed. Thus $\Delta H^\circ_{(b)} = 0$.

Brown nitrogen dioxide gas.

TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	ΔH_f° (kJ/mol)
$NH_3(g)$	−46
$NO_2(g)$	34
$H_2O(l)$	−286
$Al_2O_3(s)$	−1676
$Fe_2O_3(s)$	−826
$CO_2(g)$	−394
$CH_3OH(l)$	−239
$C_8H_{18}(l)$	−269

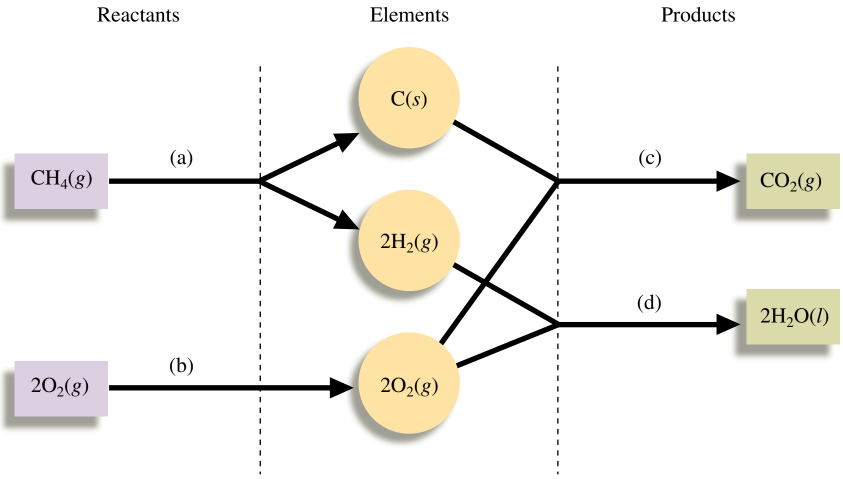


FIGURE 6.8
In this pathway for the combustion of methane, the reactants are first taken apart in reactions (a) and (b) to form the constituent elements in their standard states, which are then used to assemble the products in reactions (c) and (d).

The next steps, reactions (c) and (d), use the elements formed in reactions (a) and (b) to form the products. Note that reaction (c) is simply the formation reaction for carbon dioxide:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_f^\circ = -394\ \text{kJ/mol}$$

and

$$\Delta H^\circ_{(c)} = \Delta H_f^\circ \text{ for } CO_2(g) = -394\ \text{kJ}$$

Reaction (d) is the formation reaction for water:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f^\circ = -286\ \text{kJ/mol}$$

However, since 2 moles of water are required in the balanced equation, we must form 2 moles of water from the elements:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Thus

$$\Delta H^\circ_{(d)} = 2 \times \Delta H_f^\circ \text{ for } H_2O(l) = 2(-286\ \text{kJ}) = -572\ \text{kJ}$$

We have now completed the pathway from the reactants to the products. The change in enthalpy for the reaction is the sum of the ΔH values (including their signs) for the steps:

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &\\ &= \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)} \\ &= [-\Delta H_f^\circ \text{ for } CH_4(g)] + 0 + [\Delta H_f^\circ \text{ for } CO_2(g)] + [2 \times \Delta H_f^\circ \text{ for } H_2O(l)] \\ &= -(-75\ \text{kJ}) + 0 + (-394\ \text{kJ}) + (-572\ \text{kJ}) \\ &= -891\ \text{kJ}\end{aligned}$$

This process is diagramed in Fig. 6.9. Notice that the reactants are taken apart and converted to elements [not necessary for $O_2(g)$] that are then used to form products. You can see that this is a very exothermic reaction because very little energy is required to convert the reactants to the respective elements but a great deal of energy is released when these elements form the products. This is why this reaction is so useful for producing heat to warm homes and offices.

Let's examine carefully the pathway we used in this example. First, the reactants were broken down into the elements in their standard states. This process involved reversing

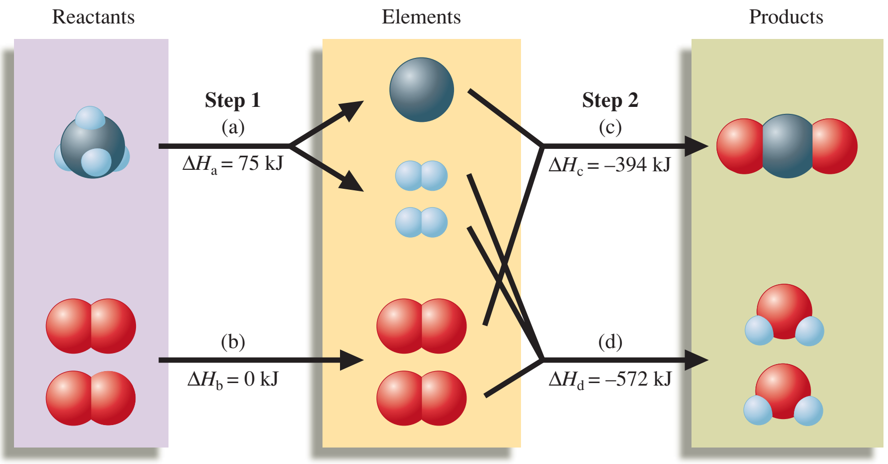


FIGURE 6.9
A schematic diagram of the energy changes for the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$.

Subtraction means to reverse the sign and add.

the formation reactions and thus switching the signs of the enthalpies of formation. The products were then constructed from these elements. This involved formation reactions and thus enthalpies of formation. We can summarize this entire process as follows: *The enthalpy change for a given reaction can be calculated by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products.* Remember to multiply the enthalpies of formation by integers as required by the balanced equation. This statement can be represented symbolically as follows:

$$\Delta H^\circ_{\text{reaction}} = \Sigma n_p \Delta H^\circ_f(\text{products}) - \Sigma n_r \Delta H^\circ_f(\text{reactants}) \qquad (6.1)$$

where the symbol Σ (sigma) means "to take the sum of the terms," and n_p and n_r represent the moles of each product or reactant, respectively.

Elements in their standard states are not included in enthalpy calculations using ΔH°_f values.

Elements are not included in the calculation because elements require no change in form. We have in effect *defined* the enthalpy of formation of an element in its standard state as zero, since we have chosen this as our reference point for calculating enthalpy changes in reactions.

Keep in Mind the Following Key Concepts When Doing Enthalpy Calculations:

- When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.
- When the balanced equation for a reaction is multiplied by an integer, the value of ΔH for that reaction must be multiplied by the same integer.
- The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^\circ_{\text{reaction}} = \Sigma n_p \Delta H^\circ_f(\text{products}) - \Sigma n_r \Delta H^\circ_f(\text{reactants})$$

- Elements in their standard states are not included in the $\Delta H_{\text{reaction}}$ calculations. That is, ΔH°_f for an element in its standard state is zero.

Sample Exercise 6.9

Enthalpies from Standard Enthalpies of Formation I

Using the standard enthalpies of formation listed in Table 6.2, calculate the standard enthalpy change for the overall reaction that occurs when ammonia is burned in air to form nitrogen dioxide and water. This is the first step in the manufacture of nitric acid.

$$4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(l)$$

Solution

We will use the pathway in which the reactants are broken down into elements in their standard states, which are then used to form the products (see Fig. 6.10).

➥ **1** *Decomposition of $NH_3(g)$ into elements* (reaction (a) in Fig. 6.10). The first step is to decompose 4 moles of NH_3 into N_2 and H_2:

$$4NH_3(g) \longrightarrow 2N_2(g) + 6H_2(g)$$

The preceding reaction is 4 times the *reverse* of the formation reaction for NH_3:

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H^\circ_f = -46 \text{ kJ/mol}$$

Thus

$$\Delta H^\circ_{(a)} = 4 \text{ mol}[-(-46 \text{ kJ/mol})] = 184 \text{ kJ}$$

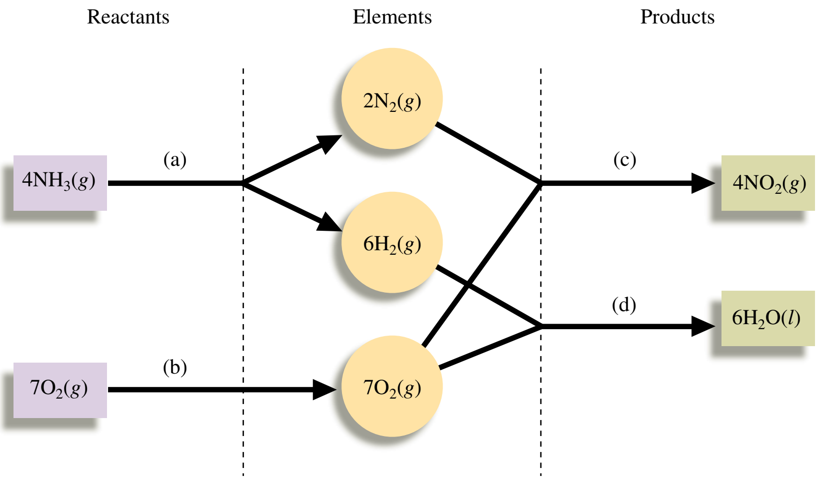


FIGURE 6.10
A pathway for the combustion of ammonia.

2 *Elemental oxygen* (reaction (b) in Fig. 6.10). Since $O_2(g)$ is an element in its standard state, $\Delta H^\circ_{(b)} = 0$.

We now have the elements $N_2(g)$, $H_2(g)$, and $O_2(g)$, which can be combined to form the products of the overall reaction.

3 *Synthesis of $NO_2(g)$ from elements* (reaction (c) in Fig. 6.10). The overall reaction equation has 4 moles of NO_2. Thus the required reaction is 4 times the formation reaction for NO_2:

$$4 \times [\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)]$$

and

$$\Delta H^\circ_{(c)} = 4 \times \Delta H_f^\circ \text{ for } NO_2(g)$$

From Table 6.2, ΔH_f° for $NO_2(g) = 34$ kJ/mol and

$$\Delta H^\circ_{(c)} = 4 \text{ mol} \times 34 \text{ kJ/mol} = 136 \text{ kJ}$$

4 *Synthesis of $H_2O(l)$ from elements* (reaction (d) in Fig. 6.10). Since the overall equation for the reaction has 6 moles of $H_2O(l)$, the required reaction is 6 times the formation reaction for $H_2O(l)$:

$$6 \times [H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)]$$

and

$$\Delta H^\circ_{(d)} = 6 \times \Delta H_f^\circ \text{ for } H_2O(l)$$

From Table 6.2, ΔH_f° for $H_2O(l) = -286$ kJ/mol and

$$\Delta H^\circ_{(d)} = 6 \text{ mol} (-286 \text{ kJ/mol}) = -1716 \text{ kJ}$$

To summarize, we have done the following:

$$\begin{matrix} 4NH_3(g) \xrightarrow{\Delta H^\circ_{(a)}} \\ 7O_2(g) \xrightarrow{\Delta H^\circ_{(b)}} \end{matrix} \left\{ \begin{matrix} 2N_2(g) + 6H_2(g) \\ 7O_2(g) \end{matrix} \right\} \begin{matrix} \xrightarrow{\Delta H^\circ_{(c)}} 4NO_2(g) \\ \xrightarrow{\Delta H^\circ_{(d)}} 6H_2O(l) \end{matrix}$$

Elements in their standard states

We add the ΔH° values for the steps to get ΔH° for the overall reaction:

$$\begin{aligned}
\Delta H^\circ_{\text{reaction}} &= \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)} \\
&= [4 \times -\Delta H_f^\circ \text{ for } NH_3(g)] + 0 + [4 \times \Delta H_f^\circ \text{ for } NO_2(g)] \\
&\qquad + [6 \times \Delta H_f^\circ \text{ for } H_2O(l)] \\
&= [4 \times \Delta H_f^\circ \text{ for } NO_2(g)] + [6 \times \Delta H_f^\circ \text{ for } H_2O(l)] \\
&\qquad - [4 \times \Delta H_f^\circ \text{ for } NH_3(g)] \\
&= \Sigma n_p \Delta H_f^\circ(\text{products}) - \Sigma n_r \Delta H_f^\circ(\text{reactants})
\end{aligned}$$

Remember that elemental reactants and products do not need to be included, since ΔH_f° for an element in its standard state is zero. Note that we have again obtained Equation (6.1). The final solution is

$$\begin{aligned}
\Delta H^\circ_{\text{reaction}} &= [4 \times (34 \text{ kJ})] + [6 \times (-286 \text{ kJ})] - [4 \times (-46 \text{ kJ})] \\
&= -1396 \text{ kJ}
\end{aligned}$$

See Exercises 6.67 and 6.68.

Now that we have shown the basis for Equation (6.1), we will make direct use of it to calculate ΔH for reactions in succeeding exercises.

Sample Exercise 6.10

Enthalpies from Standard Enthalpies of Formation II

Visualization: Thermite Reaction

Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction:

$$2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$$

This reaction occurs when a mixture of powdered aluminum and iron(III) oxide is ignited with a magnesium fuse.

The thermite reaction is one of the most energetic chemical reactions known.

Solution

We use Equation (6.1):

$$\Delta H^\circ = \Sigma n_p \Delta H_f^\circ(\text{products}) - \Sigma n_r \Delta H_f^\circ(\text{reactants})$$

where

$$\begin{aligned}
\Delta H_f^\circ \text{ for } Fe_2O_3(s) &= -826 \text{ kJ/mol} \\
\Delta H_f^\circ \text{ for } Al_2O_3(s) &= -1676 \text{ kJ/mol} \\
\Delta H_f^\circ \text{ for } Al(s) = \Delta H_f^\circ \text{ for } Fe(s) &= 0
\end{aligned}$$

Thus

$$\begin{aligned}
\Delta H^\circ_{\text{reaction}} &= \Delta H_f^\circ \text{ for } Al_2O_3(s) - \Delta H_f^\circ \text{ for } Fe_2O_3(s) \\
&= -1676 \text{ kJ} - (-826 \text{ kJ}) = -850. \text{ kJ}
\end{aligned}$$

This reaction is so highly exothermic that the iron produced is initially molten. This process is often used as a lecture demonstration and also has been used in welding massive steel objects such as ships' propellers.

See Exercises 6.71 and 6.72.

Sample Exercise 6.11 Enthalpies from Standard Enthalpies of Formation III

Methanol (CH_3OH) is often used as a fuel in high-performance engines in race cars. Using the data in Table 6.2, compare the standard enthalpy of combustion per gram of methanol with that per gram of gasoline. Gasoline is actually a mixture of compounds, but assume for this problem that gasoline is pure liquid octane (C_8H_{18}).

Solution

The combustion reaction for methanol is

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

Using the standard enthalpies of formation from Table 6.2 and Equation (6.1), we have

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= 2 \times \Delta H_f^\circ \text{ for } CO_2(g) + 4 \times \Delta H_f^\circ \text{ for } H_2O(l) - \\ &\quad 2 \times \Delta H_f^\circ \text{ for } CH_3OH(l) \\ &= 2 \times (-394 \text{ kJ}) + 4 \times (-286 \text{ kJ}) - 2 \times (-239 \text{ kJ}) \\ &= -1454 \text{ kJ}\end{aligned}$$

Thus 1454 kJ of heat is evolved when 2 moles of methanol burn. The molar mass of methanol is 32.0 g/mol. This means that 1454 kJ of energy is produced when 64.0 g methanol burns. The enthalpy of combustion per gram of methanol is

$$\frac{-1454 \text{ kJ}}{64.0 \text{ g}} = -22.7 \text{ kJ/g}$$

The combustion reaction for octane is

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l)$$

Using the standard enthalpies of information from Table 6.2 and Equation (6.1), we have

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= 16 \times \Delta H_f^\circ \text{ for } CO_2(g) + 18 \times \Delta H_f^\circ \text{ for } H_2O(l) - \\ &\quad 2 \times \Delta H_f^\circ \text{ for } C_8H_{18}(l) \\ &= 16 \times (-394 \text{ kJ}) + 18 \times (-286 \text{ kJ}) - 2 \times (-269 \text{ kJ}) \\ &= -1.09 \times 10^4 \text{ kJ}\end{aligned}$$

This is the amount of heat evolved when 2 moles of octane burn. Since the molar mass of octane is 114.2 g/mol, the enthalpy of combustion per gram of octane is

$$\frac{-1.09 \times 10^4 \text{ kJ}}{2(114.2 \text{ g})} = -47.8 \text{ kJ/g}$$

The enthalpy of combustion per gram of octane is approximately twice that per gram of methanol. On this basis, gasoline appears to be superior to methanol for use in a racing car, where weight considerations are usually very important. Why, then, is methanol used in racing cars? The answer is that methanol burns much more smoothly than gasoline in high-performance engines, and this advantage more than compensates for its weight disadvantage.

See Exercise 6.77.

6.5 Present Sources of Energy

Woody plants, coal, petroleum, and natural gas hold a vast amount of energy that originally came from the sun. By the process of photosynthesis, plants store energy that can be claimed by burning the plants themselves or the decay products that have been converted

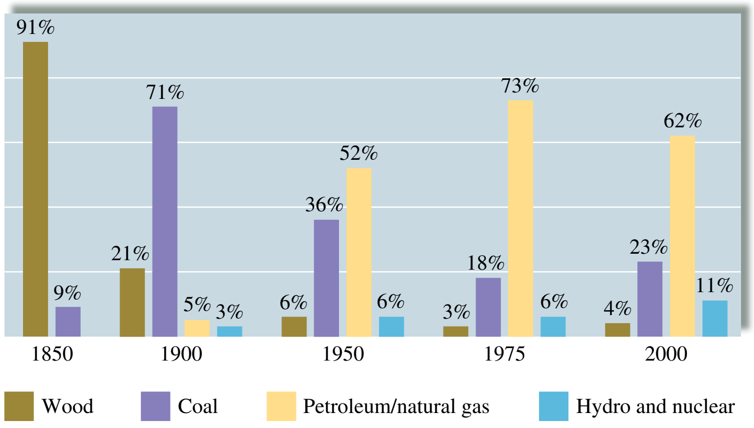


FIGURE 6.11
Energy sources used in the United States.

over millions of years to **fossil fuels.** Although the United States currently depends heavily on petroleum for energy, this dependency is a relatively recent phenomenon, as shown in Fig. 6.11. In this section we discuss some sources of energy and their effects on the environment.

This oil rig in Norway is the largest in the world.

Petroleum and Natural Gas

Although how they were produced is not completely understood, petroleum and natural gas were most likely formed from the remains of marine organisms that lived approximately 500 million years ago. **Petroleum** is a thick, dark liquid composed mostly of compounds called *hydrocarbons* that contain carbon and hydrogen. (Carbon is unique among elements in the extent to which it can bond to itself to form chains of various lengths.) Table 6.3 gives the formulas and names for several common hydrocarbons. **Natural gas,** usually associated with petroleum deposits, consists mostly of methane, but it also contains significant amounts of ethane, propane, and butane.

The composition of petroleum varies somewhat, but it consists mostly of hydrocarbons having chains that contain from 5 to more than 25 carbons. To be used efficiently, the petroleum must be separated into fractions by boiling. The lighter molecules (having the lowest boiling points) can be boiled off, leaving the heavier ones behind. The commercial uses of various petroleum fractions are shown in Table 6.4.

The petroleum era began when the demand for lamp oil during the Industrial Revolution outstripped the traditional sources: animal fats and whale oil. In response to this increased demand, Edwin Drake drilled the first oil well in 1859 at Titusville, Pennsylvania. The petroleum from this well was refined to produce *kerosene* (fraction C_{10}–C_{18}), which served as an excellent lamp oil. *Gasoline* (fraction C_5–C_{10}) had limited use and was often discarded. However, this situation soon changed. The development of the electric light decreased the need for kerosene, and the advent of the "horseless carriage" with its gasoline-powered engine signaled the birth of the gasoline age.

As gasoline became more important, new ways were sought to increase the yield of gasoline obtained from each barrel of petroleum. William Burton invented a process at Standard Oil of Indiana called *pyrolytic (high-temperature) cracking.* In this process, the heavier molecules of the kerosene fraction are heated to about 700°C, causing them to break (crack) into the smaller molecules of hydrocarbons in the gasoline fraction. As cars became larger, more efficient internal combustion engines were designed. Because of the uneven burning of the gasoline then available, these engines "knocked," producing unwanted noise and even engine damage. Intensive research to find additives that would promote smoother burning produced tetraethyl lead, $(C_2H_5)_4Pb$, a very effective "antiknock" agent.

TABLE 6.3 Names and Formulas for Some Common Hydrocarbons

Formula	Name
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane

The addition of tetraethyl lead to gasoline became a common practice, and by 1960, gasoline contained as much as 3 grams of lead per gallon. As we have discovered so often in recent years, technological advances can produce environmental problems. To prevent air pollution from automobile exhaust, catalytic converters have been added to car exhaust systems. The effectiveness of these converters, however, is destroyed by lead. The use of leaded gasoline also greatly increased the amount of lead in the environment, where it can be ingested by animals and humans. For these reasons, the use of lead in gasoline has been phased out, requiring extensive (and expensive) modifications of engines and of the gasoline refining process.

TABLE 6.4 Uses of the Various Petroleum Fractions

Petroleum Fraction in Terms of Numbers of Carbon Atoms	Major Uses
C_5–C_{10}	Gasoline
C_{10}–C_{18}	Kerosene Jet fuel
C_{15}–C_{25}	Diesel fuel Heating oil Lubricating oil
$>C_{25}$	Asphalt

Coal

Coal has variable composition depending on both its age and location.

Coal was formed from the remains of plants that were buried and subjected to high pressure and heat over long periods of time. Plant materials have a high content of cellulose, a complex molecule whose empirical formula is CH_2O but whose molar mass is around 500,000 g/mol. After the plants and trees that flourished on the earth at various times and places died and were buried, chemical changes gradually lowered the oxygen and hydrogen content of the cellulose molecules. Coal "matures" through four stages: lignite, subbituminous, bituminous, and anthracite. Each stage has a higher carbon-to-oxygen and carbon-to-hydrogen ratio; that is, the relative carbon content gradually increases. Typical elemental compositions of the various coals are given in Table 6.5. The energy available from the combustion of a given mass of coal increases as the carbon content increases. Therefore, anthracite is the most valuable coal, and lignite the least valuable.

Coal is an important and plentiful fuel in the United States, currently furnishing approximately 23% of our energy. As the supply of petroleum dwindles, the share of the energy supply from coal is expected to increase. However, coal is expensive and dangerous to mine underground, and the strip mining of fertile farmland in the Midwest or of scenic land in the West causes obvious problems. In addition, the burning of coal, especially high-sulfur coal, yields air pollutants such as sulfur dioxide, which, in turn, can lead to acid rain, as we learned in Chapter 5. However, even if coal were pure carbon, the carbon dioxide produced when it was burned would still have significant effects on the earth's climate.

Effects of Carbon Dioxide on Climate

The electromagnetic spectrum, including visible and infrared radiation, is discussed in Chapter 7.

The earth receives a tremendous quantity of radiant energy from the sun, about 30% of which is reflected back into space by the earth's atmosphere. The remaining energy passes through the atmosphere to the earth's surface. Some of this energy is absorbed by plants for photosynthesis and some by the oceans to evaporate water, but most of it is absorbed by soil, rocks, and water, increasing the temperature of the earth's surface. This energy is in turn radiated from the heated surface mainly as *infrared radiation,* often called *heat radiation.*

TABLE 6.5 Elemental Composition of Various Types of Coal

	Mass Percent of Each Element				
Type of Coal	C	H	O	N	S
Lignite	71	4	23	1	1
Subbituminous	77	5	16	1	1
Bituminous	80	6	8	1	5
Anthracite	92	3	3	1	1

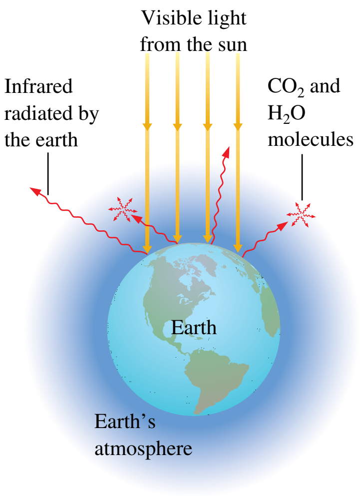


FIGURE 6.12
The earth's atmosphere is transparent to visible light from the sun. This visible light strikes the earth, and part of it is changed to infrared radiation. The infrared radiation from the earth's surface is strongly absorbed by CO_2, H_2O, and other molecules present in smaller amounts (for example, CH_4 and N_2O) in the atmosphere. In effect, the atmosphere traps some of the energy, acting like the glass in a greenhouse and keeping the earth warmer than it would otherwise be.

The average temperature of the earth's surface is 298 K. It would be 255 K without the "greenhouse gases."

The atmosphere, like window glass, is transparent to visible light but does not allow all the infrared radiation to pass back into space. Molecules in the atmosphere, principally H_2O and CO_2, strongly absorb infrared radiation and radiate it back toward the earth, as shown in Fig. 6.12, so a net amount of thermal energy is retained by the earth's atmosphere, causing the earth to be much warmer than it would be without its atmosphere. In a way, the atmosphere acts like the glass of a greenhouse, which is transparent to visible light but absorbs infrared radiation, thus raising the temperature inside the building. This **greenhouse effect** is seen even more spectacularly on Venus, where the dense atmosphere is thought to be responsible for the high surface temperature of that planet.

Thus the temperature of the earth's surface is controlled to a significant extent by the carbon dioxide and water content of the atmosphere. The effect of atmospheric moisture (humidity) is apparent in the Midwest. In summer, when the humidity is high, the heat of the sun is retained well into the night, giving very high nighttime temperatures. On the other hand, in winter, the coldest temperatures always occur on clear nights, when the low humidity allows efficient radiation of energy back into space.

The atmosphere's water content is controlled by the water cycle (evaporation and precipitation), and the average remains constant over the years. However, as fossil fuels have been used more extensively, the carbon dioxide concentration has increased by about 16% from 1880 to 1980. Comparisons of satellite data have now produced evidence that the greenhouse effect has significantly warmed the earth's atmosphere. The data compare the same areas in both 1979 and 1997. The analysis shows that more infrared radiation was blocked by CO_2, methane, and other greenhouse gases. This *could* increase the earth's average temperature by as much as 3°C, causing dramatic changes in climate and greatly affecting the growth of food crops.

How well can we predict long-term effects? Because weather has been studied for a period of time that is minuscule compared with the age of the earth, the factors that control the earth's climate in the long range are not clearly understood. For example, we do not understand what causes the earth's periodic ice ages. So it is difficult to estimate the impact of the increasing carbon dioxide levels.

In fact, the variation in the earth's average temperature over the past century is somewhat confusing. In the northern latitudes during the past century, the average temperature rose by 0.8°C over a period of 60 years, then cooled by 0.5°C during the next 25 years, and finally warmed by 0.2°C in the succeeding 15 years. Such fluctuations do not match the steady increase in carbon dioxide. However, in southern latitudes and near the equator during the past century, the average temperature showed a steady rise totaling 0.4°C.

Sheep grazing on a ranch in Australia.

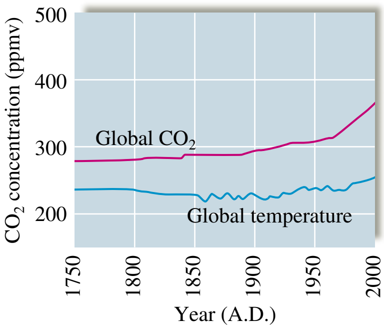


FIGURE 6.13
The atmospheric CO_2 concentration and the average global temperature over the last 250 years. Note the significant increase in CO_2 concentration in the last 50 years.
(Source: National Assessment Synthesis Team, *Climate Change Impacts on the United States: The Potential Consequences of Climate, Variability and Change, Overview,* Report for the U.S. Global Change Research Program, Cambridge University Press, Cambridge, UK, p. 13, 2000.)

This figure is in reasonable agreement with the predicted effect of the increasing carbon dioxide concentration over that period. Another significant fact is that the past 10 years constitute the warmest decade on record.

Although the exact relationship between the carbon dioxide concentration in the atmosphere and the earth's temperature is not known at present, one thing is clear: The increase in the atmospheric concentration of carbon dioxide is quite dramatic (see Fig. 6.13). We must consider the implications of this increase as we consider our future energy needs.

Methane is another greenhouse gas that is 21 times more potent than carbon dioxide. This fact is particularly significant for countries with lots of animals, because methane is produced by methanogenic archae that live in the animals' rumen. For example, sheep and cattle produce about 14% of Australia's total greenhouse emissions. To reduce this level, Australia has initiated a program to vaccinate sheep and cattle to lower the number of archae present in their digestive systems. It is hoped that this effort will reduce by 20% the amount of methane emitted by these animals.

6.6 New Energy Sources

As we search for the energy sources of the future, we need to consider economic, climatic, and supply factors. There are several potential energy sources: the sun (solar), nuclear processes (fission and fusion), biomass (plants), and synthetic fuels. Direct use of the sun's radiant energy to heat our homes and run our factories and transportation systems seems a sensible long-term goal. But what do we do now? Conservation of fossil fuels is one obvious step, but substitutes for fossil fuels also must be found. We will discuss some alternative sources of energy here. Nuclear power will be considered in Chapter 21.

Coal Conversion

One alternative energy source involves using a traditional fuel—coal—in new ways. Since transportation costs for solid coal are high, more energy-efficient fuels are being developed from coal. One possibility is to produce a gaseous fuel. Substances like coal that contain large molecules have high boiling points and tend to be solids or thick liquids. To convert coal from a solid to a gas therefore requires reducing the size of the molecules; the coal structure must be broken down in a process called *coal gasification.* This is done by treating the coal with oxygen and steam at high temperatures to break many of the carbon–carbon bonds. These bonds are replaced by carbon–hydrogen and carbon–oxygen bonds as the coal fragments react with the water and oxygen. The process is represented in Fig. 6.14. The desired product is a mixture of carbon monoxide and hydrogen called *synthetic gas,* or **syngas,** and methane (CH_4) gas. Since all the components of this product can react with oxygen to release heat in a combustion reaction, this gas is a useful fuel.

One of the most important considerations in designing an industrial process is efficient use of energy. In coal gasification, some of the reactions are exothermic:

$$\begin{aligned} C(s) + 2H_2(g) &\longrightarrow CH_4(g) \qquad \Delta H^\circ = -75\text{ kJ} \\ C(s) + \tfrac{1}{2}O_2(g) &\longrightarrow CO(g) \qquad \Delta H^\circ = -111\text{ kJ} \\ C(s) + O_2(g) &\longrightarrow CO_2(g) \qquad \Delta H^\circ = -394\text{ kJ} \end{aligned}$$

Other gasification reactions are endothermic, for example:

$$C(s) + H_2O(g) \longrightarrow H_2(g) + CO(g) \qquad \Delta H^\circ = 131\text{ kJ}$$

An industrial process must be energy efficient.

If such conditions as the rate of feed of coal, air, and steam are carefully controlled, the correct temperature can be maintained in the process without using any external energy source. That is, an energy balance is maintained.

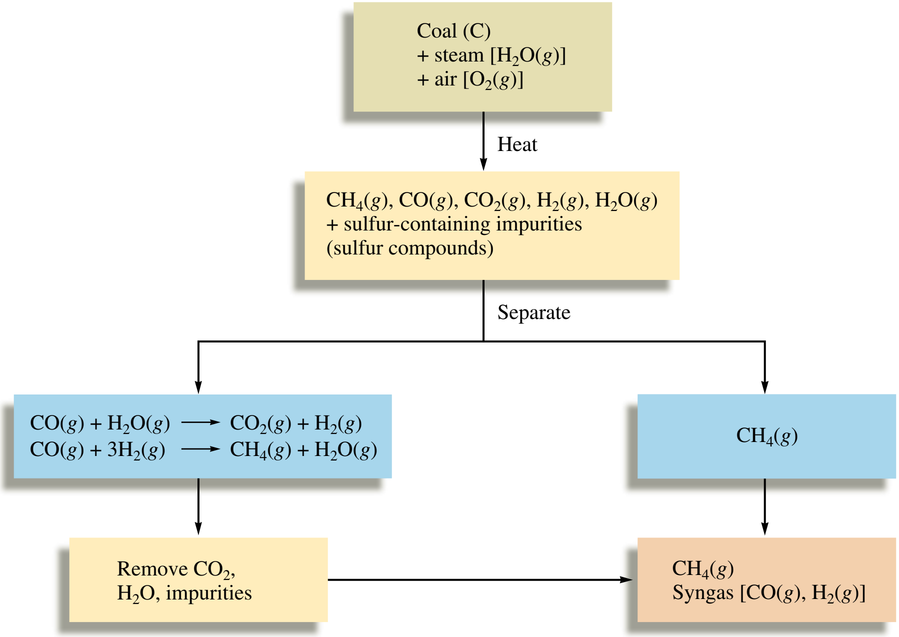


FIGURE 6.14
Coal gasification. Reaction of coal with a mixture of steam and air breaks down the large hydrocarbon molecules in the coal to smaller gaseous molecules, which can be used as fuels.

Presently only a few plants in the United States use syngas produced on site to produce electricity. These plants are being used to evaluate the economic feasibility of producing electrical power by coal gasification.

Although syngas can be used directly as a fuel, it is also important as a raw material to produce other fuels. For example, syngas can be converted directly to methanol:

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$$

Methanol is used in the production of synthetic fibers and plastics and also can be used as a fuel. In addition, it can be converted directly to gasoline. Approximately half of South Africa's gasoline supply comes from methanol produced from syngas.

In addition to coal gasification, the formation of *coal slurries* is another new use of coal. A slurry is a suspension of fine particles in a liquid, and coal must be pulverized and mixed with water to form a slurry. The slurry can be handled, stored, and burned in ways similar to those used for *residual oil,* a heavy fuel oil from petroleum accounting for almost 15% of U.S. petroleum imports. One hope is that coal slurries might replace solid coal and residual oil as fuels for electricity-generating power plants. However, the water needed for slurries might place an unacceptable burden on water resources, especially in the western states.


The main engines in the space shuttle Endeavour use hydrogen and oxygen as fuel.

Hydrogen as a Fuel

If you have ever seen a lecture demonstration where hydrogen–oxygen mixtures were ignited, you have witnessed a demonstration of hydrogen's potential as a fuel. The combustion reaction is

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -286 \text{ kJ}$$

As we saw in Sample Exercise 6.6, the heat of combustion of $H_2(g)$ per gram is approximately 2.5 times that of natural gas. In addition, hydrogen has a real advantage over fossil fuels in that the only product of hydrogen combustion is water; fossil fuels also produce carbon dioxide. However, even though it appears that hydrogen is a very logical choice as a major fuel for the future, there are three main problems: the cost of production, storage, and transport.

CHEMICAL IMPACT

Farming the Wind

In the Midwest the wind blows across fields of corn, soybeans, wheat, and wind turbines—wind turbines? It turns out that the wind that seems to blow almost continuously across the plains is now becoming the latest cash crop. One of these new-breed wind farmers is Daniel Juhl, who recently erected 17 wind turbines on six acres of land near Woodstock, Minnesota. These turbines can generate as much as 10 megawatts (MW) of electricity, which Juhl sells to the local electrical utility.

There is plenty of untapped wind-power in the United States. Wind mappers rate regions on a scale of 1 to 6 (with 6 being the best) to indicate the quality of the wind resource. Wind farms are now being developed in areas rated from 4 to 6. The farmers who own the land welcome the increased income derived from the wind blowing across their land. Economists estimate that each acre devoted to wind turbines can pay royalties to the farmers of as much as $8000 per year, or many times the revenue from growing corn on that same land. Daniel Juhl claims that farmers who construct the turbines themselves can realize as much as $20,000 per year per turbine. Globally, wind generation of electricity has nearly quadrupled in the last five years and is expected to increase by about 60% per year in the United States. The economic feasibility of wind-generated electricity has greatly improved in the last 30 years as the wind turbines have become more efficient. Today's turbines can produce electricity that costs about the same as that from other sources. The most impressive thing about wind power is the magnitude of the supply. According to the American Wind Energy Association in Washington, D.C., the wind-power potential in the United States is comparable or larger than the energy resources under the sands of Saudi Arabia.

First let's look at the production problem. Although hydrogen is very abundant on earth, virtually none of it exists as the free gas. Currently, the main source of hydrogen gas is from the treatment of natural gas with steam:

$$CH_4(g) + H_2O(g) \longrightarrow 3H_2(g) + CO(g)$$

We can calculate ΔH for this reaction using Equation (6.1):

$$\begin{aligned}\Delta H^\circ &= \Sigma n_p \Delta H_f^\circ(\text{products}) - \Sigma n_r \Delta H_f^\circ(\text{reactants}) \\ &= \Delta H_f^\circ \text{ for } CO(g) - \Delta H_f^\circ \text{ for } CH_4(g) - \Delta H_f^\circ \text{ for } H_2O(g) \\ &= -111\text{ kJ} - (-75\text{ kJ}) - (-242\text{ kJ}) = 206\text{ kJ}\end{aligned}$$

Note that this reaction is highly endothermic; treating methane with steam is not an efficient way to obtain hydrogen for fuel. It would be much more economical to burn the methane directly.

A virtually inexhaustible supply of hydrogen exists in the waters of the world's oceans. However, the reaction

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

requires 286 kJ of energy per mole of liquid water, and under current circumstances, large-scale production of hydrogen from water is not economically feasible. However, several methods for such production are currently being studied: electrolysis of water, thermal decomposition of water, thermochemical decomposition of water, and biological decomposition of water.

Electrolysis will be discussed in Chapter 17.

Electrolysis of water involves passing an electric current through it, as shown in Fig. 1.16 in Chapter 1. The present cost of electricity makes the hydrogen produced by electrolysis too expensive to be competitive as a fuel. However, if in the future we develop more efficient sources of electricity, this situation could change.

Recent research at the University of Minnesota by Lanny Schmidt and his coworkers suggests that corn could be a feasible source of hydrogen. In this process the starch from the corn is fermented to produce alcohol, which is then decomposed in a special

The biggest hurdle that must be overcome before wind power can become a significant electricity producer in the United States is construction of the transmission infrastructure—the power lines needed to move the electricity from the rural areas to the cities where most of the power is used. For example, the hundreds of turbines planned in southwest Minnesota in a development called Buffalo Ridge could supply enough electricity to power 1 million homes if transmission problems can be solved.

Another possible scenario for wind farms is to use the electrical power generated to decompose water to produce hydrogen gas that could be carried to cities by pipelines and used as a fuel. One real benefit of hydrogen is that it produces water as its only combustion product. Thus, it is essentially pollution-free.

Within a few years wind power could be a major source of electricity. There could be a fresh wind blowing across the energy landscape of the United States in the near future.

This State Line Wind Project along the Oregon-Washington border uses approximately 399 wind turbines to create enough electricity to power some 70,000 households.

reactor at 140°C with a rhodium and cerium oxide catalyst to give hydrogen. These scientists indicate that enough hydrogen gas can be obtained from a few ounces of ethanol to generate electricity to run six 60-watt bulbs for an hour.

Thermal decomposition is another method for producing hydrogen from water. This involves heating the water to several thousand degrees, where it spontaneously decomposes into hydrogen and oxygen. However, attaining temperatures in this range would be very expensive even if a practical heat source and a suitable reaction container were available.

In the thermochemical decomposition of water, chemical reactions, as well as heat, are used to "split" water into its components. One such system involves the following reactions (the temperature required for each is given in parentheses):

$$\begin{array}{rcll}
2HI & \longrightarrow & I_2 + H_2 & (425°C) \\
2H_2O + SO_2 + I_2 & \longrightarrow & H_2SO_4 + 2HI & (90°C) \\
H_2SO_4 & \longrightarrow & SO_2 + H_2O + \frac{1}{2}O_2 & (825°C) \\
\hline
\text{Net reaction: } H_2O & \longrightarrow & H_2 + \frac{1}{2}O_2 &
\end{array}$$

Note that the HI is not consumed in the net reaction. Note also that the maximum temperature required is 825°C, a temperature that is feasible if a nuclear reactor is used as a heat source. A current research goal is to find a system for which the required temperatures are low enough that sunlight can be used as the energy source.

But what about the organisms that decompose water without the aid of electricity or high temperatures? In the process of photosynthesis, green plants absorb carbon dioxide and water and use them along with energy from the sun to produce the substances needed for growth. Scientists have studied photosynthesis for years, hoping to get answers to humanity's food and energy shortages. At present, much of this research involves attempts to modify the photosynthetic process so that plants will release hydrogen gas from water instead of using the hydrogen to produce complex compounds. Small-scale experiments have shown that under certain conditions plants do produce hydrogen gas, but the yields are far from being commercially useful. At this point the economical production of hydrogen gas remains unrealized.

The storage and transportation of hydrogen also present problems. First, on metal surfaces the H_2 molecule decomposes to atoms. Since the atoms are so small, they can migrate into the metal, causing structural changes that make it brittle. This might lead to a pipeline failure if hydrogen were pumped under high pressure.

An additional problem is the relatively small amount of energy that is available *per unit volume* of hydrogen gas. Although the energy available per gram of hydrogen is significantly greater than that per gram of methane, the energy available per given volume of hydrogen is about one-third that available from the same volume of methane. This is demonstrated in Sample Exercise 6.12.

Although the use of hydrogen as a fuel solves some of the problems associated with fossil fuels, it does present some potential environmental problems of its own. Studies by John M. Eiler and his colleagues at California Institute of Technology indicate that, if hydrogen becomes a major source of energy, accidental leakage of the gas into the atmosphere could pose a threat. The Cal Tech scientists calculate that leakage could raise the concentration of H_2 in the atmosphere from its natural level of 0.5 part per million to more than 2 parts per million. As some of the H_2 eventually finds its way into the upper atmosphere, it would react with O_2 to form water, which would increase the number of ice crystals. This could lead to the destruction of some of the protective ozone because many of the chemical reactions that destroy ozone occur on the surfaces of ice crystals. However, as is the usual case with environmental issues, the situation is complicated. The scenario suggested by Eiler's team may not happen because the leaked H_2 could be consumed by soil microbes that use hydrogen as a nutrient. In fact, Eiler's studies show that 90% of the H_2 emitted into the atmosphere today from sources such as motor vehicles and forest fires is eventually absorbed by soil organisms.

The evaluation of hydrogen as a fuel illustrates how complex and interconnected the economic and environmental issues are.

Sample Exercise 6.12

Enthalpies of Combustion

Compare the energy available from the combustion of a given volume of methane and the same volume of hydrogen at the same temperature and pressure.

Solution

In Sample Exercise 6.6 we calculated the heat released for the combustion of methane and hydrogen: 55 kJ/g CH_4 and 141 kJ/g H_2. We also know from our study of gases that 1 mol $H_2(g)$ has the same volume as 1 mol $CH_4(g)$ at the same temperature and pressure (assuming ideal behavior). Thus, for molar volumes of both gases under the same conditions of temperature and pressure,

$$\frac{\text{Enthalpy of combustion of 1 molar volume of } H_2(g)}{\text{Enthalpy of combustion of 1 molar volume of } CH_4(g)}$$

$$= \frac{\text{enthalpy of combustion per mole of } H_2}{\text{enthalpy of combustion per mole of } CH_4}$$

$$= \frac{(-141\ \cancel{\text{kJ}}/\cancel{\text{g}})(2.02\ \cancel{\text{g}}\ \cancel{H_2}/\cancel{\text{mol}}\ \cancel{H_2})}{(-55\ \cancel{\text{kJ}}/\cancel{\text{g}})(16.04\ \cancel{\text{g}}\ \cancel{CH_4}/\cancel{\text{mol}}\ \cancel{CH_4})}$$

$$= \frac{-285}{-882} \approx \frac{1}{3}$$

Thus about three times the volume of hydrogen gas is needed to furnish the same energy as a given volume of methane.

See Exercise 6.78.

Could hydrogen be considered as a potential fuel for automobiles? This is an intriguing question. The internal combustion engines in automobiles can be easily adapted to burn hydrogen. In fact, BMW is now experimenting with a fleet of cars powered by hydrogen-burning internal combustion engines. However, the primary difficulty is the storage of enough hydrogen to give an automobile a reasonable range. This is illustrated by Sample Exercise 6.13.

Sample Exercise 6.13

Comparing Enthalpies of Combustion

Assuming that the combustion of hydrogen gas provides three times as much energy per gram as gasoline, calculate the volume of liquid H_2 (density = 0.0710 g/mL) required to furnish the energy contained in 80.0 L (about 20 gal) of gasoline (density = 0.740 g/mL). Calculate also the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C.

Solution

The mass of 80.0 L gasoline is

$$80.0\ \cancel{\mathrm{L}} \times \frac{1000\ \cancel{\mathrm{mL}}}{1\ \cancel{\mathrm{L}}} \times \frac{0.740\ \mathrm{g}}{\cancel{\mathrm{mL}}} = 59{,}200\ \mathrm{g}$$

Since H_2 furnishes three times as much energy per gram as gasoline, only a third as much liquid hydrogen is needed to furnish the same energy:

$$\text{Mass of } \mathrm{H_2}(l) \text{ needed} = \frac{59{,}200\ \mathrm{g}}{3} = 19{,}700\ \mathrm{g}$$

Since density = mass/volume, then volume = mass/density, and the volume of $H_2(l)$ needed is

$$\begin{aligned} V &= \frac{19{,}700\ \cancel{\mathrm{g}}}{0.0710\ \cancel{\mathrm{g}}/\mathrm{mL}} \\ &= 2.77 \times 10^5\ \mathrm{mL} = 277\ \mathrm{L} \end{aligned}$$

Thus 277 L of liquid H_2 is needed to furnish the same energy of combustion as 80.0 L of gasoline.

To calculate the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C, we use the ideal gas law:

$$PV = nRT$$

In this case

$$P = 1.00\ \mathrm{atm},\ T = 273 + 25^\circ\mathrm{C} = 298\ \mathrm{K},\ \text{and } R = 0.08206\ \mathrm{L \cdot atm/K \cdot mol}.$$

Also,

$$n = 19{,}700\ \cancel{\mathrm{g\ H_2}} \times \frac{1\ \mathrm{mol\ H_2}}{2.02\ \cancel{\mathrm{g\ H_2}}} = 9.75 \times 10^3\ \mathrm{mol\ H_2}$$

Thus

$$\begin{aligned} V = \frac{nRT}{P} &= \frac{(9.75 \times 10^3\ \cancel{\mathrm{mol}})(0.08206\ \mathrm{L} \cdot \cancel{\mathrm{atm}}/\cancel{\mathrm{K}} \cdot \cancel{\mathrm{mol}})(298\ \cancel{\mathrm{K}})}{1.00\ \cancel{\mathrm{atm}}} \\ &= 2.38 \times 10^5\ \mathrm{L} = 238{,}000\ \mathrm{L} \end{aligned}$$

At 1 atm and 25°C, the hydrogen gas needed to replace 20 gal of gasoline occupies a volume of 238,000 L.

See Exercises 6.79 and 6.80.

CHEMICAL IMPACT

Veggie Gasoline?

Gasoline usage is as high as ever, and world petroleum supplies will eventually dwindle. One possible alternative to petroleum as a source of fuels and lubricants is vegetable oil—the same vegetable oil we now use to cook french fries. Researchers believe that the oils from soybeans, corn, canola, and sunflowers all have the potential to be used in cars as well as on salads.

The use of vegetable oil for fuel is not a new idea. Rudolf Diesel reportedly used peanut oil to run one of his engines at the Paris Exposition in 1900. In addition, ethyl alcohol has been used widely as a fuel in South America and as a fuel additive in the United States.

This promotion bus both advertises biodiesel and demonstrates its usefulness

You can see from Sample Exercise 6.13 that an automobile would need a huge tank to hold enough hydrogen gas (at 1 atm) to have a typical mileage range. Clearly, hydrogen must be stored as a liquid or in some other way. Is this feasible? Because of its very low boiling point (20 K), storage of liquid hydrogen requires a superinsulated container that can withstand high pressures. Storage in this manner would be both expensive and hazardous because of the potential for explosion. Thus storage of hydrogen in the individual automobile as a liquid does not seem practical.

Metal hydrides are discussed in Chapter 18.

A much better alternative seems to be the use of metals that absorb hydrogen to form solid metal hydrides:

$$H_2(g) + M(s) \longrightarrow MH_2(s)$$

To use this method of storage, hydrogen gas would be pumped into a tank containing the solid metal in powdered form, where it would be absorbed to form the hydride, whose volume would be little more than that of the metal alone. This hydrogen would then be available for combustion in the engine by release of $H_2(g)$ from the hydride as needed:

$$MH_2(s) \longrightarrow M(s) + H_2(g)$$

Several types of solids that absorb hydrogen to form hydrides are being studied for use in hydrogen-powered vehicles. The most likely use of hydrogen in automobiles will be to power fuel cells (see Section 17.5). Ford, Honda, and Toyota are all experimenting with cars powered by hydrogen fuel cells.

Other Energy Alternatives

Many other energy sources are being considered for future use. The western states, especially Colorado, contain huge deposits of *oil shale,* which consists of a complex carbon-based material called *kerogen* contained in porous rock formations. These deposits have the potential of being a larger energy source than the vast petroleum deposits of the Middle East. The main problem with oil shale is that the trapped fuel is not fluid and cannot

Biodiesel, a fuel made by esterifying the fatty acids found in vegetable oil, has some real advantages over regular diesel fuel. Biodiesel produces fewer pollutants such as particulates, carbon monoxide, and complex organic molecules, and since vegetable oils have no sulfur, there is no noxious sulfur dioxide in the exhaust gases. Also, biodiesel can run in existing engines with little modification. In addition, biodiesel is much more biodegradable than petroleum-based fuels, so spills cause less environmental damage.

Of course, biodiesel also has some serious drawbacks. The main one is that it costs about three times as much as regular diesel fuel. Biodiesel also produces more nitrogen oxides in the exhaust than conventional diesel fuel and is less stable in storage. Biodiesel also can leave more gummy deposits in engines and must be "winterized" by removing components that tend to solidify at low temperatures.

The best solution may be to use biodiesel as an additive to regular diesel fuel. One such fuel is known as B20 because it is 20% biodiesel and 80% conventional diesel fuel. B20 is especially attractive because of the higher lubricating ability of vegetable oils, thus reducing diesel engine wear.

Vegetable oils are also being looked at as replacements for motor oils and hydraulic fluids. Tests of a sunflower seed–based engine lubricant manufactured by Renewable Lubricants of Hartville, Ohio, have shown satisfactory lubricating ability while lowering particle emissions. In addition, Lou Honary and his colleagues at the University of Northern Iowa have developed BioSOY, a vegetable oil–based hydraulic fluid for use in heavy machinery.

Veggie oil fuels and lubricants seem to have a growing market as petroleum supplies wane and as environmental laws become more stringent. In Germany's Black Forest region, for example, environmental protection laws require that farm equipment use only vegetable oil fuels and lubricants. In the near future there may be veggie oil in your garage as well as in your kitchen.

Adapted from "Fill 'Er Up . . . with Veggie Oil," by Corinna Wu, as appeared in *Science News,* Vol. 154, December 5, 1998, p. 364.

be pumped. To recover the fuel, the rock must be heated to a temperature of 250°C or higher to decompose the kerogen to smaller molecules that produce gaseous and liquid products. This process is expensive and yields large quantities of waste rock, which have a negative environmental impact.

Ethanol (C_2H_5OH) is another fuel with the potential to supplement, if not replace, gasoline. The most common method of producing ethanol is fermentation, a process in which sugar is changed to alcohol by the action of yeast. The sugar can come from virtually any source, including fruits and grains, although fuel-grade ethanol would probably come mostly from corn. Car engines can burn pure alcohol or *gasohol,* an alcohol–gasoline mixture (10% ethanol in gasoline), with little modification. Gasohol is now widely available in the United States. The use of pure alcohol as a motor fuel is not feasible in most of the United States because it does not vaporize easily when temperatures are low. However, pure ethanol could be a very practical fuel in warm climates. For example, in Brazil, large quantities of ethanol fuel are being produced for cars.


The sugars in corn are fermented and used to produce ethanol, an additive for gasoline.

Methanol (CH_3OH), an alcohol similar to ethanol, which has been used successfully for many years in race cars, is now being evaluated as a motor fuel in California. A major gasoline retailer has agreed to install pumps at 25 locations to dispense a fuel that is 85% methanol and 15% gasoline for use in specially prepared automobiles. The California Energy Commission feels that methanol has great potential for providing a secure, long-term energy supply that would alleviate air quality problems. Arizona and Colorado are also considering methanol as a major source of portable energy.

Another potential source of liquid fuels is oil squeezed from seeds (*seed oil*). For example, some farmers in North Dakota, South Africa, and Australia are now using sunflower oil to replace diesel fuel. Oil seeds, found in a wide variety of plants, can be processed to produce an oil composed mainly of carbon and hydrogen, which of course reacts with oxygen to produce carbon dioxide, water, and heat. It is hoped that oil-seed plants can be developed that will thrive under soil and climatic conditions unsuitable for corn and wheat. The main advantage of seed oil as a fuel is that it is renewable. Ideally, fuel would be grown just like food crops.

Key Terms

Section 6.1

energy
law of conservation of energy
potential energy
kinetic energy
heat
work
pathway
state function (property)
system
surroundings
exothermic
endothermic
thermodynamics
first law of thermodynamics
internal energy

Section 6.2

enthalpy
calorimeter
calorimetry
heat capacity
specific heat capacity
molar heat capacity
constant-pressure calorimetry
constant-volume calorimetry

Section 6.3

Hess's law

Section 6.4

standard enthalpy of formation
standard state

Section 6.5

fossil fuels
petroleum
natural gas
coal
greenhouse effect

Section 6.6

syngas

For Review

Energy

- The capacity to do work or produce heat
- Is conserved (first law of thermodynamics)
- Can be converted from one form to another
- Is a state function
- Potential energy: stored energy
- Kinetic energy: energy due to motion
- The internal energy for a system is the sum of its potential and kinetic energies
- The internal energy of a system can be changed by work and heat:

$$\Delta E = q + w$$

Work

- Force applied over a distance
- For an expanding/contracting gas
- Not a state function

$$w = -P\Delta V$$

Heat

- Energy flow due to a temperature difference
- Exothermic: energy as heat flows out of a system
- Endothermic: energy as heat flows into a system
- Not a state function
- Measured for chemical reactions by calorimetry

Enthalpy

- $H = E + PV$
- Is a state function
- Hess's law: the change in enthalpy in going from a given set of reactants to a given set of products is the same whether the process takes place in one step or a series of steps
- Standard enthalpies of formation (ΔH_f°) can be used to calculate ΔH for a chemical reaction

$$\Delta H^\circ_{\text{reaction}} = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H^\circ\,(\text{reactants})$$

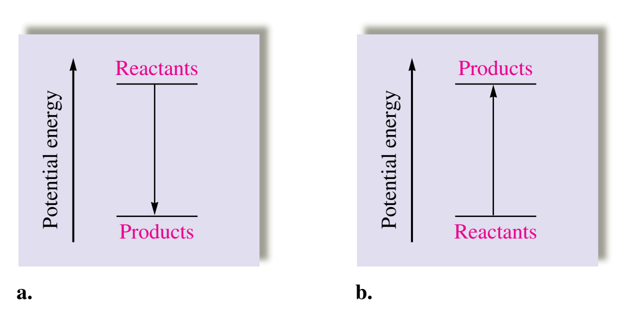
Energy use

- Energy sources from fossil fuels are associated with difficult supply and environmental impact issues
- The greenhouse effect results from release into the atmosphere of gases, including carbon dioxide, that strongly absorb infrared radiation, thus warming the earth
- Alternative fuels are being sought to replace fossil fuels:
  - Hydrogen
  - Syngas from coal
  - Biofuels from plants such as corn and certain seed-producing plants

REVIEW QUESTIONS

1. Define the following terms: potential energy, kinetic energy, path-dependent function, state function, system, surroundings.

2. Consider the following potential energy diagrams for two different reactions.



Which plot represents an exothermic reaction? In plot a, do the reactants on average have stronger or weaker bonds than the products? In plot b, reactants must gain potential energy to convert to products. How does this occur?

3. What is the first law of thermodynamics? How can a system change its internal energy, *E*? What are the sign conventions for thermodynamic quantities used in this text?
4. When a gas expands, what is the sign of *w*? Why? When a gas contracts, what is the sign of *w*? Why? What are the signs of *q* and *w* for the process of boiling water?
5. What is the heat gained/released at constant pressure equal to ($q_P = ?$)? What is the heat gained/released at constant volume equal to ($q_V = ?$)? Explain why ΔH is obtained directly from a coffee-cup calorimeter, whereas ΔE is obtained directly from a bomb calorimeter.
6. High-quality audio amplifiers generate large amounts of heat. To dissipate the heat and prevent damage to the electronic components, heat-radiating metal fins are used. Would it be better to make these fins out of iron or aluminum? Why? (See Table 6.1 for specific heat capacities.)
7. Explain how calorimetry works to calculate ΔH or ΔE for a reaction. Does the temperature of the calorimeter increase or decrease for an endothermic reaction? For an exothermic reaction? Explain.
8. What is Hess's law? When a reaction is reversed, what happens to the sign and magnitude of ΔH for that reversed reaction? When the coefficients in a balanced reaction are multiplied by a factor *n*, what happens to the sign and magnitude of ΔH for that multiplied reaction?
9. Define the standard enthalpy of formation. What are standard states for elements and for compounds? Using Hess's law, illustrate why the formula $\Delta H^\circ_{\text{reaction}} = \Sigma n_p \Delta H^\circ_f \text{ (products)} - \Sigma n_r \Delta H^\circ_f \text{ (reactants)}$ works to calculate ΔH° for a reaction.
10. What are some of the problems associated with the world's dependence on fossil fuels? What are some alternative fuels for petroleum products?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Objects placed together eventually reach the same temperature. When you go into a room and touch a piece of metal in that room, it feels colder than a piece of plastic. Explain.

2. What is meant by the term *lower in energy?* Which is lower in energy, a mixture of hydrogen and oxygen gases or liquid water? How do you know? Which of the two is more stable? How do you know?

3. A fire is started in a fireplace by striking a match and lighting crumpled paper under some logs. Explain all the energy transfers in this scenario using the terms *exothermic, endothermic, system, surroundings, potential energy,* and *kinetic energy* in the discussion.

4. Liquid water turns to ice. Is this process endothermic or exothermic? Explain what is occurring using the terms *system, surroundings, heat, potential energy,* and *kinetic energy* in the discussion.

5. Consider the following statements: “Heat is a form of energy, and energy is conserved. The heat lost by a system must be equal to the amount of heat gained by the surroundings. Therefore, heat is conserved.” Indicate everything you think is correct in these statements. Indicate everything you think is incorrect. Correct the incorrect statements and explain.

6. Consider 5.5 L of a gas at a pressure of 3.0 atm in a cylinder with a movable piston. The external pressure is changed so that the volume changes to 10.5 L.

- **a.** Calculate the work done, and indicate the correct sign.
- **b.** Use the preceding data but consider the process to occur in two steps. At the end of the first step, the volume is 7.0 L. The second step results in a final volume of 10.5 L. Calculate the work done, and indicate the correct sign.
- **c.** Calculate the work done if after the first step the volume is 8.0 L and the second step leads to a volume of 10.5 L. Does the work differ from that in part b? Explain.

7. In Question 6 the work calculated for the different conditions in the various parts of the question was different even though the system had the same initial and final conditions. Based on this information, is work a state function?

- **a.** Explain how you know that work is not a state function.
- **b.** Why does the work increase with an increase in the number of steps?
- **c.** Which two-step process resulted in more work, when the first step had the bigger change in volume or when the second step had the bigger change in volume? Explain.

8. Photosynthetic plants use the following reaction to produce glucose, cellulose, and so forth:

$$6CO_2(g) + 6H_2O(l) \xrightarrow{\text{Sunlight}} C_6H_{12}O_6(s) + 6O_2(g)$$

How might extensive destruction of forests exacerbate the greenhouse effect?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide.*

Questions

9. Consider an airplane trip from Chicago, Illinois to Denver, Colorado. List some path-dependent functions and some state functions for the plane trip

10. How is average bond strength related to relative potential energies of the reactants and the products?

11. Assuming gasoline is pure $C_8H_{18}(l)$, predict the signs of q and w for the process of combusting gasoline into $CO_2(g)$ and $H_2O(g)$.

12. What is the difference between ΔH and ΔE?

13. The enthalpy of combustion of $CH_4(g)$ when $H_2O(l)$ is formed is $^{-}891$ kJ/mol and the enthalpy of combustion of $CH_4(g)$ when $H_2O(g)$ is formed is $^{-}803$ kJ/mol. Use these data and Hess’s law to determine the enthalpy of vaporization for water.

14. Standard enthalpies of formation are relative values. What are ΔH_f° values relative to?

15. What is incomplete combustion of fossil fuels? Why can this be a problem?

16. Explain the advantages and disadvantages of hydrogen as an alternative fuel.

Exercises

In this section similar exercises are paired.

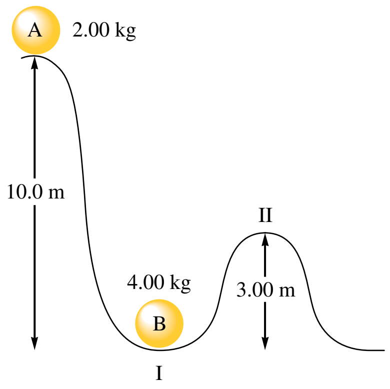
Potential and Kinetic Energy

17. Calculate the kinetic energy of a baseball (mass = 5.25 oz) with a velocity of 1.0×10^2 mi/h.

18. Calculate the kinetic energy of a 1.0×10^{-5}-g object with a velocity of 2.0×10^5 cm/s.

19. Which has the greater kinetic energy, an object with a mass of 2.0 kg and a velocity of 1.0 m/s or an object with a mass of 1.0 kg and a velocity of 2.0 m/s?

20. Consider the accompanying diagram. Ball A is allowed to fall and strike ball B. Assume that all of ball A’s energy is transferred to ball B, at point I, and that there is no loss of energy to other sources. What is the kinetic energy and the potential energy of ball B at point II? The potential energy is given by PE = mgz, where m is the mass in kilograms, g is the gravitational constant (9.81 m/s^2), and z is the distance in meters.



Heat and Work

21. Calculate ΔE for each of the following.

- **a.** $q = -47$ kJ, $w = +88$ kJ
- **b.** $q = +82$ kJ, $w = -47$ kJ
- **c.** $q = +47$ kJ, $w = 0$
- **d.** In which of these cases do the surroundings do work on the system?

22. A system undergoes a process consisting of the following two steps:

Step 1: The system absorbs 72 J of heat while 35 J of work is done on it.

Step 2: The system absorbs 35 J of heat while performing 72 J of work.

Calculate ΔE for the overall process.

23. If the internal energy of a thermodynamic system is increased by 300. J while 75 J of expansion work is done, how much heat was transferred and in which direction, to or from the system?

24. Calculate the internal energy change for each of the following.
- **a.** One hundred (100.) joules of work are required to compress a gas. At the same time, the gas releases 23 J of heat.
- **b.** A piston is compressed from a volume of 8.30 L to 2.80 L against a constant pressure of 1.90 atm. In the process, there is a heat gain by the system of 350. J.
- **c.** A piston expands against 1.00 atm of pressure from 11.2 L to 29.1 L. In the process, 1037 J of heat is absorbed.

25. A sample of an ideal gas at 15.0 atm and 10.0 L is allowed to expand against a constant external pressure of 2.00 atm at a constant temperature. Calculate the work in units of kJ for the gas expansion. (*Hint:* Boyle's law applies.)

26. A piston performs work of 210. L atm on the surroundings, while the cylinder in which it is placed expands from 10. L to 25 L. At the same time, 45 J of heat is transferred from the surroundings to the system. Against what pressure was the piston working?

27. Consider a mixture of air and gasoline vapor in a cylinder with a piston. The original volume is 40. cm^3. If the combustion of this mixture releases 950. J of energy, to what volume will the gases expand against a constant pressure of 650. torr if all the energy of combustion is converted into work to push back the piston?

28. As a system increases in volume, it absorbs 52.5 J of energy in the form of heat from the surroundings. The piston is working against a pressure of 0.500 atm. The final volume of the system is 58.0 L. What was the initial volume of the system if the internal energy of the system decreased by 102.5 J?

29. A balloon filled with 39.1 mol helium has a volume of 876 L at 0.0°C and 1.00 atm pressure. The temperature of the balloon is increased to 38.0°C as it expands to a volume of 998 L, the pressure remaining constant. Calculate q, w, and ΔE for the helium in the balloon. (The molar heat capacity for helium gas is 20.8 J/°C · mol.)

30. One mole of $H_2O(g)$ at 1.00 atm and 100.°C occupies a volume of 30.6 L. When one mole of $H_2O(g)$ is condensed to one mole of $H_2O(l)$ at 1.00 atm and 100.°C, 40.66 kJ of heat is released. If the density of $H_2O(l)$ at this temperature and pressure is 0.996 g/cm^3, calculate ΔE for the condensation of one mole of water at 1.00 atm and 100.°C.

Properties of Enthalpy

31. One of the components of polluted air is NO. It is formed in the high-temperature environment of internal combustion engines by the following reaction:

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H = 180 \text{ kJ}$$

Why are high temperatures needed to convert N_2 and O_2 to NO?

32. The reaction

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

is the last step in the commercial production of sulfuric acid. The enthalpy change for this reaction is −227 kJ. In designing a sulfuric acid plant, is it necessary to provide for heating or cooling of the reaction mixture? Explain.

33. Are the following processes exothermic or endothermic?
- **a.** When solid KBr is dissolved in water, the solution gets colder.
- **b.** Natural gas (CH_4) is burned in a furnace.
- **c.** When concentrated H_2SO_4 is added to water, the solution gets very hot.
- **d.** Water is boiled in a teakettle.

34. Are the following processes exothermic or endothermic?
- **a.** the combustion of gasoline in a car engine
- **b.** water condensing on a cold pipe
- **c.** $CO_2(s) \longrightarrow CO_2(g)$
- **d.** $F_2(g) \longrightarrow 2F(g)$

35. The overall reaction in a commercial heat pack can be represented as

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s) \qquad \Delta H = -1652 \text{ kJ}$$

- **a.** How much heat is released when 4.00 mol iron is reacted with excess O_2?
- **b.** How much heat is released when 1.00 mol Fe_2O_3 is produced?
- **c.** How much heat is released when 1.00 g iron is reacted with excess O_2?
- **d.** How much heat is released when 10.0 g Fe and 2.00 g O_2 are reacted?

36. Consider the following reaction:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -572 \text{ kJ}$$

- **a.** How much heat is evolved for the production of 1.00 mol of $H_2O(l)$?
- **b.** How much heat is evolved when 4.03 g of hydrogen is reacted with excess oxygen?
- **c.** How much heat is evolved when 186 g of oxygen is reacted wih excess hydrogen?
- **d.** The total volume of hydrogen gas needed to fill the *Hindenburg* was 2.0×10^8 L at 1.0 atm and 25°C. How much heat was evolved when the *Hindenburg* exploded, assuming all of the hydrogen reacted?

37. Consider the combustion of propane:

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2221 \text{ kJ}$$

Assume that all the heat in Sample Exercise 6.3 comes from the combustion of propane. What mass of propane must be burned to furnish this amount of energy assuming the heat transfer process is 60.% efficient?

38. Consider the following reaction:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -891 \text{ kJ}$$

Calculate the enthalpy change for each of the following cases:
- **a.** 1.00 g methane is burned in excess oxygen.
- **b.** 1.00×10^3 L methane gas at 740. torr and 25°C is burned in excess oxygen.

39. For the process $H_2O(l) \longrightarrow H_2O(g)$ at 298 K and 1.0 atm, ΔH is more positive than ΔE by 2.5 kJ/mol. What does the 2.5 kJ/mol quantity represent?

40. For the following reactions at constant pressure, predict if $\Delta H > \Delta E$, $\Delta H < \Delta E$, or $\Delta H = \Delta E$.

a. $2HF(g) \longrightarrow H_2(g) + F_2(g)$

b. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

c. $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

Calorimetry and Heat Capacity

41. Consider the substances in Table 6.1. Which substance requires the largest amount of energy to raise the temperature of 25.0 g of the substance from 15.0°C to 37.0°C? Calculate the energy. Which substance in Table 6.1 has the largest temperature change when 550. g of the substance absorbs 10.7 kJ of energy? Calculate the temperature change.

42. The specific heat capacity of silver is 0.24 J/°C · g.

a. Calculate the energy required to raise the temperature of 150.0 g Ag from 273 K to 298 K.

b. Calculate the energy required to raise the temperature of 1.0 mol Ag by 1.0°C (called the *molar heat capacity* of silver).

c. It takes 1.25 kJ of energy to heat a sample of pure silver from 12.0°C to 15.2°C. Calculate the mass of the sample of silver.

43. A 5.00-g sample of one of the substances listed in Table 6.1 was heated from 25.2°C to 55.1°C, requiring 133 J to do so. What substance was it?

44. It takes 585 J of energy to raise the temperature of 125.6 g mercury from 20.0°C to 53.5°C. Calculate the specific heat capacity and the molar heat capacity of mercury.

45. A 30.0-g sample of water at 280. K is mixed with 50.0 g of water at 330. K. Calculate the final temperature of the mixture assuming no heat loss to the surroundings.

46. A biology experiment requires the preparation of a water bath at 37.0°C (body temperature). The temperature of the cold tap water is 22.0°C, and the temperature of the hot tap water is 55.0°C. If a student starts with 90.0 g of cold water, what mass of hot water must be added to reach 37.0°C?

47. A 5.00-g sample of aluminum pellets (specific heat capacity = 0.89 J/°C · g) and a 10.00-g sample of iron pellets (specific heat capacity = 0.45 J/°C · g) are heated to 100.0°C. The mixture of hot iron and aluminum is then dropped into 97.3 g of water at 22.0°C. Calculate the final temperature of the metal and water mixture, assuming no heat loss to the surroundings.

48. Hydrogen gives off 120. J/g of energy when burned in oxygen, and methane gives off 50. J/g under the same circumstances. If a mixture of 5.0 g of hydrogen and 10. g of methane is burned, and the heat released is transferred to 50.0 g of water at 25.0°C, what final temperature will be reached by the water?

49. A 150.0-g sample of a metal at 75.0°C is added to 150.0 g of H_2O at 15.0°C. The temperature of the water rises to 18.3°C. Calculate the specific heat capacity of the metal, assuming that all the heat lost by the metal is gained by the water.

50. A 110.-g sample of copper (specific heat capacity = 0.20 J/°C · g) is heated to 82.4°C and then placed in a container of water at 22.3°C. The final temperature of the water and copper is 24.9°C. What is the mass of the water in the container, assuming that all the heat lost by the copper is gained by the water?

51. In a coffee-cup calorimeter, 50.0 mL of 0.100 *M* $AgNO_3$ and 50.0 mL of 0.100 *M* HCl are mixed to yield the following reaction:

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

The two solutions were initially at 22.60°C, and the final temperature is 23.40°C. Calculate the heat that accompanies this reaction in kJ/mol of AgCl formed. Assume that the combined solution has a mass of 100.0 g and a specific heat capacity of 4.18 J/°C · g.

52. In a coffee-cup calorimeter, 1.60 g of NH_4NO_3 is mixed with 75.0 g of water at an initial temperature of 25.00°C. After dissolution of the salt, the final temperature of the calorimeter contents is 23.34°C. Assuming the solution has a heat capacity of 4.18 J/°C · g and assuming no heat loss to the calorimeter, calculate the enthalpy change for the dissolution of NH_4NO_3 in units of kJ/mol.

53. Consider the dissolution of $CaCl_2$:

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq) \qquad \Delta H = -81.5 \text{ kJ}$$

An 11.0-g sample of $CaCl_2$ is dissolved in 125 g of water, with both substances at 25.0°C. Calculate the final temperature of the solution assuming no heat lost to the surroundings and assuming the solution has a specific heat capacity of 4.18 J/°C · g.

54. Consider the reaction

$$2HCl(aq) + Ba(OH)_2(aq) \longrightarrow BaCl_2(aq) + 2H_2O(l) \qquad \Delta H = -118 \text{ kJ}$$

Calculate the heat when 100.0 mL of 0.500 *M* HCl is mixed with 300.0 mL of 0.100 *M* $Ba(OH)_2$. Assuming that the temperature of both solutions was initially 25.0°C and that the final mixture has a mass of 400.0 g and a specific heat capacity of 4.18 J/°C · g, calculate the final temperature of the mixture.

55. The heat capacity of a bomb calorimeter was determined by burning 6.79 g of methane (energy of combustion = −802 kJ/mol CH_4) in the bomb. The temperature changed by 10.8°C.

a. What is the heat capacity of the bomb?

b. A 12.6-g sample of acetylene, C_2H_2, produced a temperature increase of 16.9°C in the same calorimeter. What is the energy of combustion of acetylene (in kJ/mol)?

56. A 0.1964-g sample of quinone ($C_6H_4O_2$) is burned in a bomb calorimeter that has a heat capacity of 1.56 kJ/°C. The temperature of the calorimeter increases by 3.2°C. Calculate the energy of combustion of quinone per gram and per mole.

Hess's Law

57. The enthalpy of combustion of solid carbon to form carbon dioxide is −393.7 kJ/mol carbon, and the enthalpy of combustion of carbon monoxide to form carbon dioxide is −283.3 kJ/mol CO. Use these data to calculate ΔH for the reaction

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

58. Combustion reactions involve reacting a substance with oxygen. When compounds containing carbon and hydrogen are combusted, carbon dioxide and water are the products. Using the enthalpies of combustion for C_4H_4 (−2341 kJ/mol), C_4H_8 (−2755 kJ/mol), and H_2 (−286 kJ/mol), calculate ΔH for the reaction

$$C_4H_4(g) + 2H_2(g) \longrightarrow C_4H_8(g)$$

59. Given the following data

$$\begin{aligned} NH_3(g) &\longrightarrow \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) & \Delta H &= 46\text{ kJ} \\ 2H_2(g) + O_2(g) &\longrightarrow 2H_2O(g) & \Delta H &= -484\text{ kJ} \end{aligned}$$

calculate ΔH for the reaction

$$2N_2(g) + 6H_2O(g) \longrightarrow 3O_2(g) + 4NH_3(g)$$

On the basis of the enthalpy change, is this a useful reaction for the synthesis of ammonia?

60. Given the following data

$$\begin{aligned} 2ClF(g) + O_2(g) &\longrightarrow Cl_2O(g) + F_2O(g) & \Delta H &= 167.4\text{ kJ} \\ 2ClF_3(g) + 2O_2(g) &\longrightarrow Cl_2O(g) + 3F_2O(g) & \Delta H &= 341.4\text{ kJ} \\ 2F_2(g) + O_2(g) &\longrightarrow 2F_2O(g) & \Delta H &= -43.4\text{ kJ} \end{aligned}$$

calculate ΔH for the reaction

$$ClF(g) + F_2(g) \longrightarrow ClF_3(g)$$

61. Given the following data

$$\begin{aligned} 2O_3(g) &\longrightarrow 3O_2(g) & \Delta H &= -427\text{ kJ} \\ O_2(g) &\longrightarrow 2O(g) & \Delta H &= +495\text{ kJ} \\ NO(g) + O_3(g) &\longrightarrow NO_2(g) + O_2(g) & \Delta H &= -199\text{ kJ} \end{aligned}$$

calculate ΔH for the reaction

$$NO(g) + O(g) \longrightarrow NO_2(g)$$

62. The bombardier beetle uses an explosive discharge as a defensive measure. The chemical reaction involved is the oxidation of hydroquinone by hydrogen peroxide to produce quinone and water:

$$C_6H_4(OH)_2(aq) + H_2O_2(aq) \longrightarrow C_6H_4O_2(aq) + 2H_2O(l)$$

Calculate ΔH for this reaction from the following data:

$$\begin{aligned} C_6H_4(OH)_2(aq) &\longrightarrow C_6H_4O_2(aq) + H_2(g) \\ & & \Delta H &= +177.4\text{ kJ} \\ H_2(g) + O_2(g) &\longrightarrow H_2O_2(aq) & \Delta H &= -191.2\text{ kJ} \\ H_2(g) + \tfrac{1}{2}O_2(g) &\longrightarrow H_2O(g) & \Delta H &= -241.8\text{ kJ} \\ H_2O(g) &\longrightarrow H_2O(l) & \Delta H &= -43.8\text{ kJ} \end{aligned}$$

63. Given the following data

$$\begin{aligned} Ca(s) + 2C(graphite) &\longrightarrow CaC_2(s) & \Delta H &= -62.8\text{ kJ} \\ Ca(s) + \tfrac{1}{2}O_2(g) &\longrightarrow CaO(s) & \Delta H &= -635.5\text{ kJ} \\ CaO(s) + H_2O(l) &\longrightarrow Ca(OH)_2(aq) & \Delta H &= -653.1\text{ kJ} \\ C_2H_2(g) + \tfrac{5}{2}O_2(g) &\longrightarrow 2CO_2(g) + H_2O(l) & \Delta H &= -1300.\text{ kJ} \\ C(graphite) + O_2(g) &\longrightarrow CO_2(g) & \Delta H &= -393.5\text{ kJ} \end{aligned}$$

calculate ΔH for the reaction

$$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + C_2H_2(g)$$

64. Given the following data

$$\begin{aligned} P_4(s) + 6Cl_2(g) &\longrightarrow 4PCl_3(g) & \Delta H &= -1225.6\text{ kJ} \\ P_4(s) + 5O_2(g) &\longrightarrow P_4O_{10}(s) & \Delta H &= -2967.3\text{ kJ} \\ PCl_3(g) + Cl_2(g) &\longrightarrow PCl_5(g) & \Delta H &= -84.2\text{ kJ} \\ PCl_3(g) + \tfrac{1}{2}O_2(g) &\longrightarrow Cl_3PO(g) & \Delta H &= -285.7\text{ kJ} \end{aligned}$$

calculate ΔH for the reaction

$$P_4O_{10}(s) + 6PCl_5(g) \longrightarrow 10Cl_3PO(g)$$

Standard Enthalpies of Formation

65. Give the definition of the standard enthalpy of formation for a substance. Write separate reactions for the formation of NaCl, H_2O, $C_6H_{12}O_6$, and $PbSO_4$ that have ΔH° values equal to ΔH_f° for each compound.

66. Write reactions for which the enthalpy change will be

a. ΔH_f° for solid aluminum oxide.

b. The standard enthalpy of combustion of liquid ethanol, $C_2H_5OH(l)$.

c. The standard enthalpy of neutralization of sodium hydroxide solution by hydrochloric acid.

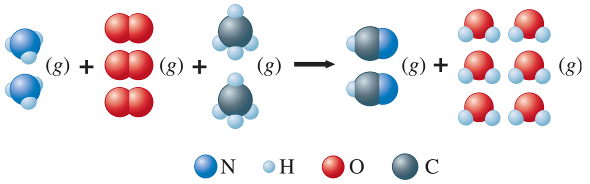
d. ΔH_f° for gaseous vinyl chloride, $C_2H_3Cl(g)$.

e. The enthalpy of combustion of liquid benzene, $C_6H_6(l)$.

f. The enthalpy of solution of solid ammonium bromide.

67. Use the values of ΔH_f° in Appendix 4 to calculate ΔH° for the following reactions.

a.

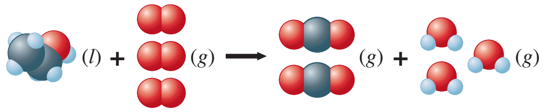


b. $Ca_3(PO_4)_2(s) + 3H_2SO_4(l) \longrightarrow 3CaSO_4(s) + 2H_3PO_4(l)$

c. $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

68. Use the values of ΔH_f° in Appendix 4 to calculate ΔH° for the following reactions. (See Exercise 67.)

a.



b. $SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$

c. $MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(s)$

69. The Ostwald process for the commercial production of nitric acid from ammonia and oxygen involves the following steps:

$$\begin{aligned} 4NH_3(g) + 5O_2(g) &\longrightarrow 4NO(g) + 6H_2O(g) \\ 2NO(g) + O_2(g) &\longrightarrow 2NO_2(g) \\ 3NO_2(g) + H_2O(l) &\longrightarrow 2HNO_3(aq) + NO(g) \end{aligned}$$

a. Use the values of ΔH_f° in Appendix 4 to calculate the value of ΔH° for each of the preceding reactions.

b. Write the overall equation for the production of nitric acid by the Ostwald process by combining the preceding equations. (Water is also a product.) Is the overall reaction exothermic or endothermic?

70. Calculate $\Delta H°$ for each of the following reactions using the data in Appendix 4:

$$4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$$
$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$
$$2Na(s) + CO_2(g) \longrightarrow Na_2O(s) + CO(g)$$

Explain why a water or carbon dioxide fire extinguisher might not be effective in putting out a sodium fire.

71. The reusable booster rockets of the space shuttle use a mixture of aluminum and ammonium perchlorate as fuel. A possible reaction is

$$3Al(s) + 3NH_4ClO_4(s) \longrightarrow Al_2O_3(s) + AlCl_3(s) + 3NO(g) + 6H_2O(g)$$

Calculate $\Delta H°$ for this reaction.

72. The space shuttle orbiter utilizes the oxidation of methylhydrazine by dinitrogen tetroxide for propulsion:

$$4N_2H_3CH_3(l) + 5N_2O_4(l) \longrightarrow 12H_2O(g) + 9N_2(g) + 4CO_2(g)$$

Calculate $\Delta H°$ for this reaction.

73. Consider the reaction

$$2ClF_3(g) + 2NH_3(g) \longrightarrow N_2(g) + 6HF(g) + Cl_2(g) \qquad \Delta H° = -1196 \text{ kJ}$$

Calculate $\Delta H_f°$ for $ClF_3(g)$.

74. The standard enthalpy of combustion of ethene gas, $C_2H_4(g)$, is −1411.1 kJ/mol at 298 K. Given the following enthalpies of formation, calculate $\Delta H_f°$ for $C_2H_4(g)$.

$CO_2(g)$	−393.5 kJ/mol
$H_2O(l)$	−285.8 kJ/mol

Energy Consumption and Sources

75. Ethanol (C_2H_5OH) has been proposed as an alternative fuel. Calculate the standard of enthalpy of combustion per gram of liquid ethanol.

76. Methanol (CH_3OH) has also been proposed as an alternative fuel. Calculate the standard enthalpy of combustion per gram of liquid methanol and compare this answer to that for ethanol in Exercise 75.

77. Some automobiles and buses have been equipped to burn propane (C_3H_8). Compare the amounts of energy that can be obtained per gram of $C_3H_8(g)$ and per gram of gasoline, assuming that gasoline is pure octane, $C_8H_{18}(l)$. (See Sample Exercise 6.11.) Look up the boiling point of propane. What disadvantages are there to using propane instead of gasoline as a fuel?

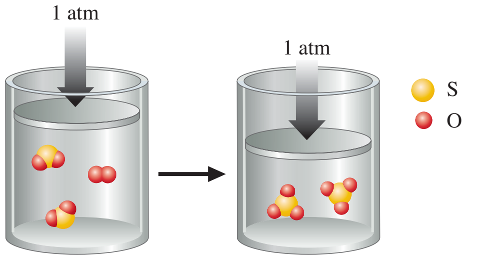
78. Acetylene (C_2H_2) and butane (C_4H_{10}) are gaseous fuels with enthalpies of combustion of −49.9 kJ/g and −49.5 kJ/g, respectively. Compare the energy available from the combustion of a given volume of acetylene to the combustion energy from the same volume of butane at the same temperature and pressure.

79. Assume that 4.19×10^6 kJ of energy is needed to heat a home. If this energy is derived from the combustion of methane (CH_4), what volume of methane, measured at STP, must be burned? ($\Delta H°_{\text{combustion}}$ for $CH_4 = -891$ kJ/mol)

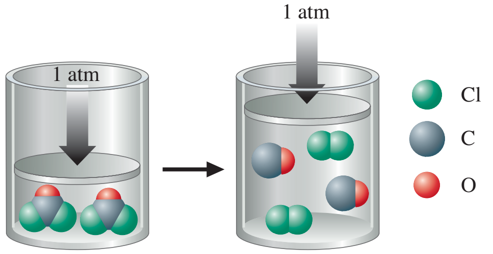
80. The complete combustion of acetylene, $C_2H_2(g)$, produces 1300. kJ of energy per mole of acetylene consumed. How many grams of acetylene must be burned to produce enough heat to raise the temperature of 1.00 gal of water by 10.0°C if the process is 80.0% efficient? Assume the density of water is 1.00 g/cm^3.

Additional Exercises

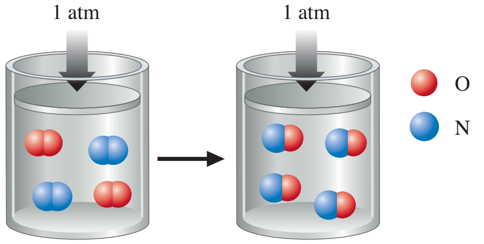
81. Three gas-phase reactions were run in a constant-pressure piston apparatus as illustrated below. For each reaction, give the balanced reaction and predict the sign of w (the work done) for the reaction.



a.



b.



c.

If just the balanced reactions were given, how could you predict the sign of w for a reaction?

82. Consider the following changes:

a. $N_2(g) \longrightarrow N_2(l)$
b. $CO(g) + H_2O(g) \longrightarrow H_2(g) + CO_2(g)$
c. $Ca_3P_2(s) + 6H_2O(l) \longrightarrow 3Ca(OH)_2(s) + 2PH_3(g)$
d. $2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$
e. $I_2(s) \longrightarrow I_2(g)$

At constant temperature and pressure, in which of these changes is work done by the system on the surroundings? By the surroundings on the system? In which of them is no work done?

83. Consider the following cyclic process carried out in two steps on a gas:

Step 1: 45 J of heat is added to the gas, and 10. J of expansion work is performed.

Step 2: 60. J of heat is removed from the gas as the gas is compressed back to the initial state.

Calculate the work for the gas compression in Step 2.

84. Calculate $\Delta H°$ for the reaction

$$2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$$

A 5.00-g chunk of potassium is dropped into 1.00 kg water at 24.0°C. What is the final temperature of the water after the preceding reaction occurs? Assume that all the heat is used to raise the temperature of the water. (Never run this reaction. It is very dangerous; it bursts into flame!)

85. The enthalpy of neutralization for the reaction of a strong acid with a strong base is −56 kJ/mol of water produced. How much energy will be released when 200.0 mL of 0.400 *M* HCl is mixed with 150.0 mL of 0.500 *M* NaOH?

86. When 1.00 L of 2.00 *M* Na_2SO_4 solution at 30.0°C is added to 2.00 L of 0.750 *M* $Ba(NO_3)_2$ solution at 30.0°C in a calorimeter, a white solid ($BaSO_4$) forms. The temperature of the mixture increases to 42.0°C. Assuming that the specific heat capacity of the solution is 6.37 J/°C · g and that the density of the final solution is 2.00 g/mL, calculate the enthalpy change per mole of $BaSO_4$ formed.

87. If a student performs an endothermic reaction in a calorimeter, how does the calculated value of ΔH differ from the actual value if the heat exchanged with the calorimeter is not taken into account?

88. In a bomb calorimeter, the reaction vessel is surrounded by water that must be added for each experiment. Since the amount of water is not constant from experiment to experiment, the mass of water must be measured in each case. The heat capacity of the calorimeter is broken down into two parts: the water and the calorimeter components. If a calorimeter contains 1.00 kg water and has a total heat capacity of 10.84 kJ/°C, what is the heat capacity of the calorimeter components?

89. The bomb calorimeter in Exercise 88 is filled with 987 g of water. The initial temperature of the calorimeter contents is 23.32°C. A 1.056-g sample of benzoic acid ($\Delta E_{\text{comb}} = -26.42$ kJ/g) is combusted in the calorimeter. What is the final temperature of the calorimeter contents?

90. Given the following data

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H° = -23 \text{ kJ}$$
$$3Fe_2O_3(s) + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g) \qquad \Delta H° = -39 \text{ kJ}$$
$$Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g) \qquad \Delta H° = +18 \text{ kJ}$$

calculate $\Delta H°$ for the reaction

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

91. At 298 K, the standard enthalpies of formation for $C_2H_2(g)$ and $C_6H_6(l)$ are 227 kJ/mol and 49 kJ/mol, respectively.

a. Calculate $\Delta H°$ for

$$C_6H_6(l) \longrightarrow 3C_2H_2(g)$$

b. Both acetylene (C_2H_2) and benzene (C_6H_6) can be used as fuels. Which compound would liberate more energy per gram when combusted in air?

92. Using the following data, calculate the standard heat of formation of ICl(*g*) in kJ/mol:

$$Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H° = 242.3 \text{ kJ}$$
$$I_2(g) \longrightarrow 2I(g) \qquad \Delta H° = 151.0 \text{ kJ}$$
$$ICl(g) \longrightarrow I(g) + Cl(g) \qquad \Delta H° = 211.3 \text{ kJ}$$
$$I_2(s) \longrightarrow I_2(g) \qquad \Delta H° = 62.8 \text{ kJ}$$

93. Calculate $\Delta H°$ for each of the following reactions, which occur in the atmosphere.

a. $C_2H_4(g) + O_3(g) \longrightarrow CH_3CHO(g) + O_2(g)$

b. $O_3(g) + NO(g) \longrightarrow NO_2(g) + O_2(g)$

c. $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$

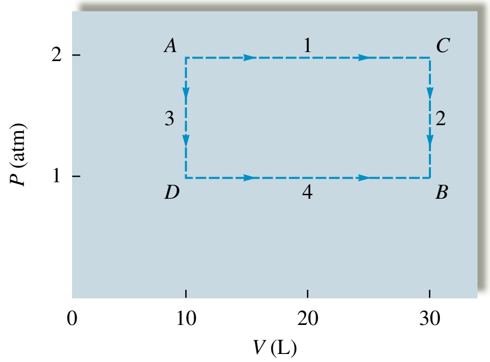
d. $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Challenge Problems

94. Consider 2.00 mol of an ideal gas that is taken from state *A* (P_A = 2.00 atm, V_A = 10.0 L) to state *B* (P_B = 1.00 atm, V_B = 30.0 L) by two different pathways:

$$\begin{tikzcd}
 & \begin{pmatrix} V_C = 30.0\text{ L} \\ P_C = 2.00\text{ atm} \end{pmatrix} \arrow[dr, "2"] & \\
\text{State } A \; \begin{pmatrix} V_A = 10.0\text{ L} \\ P_A = 2.00\text{ atm} \end{pmatrix} \arrow[ur, "1"] \arrow[dr, "3"'] & & \text{State } B \; \begin{pmatrix} V_B = 30.0\text{ L} \\ P_B = 1.00\text{ atm} \end{pmatrix} \\
 & \begin{pmatrix} V_D = 10.0\text{ L} \\ P_D = 1.00\text{ atm} \end{pmatrix} \arrow[ur, "4"'] &
\end{tikzcd}$$

These pathways are summarized on the following graph of *P* versus *V*:



Calculate the work (in units of J) associated with the two pathways. Is work a state function? Explain.

95. Combustion of table sugar produces $CO_2(g)$ and $H_2O(l)$. When 1.46 g of table sugar is combusted in a constant-volume (bomb) calorimeter, 24.00 kJ of heat is liberated.

a. Assuming that table sugar is pure sucrose, $C_{12}H_{22}O_{11}(s)$, write the balanced equation for the combustion reaction.

b. Calculate ΔE in kJ/mol $C_{12}H_{22}O_{11}$ for the combustion reaction of sucrose.

c. Calculate ΔH in kJ/mol $C_{12}H_{22}O_{11}$ for the combustion reaction of sucrose at 25°C.

96. The sun supplies energy at a rate of about 1.0 kilowatt per square meter of surface area (1 watt = 1 J/s). The plants in an agricultural field produce the equivalent of 20. kg of sucrose ($C_{12}H_{22}O_{11}$) per hour per hectare (1 ha = 10,000 m^2). Assuming that sucrose is produced by the reaction

$$12CO_2(g) + 11H_2O(l) \longrightarrow C_{12}H_{22}O_{11}(s) + 12O_2(g) \qquad \Delta H = 5640 \text{ kJ}$$

calculate the percentage of sunlight used to produce the sucrose—that is, determine the efficiency of photosynthesis.

97. The best solar panels currently available are about 13% efficient in converting sunlight to electricity. A typical home will use about 40. kWh of electricity per day (1 kWh = 1 kilowatt hour; 1 kW = 1000 J/s). Assuming 8.0 hours of useful sunlight per day, calculate the minimum solar panel surface area necessary to provide all of a typical home's electricity. (See Exercise 96 for the energy rate supplied by the sun.)

98. On Easter Sunday, April 3, 1983, nitric acid spilled from a tank car near downtown Denver, Colorado. The spill was neutralized with sodium carbonate:

$$2HNO_3(aq) + Na_2CO_3(s) \longrightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$$

a. Calculate $\Delta H°$ for this reaction. Approximately 2.0×10^4 gal nitric acid was spilled. Assume that the acid was an aqueous solution containing 70.0% HNO_3 by mass with a density of 1.42 g/cm^3. How much sodium carbonate was required for complete neutralization of the spill, and how much heat was evolved? ($\Delta H_f°$ for $NaNO_3(aq) = -467$ kJ/mol)

b. According to *The Denver Post* for April 4, 1983, authorities feared that dangerous air pollution might occur during the neutralization. Considering the magnitude of $\Delta H°$, what was their major concern?

99. A piece of chocolate cake contains about 400 Calories. A nutritional Calorie is equal to 1000 calories (thermochemical calories), which is equal to 4.184 kJ. How many 8-in-high steps must a 180-lb man climb to expend the 400 Cal from the piece of cake? See Exercise 20 for the formula for potential energy.

100. The standard enthalpy of formation of $H_2O(l)$ at 298 K is −285.8 kJ/mol. Calculate the change in internal energy for the following process at 298 K and 1 atm:

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta E° = ?$$

(*Hint:* Using the ideal gas equation, derive an expression for work in terms of *n, R,* and *T.*)

101. You have a 1.00-mol sample of water at −30.°C and you heat it until you have gaseous water at 140.°C. Calculate q for the entire process. Use the following data.

Specific heat capacity of ice = 2.03 J/°C · g
Specific heat capacity of water = 4.18 J/°C · g
Specific heat capacity of steam = 2.02 J/°C · g

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H_{\text{fusion}} = 6.02 \text{ kJ/mol (at 0°C)}$$
$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H_{\text{vaporization}} = 40.7 \text{ kJ/mol (at 100.°C)}$$

102. A 500.0-g sample of an element at 195°C is dropped into an ice–water mixture; 109.5 g of ice melts and an ice–water mixture remains. Calculate the specific heat of the element. See Exercise 101 for pertinent information.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

103. The preparation of $NO_2(g)$ from $N_2(g)$ and $O_2(g)$ is an endothermic reaction:

$$N_2(g) + O_2(g) \longrightarrow NO_2(g) \text{ (unbalanced)}$$

The enthalpy change of reaction for the balanced equation (with lowest whole-number coefficients) is $\Delta H = 67.7$ kJ. If 2.50×10^2 mL of $N_2(g)$ at 100.°C and 3.50 atm and 4.50×10^2 mL of $O_2(g)$ at 100.°C and 3.50 atm are mixed, what amount of heat is necessary to synthesize $NO_2(g)$?

104. Nitromethane, CH_3NO_2, can be used as a fuel. When the liquid is burned, the (unbalanced) reaction is mainly

$$CH_3NO_2(l) + O_2(g) \longrightarrow CO_2(g) + N_2(g) + H_2O(g)$$

a. The standard enthalpy change of reaction ($\Delta H°_{\text{rxn}}$) for the balanced reaction (with lowest whole-number coefficients) is −1288.5 kJ. Calculate the $\Delta H_f°$ for nitromethane.

b. A 15.0-L flask containing a sample of nitromethane is filled with O_2 and the flask is heated to 100.ºC. At this temperature, and after the reaction is complete, the total pressure of all the gases inside the flask is 950. torr. If the mole fraction of nitrogen (χ_{nitrogen}) is 0.134 after the reaction is complete, what mass of nitrogen was produced?

105. A cubic piece of uranium metal (specific heat capacity = 0.117 J/°C · g) at 200.0°C is dropped into 1.00 L of deuterium oxide ("heavy water," specific heat capacity = 4.211 J/°C · g) at 25.5°C. The final temperature of the uranium and deuterium oxide mixture is 28.5°C. Given the densities of uranium (19.05 g/cm^3) and deuterium oxide (1.11 g/mL), what is the edge length of the cube of uranium?

Marathon Problems*

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

106. A sample consisting of 22.7 g of a nongaseous, unstable compound X is placed inside a metal cylinder with a radius of 8.00 cm, and a piston is carefully placed on the surface of the compound so that, for all practical purposes, the distance between the bottom of the cylinder and the piston is zero. (A hole in the piston allows trapped air to escape as the piston is placed on the compound; then this hole is plugged so that nothing in-

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side the cylinder can escape.) The piston-and-cylinder apparatus is carefully placed in 10.00 kg of water at 25.00°C. The barometric pressure is 778 torr.

When the compound spontaneously decomposes, the piston moves up, the temperature of the water reaches a maximum of 29.52°C, and then it gradually decreases as the water loses heat to the surrounding air. The distance between the piston and the bottom of the cylinder, at the maximum temperature, is 59.8 cm. Chemical analysis shows that the cylinder contains 0.300 mol carbon dioxide, 0.250 mol liquid water, 0.025 mol oxygen gas, and an undetermined amount of a gaseous element A.

It is known that the enthalpy change for the decomposition of X, according to the reaction described above, is −1893 kJ/mol X. The standard enthalpies of formation for gaseous carbon dioxide and liquid water are −393.5 kJ/mol and −286 kJ/mol, respectively. The heat capacity for water is 4.184 J/°C · g. The conversion factor between L · atm and J can be determined from the two values for the gas constant *R*, namely, 0.08206 L · atm/mol · K and 8.3145 J/mol · K. The vapor pressure of water at 29.5°C is 31 torr. Assume that the heat capacity of the piston-and-cylinder apparatus is negligible and that the piston has negligible mass.

Given the preceding information, determine

a. The formula for X.

b. The pressure–volume work (in kJ) for the decomposition of the 22.7-g sample of X.

c. The *molar* change in internal energy for the decomposition of X and the approximate standard enthalpy of formation for X.

107. A gaseous hydrocarbon reacts completely with oxygen gas to form carbon dioxide and water vapor. Given the following data, determine ΔH_f° for the hydrocarbon:

$$\Delta H^\circ_{\text{rxn}} = -2044.5 \text{ kJ/mol hydrocarbon}$$
$$\Delta H_f^\circ \ (CO_2) = -393.5 \text{ kJ/mol}$$
$$\Delta H_f^\circ \ (H_2O) = -242 \text{ kJ/mol}$$

Density of CO_2 and H_2O product mixture at 1.00 atm, 200.°C = 0.751g/L

The density of the hydrocarbon is less than the density of Kr at the same conditions.

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **College.hmco.com/PIC/Zumdahl7e.**