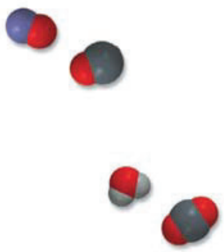
Chapter Outline

A Look Ahead

- We begin by studying the nature and different types of energy, which, in principle, are interconvertible. (6.1)
- Next, we build up our vocabulary in learning thermochemistry, which is the study of heat change in chemical reactions. We see that the vast majority of reactions are either endothermic (absorbing heat) or exothermic (releasing heat). (6.2)
- We learn that thermochemistry is part of a broader subject called the first law of thermodynamics, which is based on the law of conservation of energy. We see that the change in internal energy can be expressed in terms of the changes in heat and work done of a system. (6.3)
- We then become acquainted with a new term for energy, called enthalpy, whose change applies to processes carried out under constant-pressure conditions. (6.4)
- We learn ways to measure the heats of reaction or calorimetry, and the meaning of specific heat and heat capacity, quantities used in experimental work. (6.5)
- Knowing the standard enthalpies of formation of reactants and products enables us to calculate the enthalpy of a reaction. We will discuss ways to determine these quantities either by the direct method from the elements or by the indirect method, which is based on Hess's law of heat summation. (6.6)
- Finally, we will study the heat changes when a solute dissolves in a solvent (heat of solution) and when a solution is diluted (heat of dilution). (6.7)

Every chemical reaction obeys two fundamental laws: the law of conservation of mass and the law of conservation of energy. We discussed the mass relationship between reactants and products in Chapter 3; here we will look at the energy changes that accompany chemical reactions.



6.1 The Nature of Energy and Types of Energy

"Energy" is a much-used term that represents a rather abstract concept. For instance, when we feel tired, we might say we haven't any *energy;* and we read about the need to find alternatives to nonrenewable *energy* sources. Unlike matter, energy is known and recognized by its effects. It cannot be seen, touched, smelled, or weighed.

Energy is usually defined as *the capacity to do work.* In Chapter 5 we defined work as "force × distance," but we will soon see that there are other kinds of work. All forms of energy are capable of doing work (that is, of exerting a force over a distance), but not all of them are equally relevant to chemistry. The energy contained in tidal waves, for example, can be harnessed to perform useful work, but the relationship between tidal waves and chemistry is minimal. Chemists define ***work*** as *directed energy change resulting from a process.* Kinetic energy—the energy produced by a moving object—is one form of energy that is of particular interest to chemists. Others include radiant energy, thermal energy, chemical energy, and potential energy.

Kinetic energy was introduced in Chapter 5 (p. 203).

Radiant energy, or *solar energy, comes from the sun* and is Earth's primary energy source. Solar energy heats the atmosphere and Earth's surface, stimulates the growth of vegetation through the process known as photosynthesis, and influences global climate patterns.

Thermal energy is *the energy associated with the random motion of atoms and molecules.* In general, thermal energy can be calculated from temperature measurements. The more vigorous the motion of the atoms and molecules in a sample of matter, the hotter the sample is and the greater its thermal energy. However, we need to distinguish carefully between thermal energy and temperature. A cup of coffee at 70°C has a higher temperature than a bathtub filled with warm water at 40°C, but much more thermal energy is stored in the bathtub water because it has a much larger volume and greater mass than the coffee and therefore more water molecules and more molecular motion.

Chemical energy is *stored within the structural units of chemical substances;* its quantity is determined by the type and arrangement of constituent atoms. When substances participate in chemical reactions, chemical energy is released, stored, or converted to other forms of energy.

As the water falls over the dam, its potential energy is converted to kinetic energy. Use of this energy to generate electricity is called hydroelectric power.

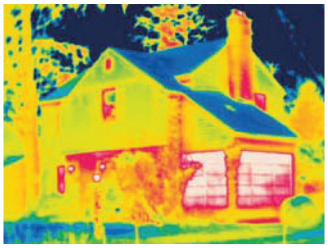
Potential energy is *energy available by virtue of an object's position.* For instance, because of its altitude, a rock at the top of a cliff has more potential energy and will make a bigger splash if it falls into the water below than a similar rock located partway down the cliff. Chemical energy can be considered a form of potential energy because it is associated with the relative positions and arrangements of atoms within a given substance.

All forms of energy can be converted (at least in principle) from one form to another. We feel warm when we stand in sunlight because radiant energy is converted to thermal energy on our skin. When we exercise, chemical energy stored in our bodies is used to produce kinetic energy. When a ball starts to roll downhill, its potential energy is converted to kinetic energy. You can undoubtedly think of many other examples. Although energy can assume many different forms that are interconvertible, scientists have concluded that energy can be neither destroyed nor created. When one form of energy disappears, some other form of energy (of equal magnitude) must appear, and vice versa. This principle is summarized by the ***law of conservation of energy:*** *the total quantity of energy in the universe is assumed constant.*

6.2 Energy Changes in Chemical Reactions

Often the energy changes that take place during chemical reactions are of as much practical interest as the mass relationships we discussed in Chapter 3. For example, combustion reactions involving fuels such as natural gas and oil are carried out in daily life more for the thermal energy they release than for their products, which are water and carbon dioxide.

Almost all chemical reactions absorb or produce (release) energy, generally in the form of heat. It is important to understand the distinction between thermal energy and heat. ***Heat*** is *the transfer of thermal energy between two bodies that are at different temperatures.* Thus, we often speak of the "heat flow" from a hot object to a cold one. Although the term "heat" by itself implies the transfer of energy, we customarily talk of "heat absorbed" or "heat released" when describing the energy changes that occur during a process. ***Thermochemistry*** is *the study of heat change in chemical reactions.*



This infrared photo shows where energy (heat) leaks through the house. The more red the color, the more energy is lost to the outside.

Animation
Heat Flow

When heat is absorbed or released during a process, energy is conserved, but it is transferred between system and surroundings.

To analyze energy changes associated with chemical reactions we must first define the ***system,*** or *the specific part of the universe that is of interest to us.* For chemists, systems usually include substances involved in chemical and physical changes. For example, in an acid-base neutralization experiment, the system may be a beaker containing 50 mL of HCl to which 50 mL of NaOH is added. The ***surroundings*** are *the rest of the universe outside the system.*

There are three types of systems. An ***open system*** *can exchange mass and energy, usually in the form of heat with its surroundings.* For example, an open system may consist of a quantity of water in an open container, as shown in Figure 6.1(a). If we close the flask, as in Figure 6.1(b), so that no water vapor can escape from or condense into the container, we create a ***closed system,*** which *allows the transfer of energy (heat) but not mass.* By placing the water in a totally insulated container, we can construct an ***isolated system,*** which *does not allow the transfer of either mass or energy,* as shown in Figure 6.1(c).

The combustion of hydrogen gas in oxygen is one of many chemical reactions that release considerable quantities of energy (Figure 6.2):

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) + \text{energy}$$

In this case, we label the reacting mixture (hydrogen, oxygen, and water molecules) the *system* and the rest of the universe the *surroundings.* Because energy cannot be

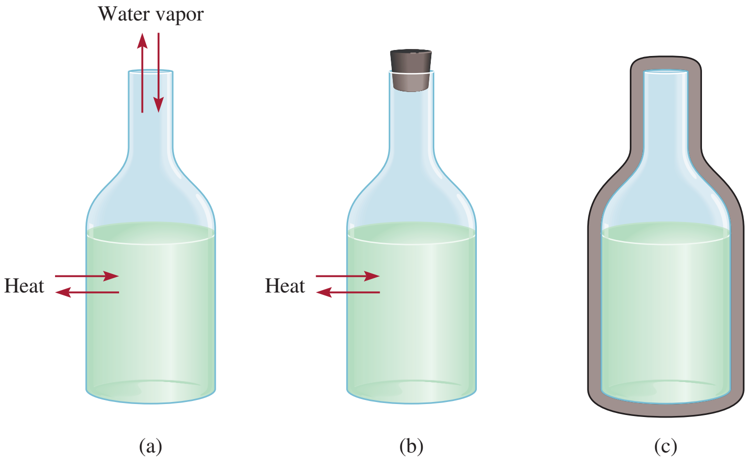


Figure 6.1 *Three systems represented by water in a flask: (a) an open system, which allows the exchange of both energy and mass with surroundings; (b) a closed system, which allows the exchange of energy but not mass; and (c) an isolated system, which allows neither energy nor mass to be exchanged (here the flask is enclosed by a vacuum jacket).*

Figure 6.2 *The Hindenburg disaster. The Hindenburg, a German airship filled with hydrogen gas, was destroyed in a spectacular fire at Lakehurst, New Jersey, in 1937.*

Exo- comes from the Greek word meaning "outside"; endo- means "within."

created or destroyed, any energy lost by the system must be gained by the surroundings. Thus, the heat generated by the combustion process is transferred from the system to its surroundings. This reaction is an example of an ***exothermic process,*** which is *any process that gives off heat*—that is, *transfers thermal energy to the surroundings.* Figure 6.3(a) shows the energy change for the combustion of hydrogen gas.

Now consider another reaction, the decomposition of mercury(II) oxide (HgO) at high temperatures:

$$\text{energy} + 2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$$

This reaction is an ***endothermic process,*** *in which heat has to be supplied to the system* (that is, to HgO) *by the surroundings* [Figure 6.3(b)].

From Figure 6.3 you can see that in exothermic reactions, the total energy of the products is less than the total energy of the reactants. The difference is the heat supplied by the system to the surroundings. Just the opposite happens in endothermic reactions. Here, the difference between the energy of the products and the energy of the reactants is equal to the heat supplied to the system by the surroundings.

On heating, HgO decomposes to give Hg and O_2.

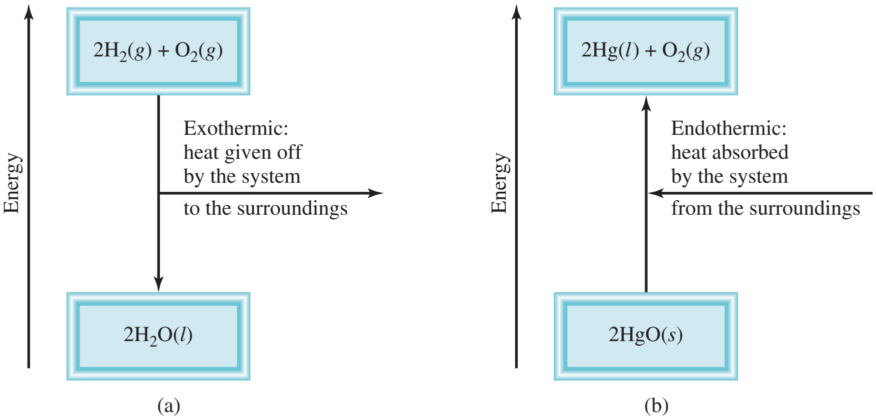


Figure 6.3 *(a) An exothermic process. (b) An endothermic process. Parts (a) and (b) are not drawn to the same scale; that is, the heat released in the formation of H_2O from H_2 and O_2 is not equal to the heat absorbed in the decomposition of HgO.*

6.3 Introduction to Thermodynamics

Thermochemistry is part of a broader subject called ***thermodynamics,*** which is *the scientific study of the interconversion of heat and other kinds of energy.* The laws of thermodynamics provide useful guidelines for understanding the energetics and directions of processes. In this section we will concentrate on the first law of thermodynamics, which is particularly relevant to the study of thermochemistry. We will continue our discussion of thermodynamics in Chapter 18.

In thermodynamics, we study changes in the ***state of a system,*** which is defined by *the values of all relevant macroscopic properties, for example, composition, energy, temperature, pressure, and volume.* Energy, pressure, volume, and temperature are said to be ***state functions***—*properties that are determined by the state of the system, regardless of how that condition was achieved.* In other words, when the state of a system changes, the magnitude of change in any state function depends only on the initial and final states of the system and not on how the change is accomplished.

Changes in state functions do not depend on the pathway, but only on the initial and final state.

The Greek letter *delta*, Δ, symbolizes change. We use Δ in this text to mean final − initial.

The First Law of Thermodynamics

The ***first law of thermodynamics,*** which is based on the law of conservation of energy, states that *energy can be converted from one form to another, but cannot be created or destroyed.*[†]

Recall that an object possesses potential energy by virtue of its position or chemical composition.

6.4 Enthalpy of Chemical Reactions

Our next step is to see how the first law of thermodynamics can be applied to processes carried out under different conditions. Specifically, we will consider two situations most commonly encountered in the laboratory; one in which the volume of the system is kept constant and one in which the pressure applied on the system is kept constant.

[†] See footnote on p. 43 (Chapter 2) for a discussion of mass and energy relationship in chemical reactions.

Enthalpy

In Section 6.5 we will discuss ways to measure heat changes at constant volume and constant pressure.

Enthalpy of Reactions

Because most reactions are constant-pressure processes, we can equate the heat change in these cases to the change in enthalpy. For any reaction of the type

$$\text{reactants} \longrightarrow \text{products}$$

we define the change in enthalpy, called the ***enthalpy of reaction, ΔH,*** as *the difference between the enthalpies of the products and the enthalpies of the reactants:*

$$\Delta H = H(\text{products}) - H(\text{reactants}) \qquad (6.9)$$

The enthalpy of reaction can be positive or negative, depending on the process. For an endothermic process (heat absorbed by the system from the surroundings), ΔH is positive (that is, $\Delta H > 0$). For an exothermic process (heat released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$).

An analogy for enthalpy change is a change in the balance in your bank account. Suppose your initial balance is \$100. After a transaction (deposit or withdrawal), the change in your bank balance, ΔX, is given by

This analogy assumes that you will not overdraw your bank account. The enthalpy of a substance *cannot* be negative.

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

where X represents the bank balance. If you deposit \$80 into your account, then $\Delta X = \$180 - \$100 = \$80$. This corresponds to an endothermic reaction. (The balance increases and so does the enthalpy of the system.) On the other hand, a withdrawal of \$60 means $\Delta X = \$40 - \$100 = -\$60$. The negative sign of ΔX means your balance has decreased. Similarly, a negative value of ΔH reflects a decrease in enthalpy of the system as a result of an exothermic process. The difference between this analogy and Equation (6.9) is that while you always know your exact bank balance, there is no way to know the enthalpies of individual products and reactants. In practice, we can only measure the *difference* in their values.

Now let us apply the idea of enthalpy changes to two common processes, the first involving a physical change, the second a chemical change.

Thermochemical Equations

At 0°C and a pressure of 1 atm, ice melts to form liquid water. Measurements show that for every mole of ice converted to liquid water under these conditions, 6.01 kilojoules (kJ) of heat energy are absorbed by the system (ice). Because the pressure is constant, the heat change is equal to the enthalpy change, ΔH. Furthermore, this is an endothermic process, as expected for the energy-absorbing change of melting ice [Figure 6.6(a)]. Therefore, ΔH is a positive quantity. The equation for this physical change is

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = 6.01 \text{ kJ/mol}$$

The "per mole" in the unit for ΔH means that this is the enthalpy change *per mole of the reaction (or process) as it is written;* that is, when 1 mole of ice is converted to 1 mole of liquid water.

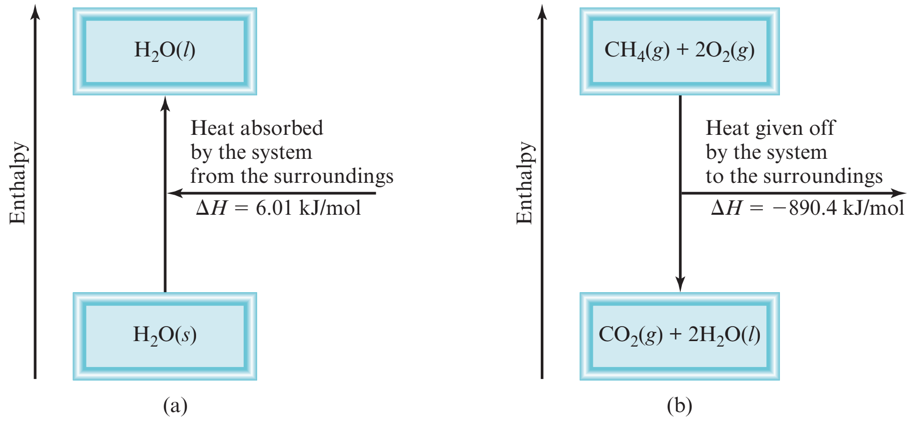


Figure 6.6 *(a) Melting 1 mole of ice at 0°C (an endothermic process) results in an enthalpy increase in the system of 6.01 kJ. (b) Burning 1 mole of methane in oxygen gas (an exothermic process) results in an enthalpy decrease in the system of 890.4 kJ. Parts (a) and (b) are not drawn to the same scale.*

As another example, consider the combustion of methane (CH_4), the principal component of natural gas:

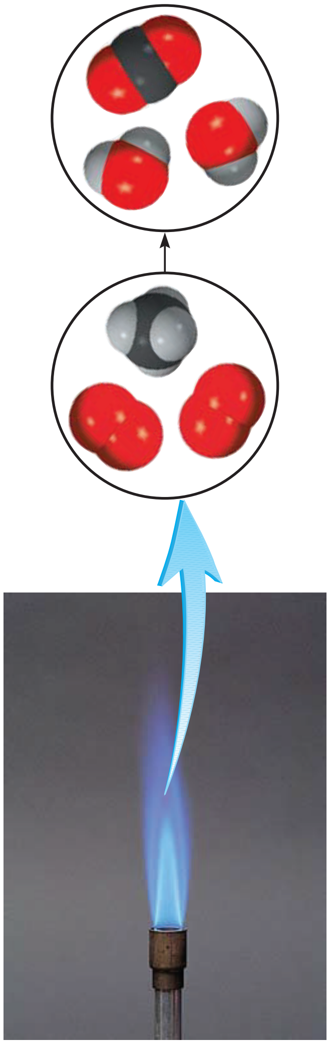
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.4 \text{ kJ/mol}$$

From experience we know that burning natural gas releases heat to the surroundings, so it is an exothermic process. Under constant-pressure condition this heat change is equal to enthalpy change and ΔH must have a negative sign [Figure 6.6(b)]. Again, the per mole of reaction unit for ΔH means that when 1 mole of CH_4 reacts with 2 moles of O_2 to produce 1 mole of CO_2 and 2 moles of liquid H_2O, 890.4 kJ of heat energy are released to the surroundings. It is important to keep in mind that the ΔH value does not refer to a particular reactant or product. It simply means that the quoted ΔH value refers to all the reacting species in molar quantities. Thus, the following conversion factors can be created:

$$\frac{-890.4 \text{ kJ}}{1 \text{ mol } CH_4} \qquad \frac{-890.4 \text{ kJ}}{2 \text{ mol } O_2} \qquad \frac{-890.4 \text{ kJ}}{1 \text{ mol } CO_2} \qquad \frac{-890.4 \text{ kJ}}{2 \text{ mol } H_2O}$$

Expressing ΔH in units of kJ/mol (rather than just kJ) conforms to the standard convention; its merit will become apparent when we continue our study of thermodynamics in Chapter 18.

The equations for the melting of ice and the combustion of methane are examples of ***thermochemical equations,*** which *show the enthalpy changes as well as the mass relationships.* It is essential to specify a balanced equation when quoting the enthalpy change of a reaction. The following guidelines are helpful in writing and interpreting thermochemical equations.



Methane gas burning from a Bunsen burner.

1. When writing thermochemical equations, we must always specify the physical states of all reactants and products, because they help determine the actual enthalpy changes. For example, in the equation for the combustion of methane, if we show water vapor rather than liquid water as a product,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H = -802.4 \text{ kJ/mol}$$

the enthalpy change is −802.4 kJ rather than −890.4 kJ because 88.0 kJ are needed to convert 2 moles of liquid water to water vapor; that is,

$$2H_2O(l) \longrightarrow 2H_2O(g) \qquad \Delta H = 88.0 \text{ kJ/mol}$$

Note that H is an extensive quantity.

2. If we multiply both sides of a thermochemical equation by a factor n, then ΔH must also change by the same factor. Returning to the melting of ice

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = 6.01\ \text{kJ/mol}$$

If we multiply the equation throughout by 2; that is, if we set $n = 2$, then

$$2H_2O(s) \longrightarrow 2H_2O(l) \qquad \Delta H = 2(6.01\ \text{kJ/mol}) = 12.0\ \text{kJ/mol}$$

3. When we reverse an equation, we change the roles of reactants and products. Consequently, the magnitude of ΔH for the equation remains the same, but its sign changes. For example, if a reaction consumes thermal energy from its surroundings (that is, if it is endothermic), then the reverse reaction must release thermal energy back to its surroundings (that is, it must be exothermic) and the enthalpy change expression must also change its sign. Thus, reversing the melting of ice and the combustion of methane, the thermochemical equations become

$$H_2O(l) \longrightarrow H_2O(s) \qquad \Delta H = -6.01\ \text{kJ/mol}$$
$$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \qquad \Delta H = 890.4\ \text{kJ/mol}$$

and what was an endothermic process becomes exothermic, and vice versa.

EXAMPLE 6.3

Given the thermochemical equation

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta H = -198.2\ \text{kJ/mol}$$

calculate the heat evolved when 87.9 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3.

Strategy The thermochemical equation shows that for every 2 moles of SO_2 reacted, 198.2 kJ of heat are given off (note the negative sign). Therefore, the conversion factor is

$$\frac{-198.2\ \text{kJ}}{2\ \text{mol}\ SO_2}$$

How many moles of SO_2 are in 87.9 g of SO_2? What is the conversion factor between grams and moles?

Solution We need to first calculate the number of moles of SO_2 in 87.9 g of the compound and then find the number of kilojoules produced from the exothermic reaction. The sequence of conversions is as follows:

$$\text{grams of } SO_2 \longrightarrow \text{moles of } SO_2 \longrightarrow \text{kilojoules of heat generated}$$

Therefore, the enthalpy change for this reaction is given by

$$\Delta H = 87.9\ \cancel{\text{g}\ SO_2} \times \frac{1\ \cancel{\text{mol}\ SO_2}}{64.07\ \cancel{\text{g}\ SO_2}} \times \frac{-198.2\ \text{kJ}}{2\ \cancel{\text{mol}\ SO_2}} = \boxed{-136\ \text{kJ}}$$

and the heat released to the surroundings is 136 kJ.

(Continued)

Check Because 87.9 g is less than twice the molar mass of SO_2 (2 × 64.07 g) as shown in the preceding thermochemical equation, we expect the heat released to be smaller than 198.2 kJ.

Similar problem: 6.26.

Practice Exercise Calculate the heat evolved when 266 g of white phosphorus (P_4) burns in air according to the equation

$$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s) \qquad \Delta H = -3013 \text{ kJ/mol}$$

Sodium reacting with water to form hydrogen gas.

Recall that 1 L · atm = 101.3 J.

For reactions that do not result in a change in the number of moles of gases from reactants to products [for example, $H_2(g) + F_2(g) \longrightarrow 2HF(g)$], $\Delta E = \Delta H$.

6.5 Calorimetry

In the laboratory, heat changes in physical and chemical processes are measured with a *calorimeter,* a closed container designed specifically for this purpose. Our discussion of ***calorimetry,*** *the measurement of heat changes,* will depend on an understanding of specific heat and heat capacity, so let us consider them first.

Figure 6.7 *(a) A beaker of water inside a cylinder fitted with a movable piston. The pressure inside is equal to the atmospheric pressure. (b) As the sodium metal reacts with water, the hydrogen gas generated pushes the piston upward (doing work on the surroundings) until the pressure inside is again equal to the pressure outside.*

(a) (b)

TABLE 6.2

The Specific Heats of Some Common Substances

Substance	Specific Heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

Specific Heat and Heat Capacity

The ***specific heat*** (***s***) of a substance is *the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius.* It has the units J/g · °C. The ***heat capacity*** (***C***) of a substance is *the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius.* Its units are J/°C. Specific heat is an intensive property whereas heat capacity is an extensive property. The relationship between the heat capacity and specific heat of a substance is

$$C = ms \tag{6.11}$$

where m is the mass of the substance in grams. For example, the specific heat of water is 4.184 J/g · °C, and the heat capacity of 60.0 g of water is

$$(60.0\text{ g})(4.184\text{ J/g}\cdot{}^\circ\text{C}) = 251\text{ J/}^\circ\text{C}$$

Table 6.2 shows the specific heat of some common substances.

If we know the specific heat and the amount of a substance, then the change in the sample's temperature (Δt) will tell us the amount of heat (q) that has been absorbed or released in a particular process. The equations for calculating the heat change are given by

$$q = ms\Delta t \tag{6.12}$$

$$q = C\Delta t \tag{6.13}$$

where Δt is the temperature change:

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

The sign convention for q is the same as that for enthalpy change; q is positive for endothermic processes and negative for exothermic processes.

EXAMPLE 6.5

A 466-g sample of water is heated from 8.50°C to 74.60°C. Calculate the amount of heat absorbed (in kilojoules) by the water.

Strategy We know the quantity of water and the specific heat of water. With this information and the temperature rise, we can calculate the amount of heat absorbed (q).

Solution Using Equation (6.12), we write

$$\begin{aligned} q &= ms\Delta t \\ &= (466\text{ g})(4.184\text{ J/g}\cdot{}^\circ\text{C})(74.60^\circ\text{C} - 8.50^\circ\text{C}) \\ &= 1.29 \times 10^5\text{ J} \times \frac{1\text{ kJ}}{1000\text{ J}} \\ &= 129\text{ kJ} \end{aligned}$$

Check The units g and °C cancel, and we are left with the desired unit kJ. Because heat is absorbed by the water from the surroundings, it has a positive sign.

Similar problem: 6.33.

Practice Exercise An iron bar of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

Constant-Volume Calorimetry

Heat of combustion is usually measured by placing a known mass of a compound in a steel container called a *constant-volume bomb calorimeter,* which is filled with oxygen at about 30 atm of pressure. The closed bomb is immersed in a known amount of water, as shown in Figure 6.8. The sample is ignited electrically, and the heat produced by the combustion reaction can be calculated accurately by recording the rise in temperature of the water. The heat given off by the sample is absorbed by the water and the bomb. The special design of the calorimeter enables us to assume that no heat (or mass) is lost to the surroundings during the time it takes to make measurements. Therefore, we can call the bomb and the water in which it is submerged an isolated system. Because no heat enters or leaves the system throughout the process, the heat change of the system (q_{system}) must be zero and we can write

"Constant volume" refers to the volume of the container, which does not change during the reaction. Note that the container remains intact after the measurement. The term "bomb calorimeter" connotes the explosive nature of the reaction (on a small scale) in the presence of excess oxygen gas.

$$\begin{aligned} q_{\text{system}} &= q_{\text{cal}} + q_{\text{rxn}} \\ &= 0 \end{aligned} \tag{6.14}$$

where q_{cal} and q_{rxn} are the heat changes for the calorimeter and the reaction, respectively. Thus,

$$q_{\text{rxn}} = -q_{\text{cal}} \tag{6.15}$$

To calculate q_{cal}, we need to know the heat capacity of the calorimeter (C_{cal}) and the temperature rise, that is,

Note that C_{cal} comprises both the bomb and the surrounding water.

$$q_{\text{cal}} = C_{\text{cal}}\Delta t \tag{6.16}$$

The quantity C_{cal} is calibrated by burning a substance with an accurately known heat of combustion. For example, it is known that the combustion of 1 g of benzoic acid

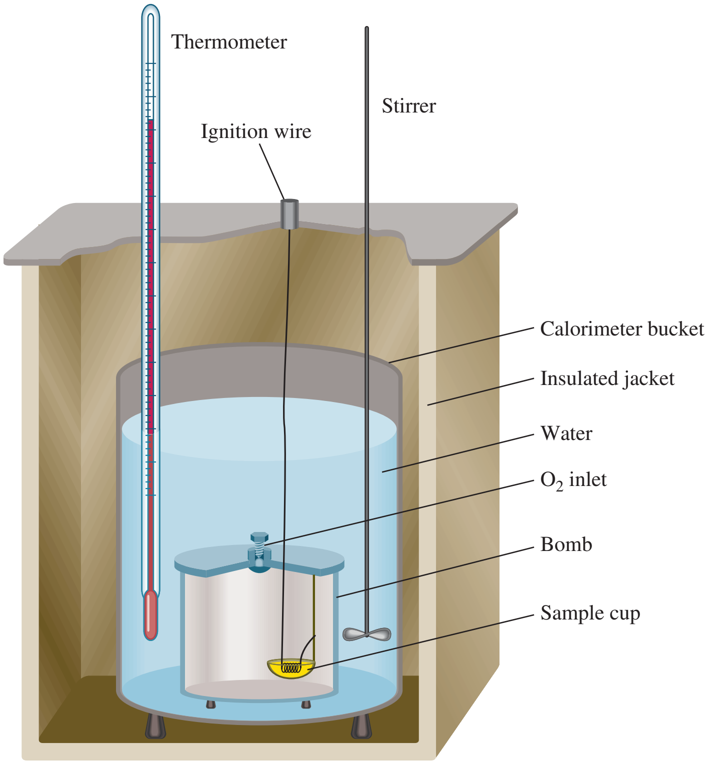


Figure 6.8 *A constant-volume bomb calorimeter. The calorimeter is filled with oxygen gas before it is placed in the bucket. The sample is ignited electrically, and the heat produced by the reaction can be accurately determined by measuring the temperature increase in the known amount of surrounding water.*

(C_6H_5COOH) releases 26.42 kJ of heat. If the temperature rise is 4.673°C, then the heat capacity of the calorimeter is given by

Note that although the combustion reaction is exothermic, q_{cal} is a positive quantity because it represents the heat absorbed by the calorimeter.

$$\begin{aligned} C_{\text{cal}} &= \frac{q_{\text{cal}}}{\Delta t} \\ &= \frac{26.42\ \text{kJ}}{4.673°\text{C}} = 5.654\ \text{kJ/°C} \end{aligned}$$

Once C_{cal} has been determined, the calorimeter can be used to measure the heat of combustion of other substances.

Note that because reactions in a bomb calorimeter occur under constant-volume rather than constant-pressure conditions, the heat changes *do not* correspond to the enthalpy change ΔH (see Section 6.4). It is possible to correct the measured heat changes so that they correspond to ΔH values, but the corrections usually are quite small so we will not concern ourselves with the details here. Finally, it is interesting to note that the energy contents of food and fuel (usually expressed in calories where 1 cal = 4.184 J) are measured with constant-volume calorimeters.

$C_{10}H_8$

EXAMPLE 6.6

A quantity of 1.435 g of naphthalene ($C_{10}H_8$), a pungent-smelling substance used in moth repellents, was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 20.28°C to 25.95°C. If the heat capacity of the bomb plus water was 10.17 kJ/°C, calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.

Strategy Knowing the heat capacity and the temperature rise, how do we calculate the heat absorbed by the calorimeter? What is the heat generated by the combustion of 1.435 g of naphthalene? What is the conversion factor between grams and moles of naphthalene?

Solution The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change. From Equation (6.16), assuming no heat is lost to the surroundings, we write

$$\begin{aligned} q_{\text{cal}} &= C_{\text{cal}}\Delta t \\ &= (10.17\ \text{kJ/°C})(25.95°\text{C} - 20.28°\text{C}) \\ &= 57.66\ \text{kJ} \end{aligned}$$

Because $q_{\text{sys}} = q_{\text{cal}} + q_{\text{rxn}} = 0$, $q_{\text{cal}} = -q_{\text{rxn}}$. The heat change of the reaction is -57.66 kJ. This is the heat released by the combustion of 1.435 g of $C_{10}H_8$; therefore, we can write the conversion factor as

$$\frac{-57.66\ \text{kJ}}{1.435\ \text{g}\ C_{10}H_8}$$

The molar mass of naphthalene is 128.2 g, so the heat of combustion of 1 mole of naphthalene is

$$\begin{aligned} \text{molar heat of combustion} &= \frac{-57.66\ \text{kJ}}{1.435\ \cancel{\text{g}\ C_{10}H_8}} \times \frac{128.2\ \cancel{\text{g}\ C_{10}H_8}}{1\ \text{mol}\ C_{10}H_8} \\ &= -5.151 \times 10^3\ \text{kJ/mol} \end{aligned}$$

(Continued)

Check Knowing that the combustion reaction is exothermic and that the molar mass of naphthalene is much greater than 1.4 g, is the answer reasonable? Under the reaction conditions, can the heat change (−57.66 kJ) be equated to the enthalpy change of the reaction?

Similar problem: 6.37.

Practice Exercise A quantity of 1.922 g of methanol (CH_3OH) was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose by 4.20°C. If the heat capacity of the bomb plus water was 10.4 kJ/°C, calculate the molar heat of combustion of methanol.

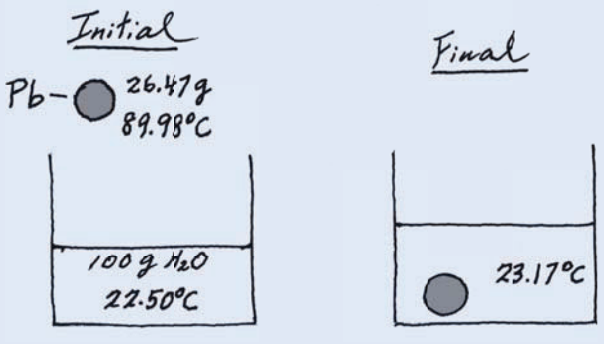
Constant-Pressure Calorimetry

A simpler device than the constant-volume calorimeter is the constant-pressure calorimeter, which is used to determine the heat changes for noncombustion reactions. A crude constant-pressure calorimeter can be constructed from two Styrofoam coffee cups, as shown in Figure 6.9. This device measures the heat effects of a variety of reactions, such as acid-base neutralization, as well as the heat of solution and heat of dilution. Because the pressure is constant, the heat change for the process (q_{rxn}) is equal to the enthalpy change (ΔH). As in the case of a constant-volume calorimeter, we treat the calorimeter as an isolated system. Furthermore, we neglect the small heat capacity of the coffee cups in our calculations. Table 6.3 lists some reactions that have been studied with the constant-pressure calorimeter.

EXAMPLE 6.7

A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat of the lead pellet?

Strategy A sketch of the initial and final situation is as follows:



(Continued)

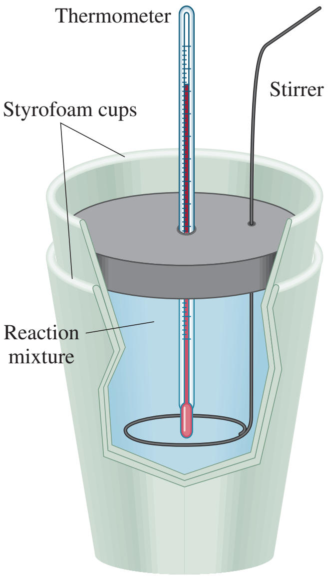


Figure 6.9 *A constant-pressure calorimeter made of two Styrofoam coffee cups. The outer cup helps to insulate the reacting mixture from the surroundings. Two solutions of known volume containing the reactants at the same temperature are carefully mixed in the calorimeter. The heat produced or absorbed by the reaction can be determined by measuring the temperature change.*

TABLE 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	−56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	44.0*
Heat of reaction	$MgCl_2(s) + 2Na(l) \longrightarrow 2NaCl(s) + Mg(s)$	−180.2

*Measured at 25°C. At 100°C, the value is 40.79 kJ.

We know the masses of water and the lead pellet as well as the initial and final temperatures. Assuming no heat is lost to the surroundings, we can equate the heat lost by the lead pellet to the heat gained by the water. Knowing the specific heat of water, we can then calculate the specific heat of lead.

Solution Treating the calorimeter as an isolated system (no heat lost to the surroundings), we write

$$q_{\text{Pb}} + q_{\text{H}_2\text{O}} = 0$$

or

$$q_{\text{Pb}} = -q_{\text{H}_2\text{O}}$$

The heat gained by the water is given by

$$q_{\text{H}_2\text{O}} = ms\Delta t$$

where m and s are the mass and specific heat and $\Delta t = t_{\text{final}} - t_{\text{initial}}$. Therefore,

$$\begin{aligned} q_{\text{H}_2\text{O}} &= (100.0\ \text{g})(4.184\ \text{J/g}\cdot{}^\circ\text{C})(23.17^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 280.3\ \text{J} \end{aligned}$$

Because the heat lost by the lead pellet is equal to the heat gained by the water, so $q_{\text{Pb}} = -280.3$ J. Solving for the specific heat of Pb, we write

$$\begin{aligned} q_{\text{Pb}} &= ms\Delta t \\ -280.3\ \text{J} &= (26.47\ \text{g})(s)(23.17^\circ\text{C} - 89.98^\circ\text{C}) \\ s &= 0.158\ \text{J/g}\cdot{}^\circ\text{C} \end{aligned}$$

Similar problem: 6.82.

Check The specific heat falls within the metals shown in Table 6.2.

Practice Exercise A 30.14-g stainless steel ball bearing at 117.82°C is placed in a constant-pressure calorimeter containing 120.0 mL of water at 18.44°C. If the specific heat of the ball bearing is 0.474 J/g · °C, calculate the final temperature of the water. Assume the calorimeter to have negligible heat capacity.

EXAMPLE 6.8

A quantity of 1.00×10^2 mL of 0.500 M HCl was mixed with 1.00×10^2 mL of 0.500 M NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same, 22.50°C, and the final temperature of the mixed solution was 25.86°C. Calculate the heat change for the neutralization reaction on a molar basis

$$\text{NaOH}(aq) + \text{HCl}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 4.184 J/g · °C, respectively).

Strategy Because the temperature rose, the neutralization reaction is exothermic. How do we calculate the heat absorbed by the combined solution? What is the heat of the reaction? What is the conversion factor for expressing the heat of reaction on a molar basis?

Solution Assuming no heat is lost to the surroundings, $q_{\text{sys}} = q_{\text{soln}} + q_{\text{rxn}} = 0$, so $q_{\text{rxn}} = -q_{\text{soln}}$, where q_{soln} is the heat absorbed by the combined solution. Because

(Continued)

CHEMISTRY *in Action*

Fuel Values of Foods and Other Substances

The food we eat is broken down, or metabolized, in stages by a group of complex biological molecules called enzymes. Most of the energy released at each stage is captured for function and growth. One interesting aspect of metabolism is that the overall change in energy is the same as it is in combustion. For example, the total enthalpy change for the conversion of glucose ($C_6H_{12}O_6$) to carbon dioxide and water is the same whether we burn the substance in air or digest it in our bodies:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2801 \text{ kJ/mol}$$

The important difference between metabolism and combustion is that the latter is usually a one-step, high-temperature process. Consequently, much of the energy released by combustion is lost to the surroundings.

Various foods have different compositions and hence different energy contents. The energy content of food is generally measured in calories. The *calorie* (*cal*) is a non-SI unit of energy that is equivalent to 4.184 J:

$$1 \text{ cal} = 4.184 \text{ J}$$

In the context of nutrition, however, the calorie we speak of (sometimes called a "big calorie") is actually equal to a *kilocalorie;* that is,

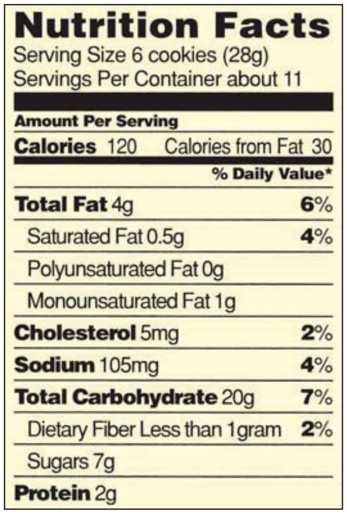
$$1 \text{ Cal} = 1000 \text{ cal} = 4184 \text{ J}$$

Note the use of a capital "C" to represent the "big calorie."

The bomb calorimeter described in Section 6.5 is ideally suited for measuring the energy content, or "fuel value," of foods. Fuel values are just the enthalpies of combustion (see table). In order to be analyzed in a bomb calorimeter, food must be dried first because most foods contain a considerable amount of water. Because the composition of particular foods is often not known, fuel values are expressed in terms of kJ/g rather than kJ/mol.

Fuel Values of Foods and Some Common Fuels

Substance	$\Delta H_{\text{combustion}}$ (kJ/g)
Apple	−2
Beef	−8
Beer	−1.5
Bread	−11
Butter	−34
Cheese	−18
Eggs	−6
Milk	−3
Potatoes	−3
Charcoal	−35
Coal	−30
Gasoline	−34
Kerosene	−37
Natural gas	−50
Wood	−20



Nutrition Facts
Serving Size 6 cookies (28g)
Servings Per Container about 11

Amount Per Serving	
Calories 120	Calories from Fat 30
	% Daily Value*
Total Fat 4g	**6%**
Saturated Fat 0.5g	**4%**
Polyunsaturated Fat 0g	
Monounsaturated Fat 1g	
Cholesterol 5mg	**2%**
Sodium 105mg	**4%**
Total Carbohydrate 20g	**7%**
Dietary Fiber Less than 1gram	**2%**
Sugars 7g	
Protein 2g	

The labels on food packages reveal the calorie content of the food inside.

the density of the solution is 1.00 g/mL, the mass of a 100-mL solution is 100 g. Thus,

$$\begin{aligned} q_{\text{soln}} &= ms\Delta t \\ &= (1.00 \times 10^2\ \text{g} + 1.00 \times 10^2\ \text{g})(4.184\ \text{J/g} \cdot {}^\circ\text{C})(25.86^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 2.81 \times 10^3\ \text{J} \\ &= 2.81\ \text{kJ} \end{aligned}$$

Because $q_{\text{rxn}} = -q_{\text{soln}}$, $q_{\text{rxn}} = -2.81$ kJ.

From the molarities given, the number of moles of both HCl and NaOH in 1.00×10^2 mL solution is

$$\frac{0.500\ \text{mol}}{1\ \text{L}} \times 0.100\ \text{L} = 0.0500\ \text{mol}$$

Therefore, the heat of neutralization when 1.00 mole of HCl reacts with 1.00 mole of NaOH is

$$\text{heat of neutralization} = \frac{-2.81\ \text{kJ}}{0.0500\ \text{mol}} = -56.2\ \text{kJ/mol}$$

Check Is the sign consistent with the nature of the reaction? Under the reaction condition, can the heat change be equated to the enthalpy change?

Practice Exercise A quantity of 4.00×10^2 mL of 0.600 *M* HNO_3 is mixed with 4.00×10^2 mL of 0.300 *M* $Ba(OH)_2$ in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of both solutions is the same at 18.46°C. What is the final temperature of the solution? (Use the result in Example 6.8 for your calculation.)

6.6 Standard Enthalpy of Formation and Reaction

So far we have learned that we can determine the enthalpy change that accompanies a reaction by measuring the heat absorbed or released (at constant pressure). From Equation (6.9) we see that ΔH can also be calculated if we know the actual enthalpies of all reactants and products. However, as mentioned earlier, there is no way to measure the *absolute* value of the enthalpy of a substance. Only values *relative* to an arbitrary reference can be determined. This problem is similar to the one geographers face in expressing the elevations of specific mountains or valleys. Rather than trying to devise some type of "absolute" elevation scale (perhaps based on distance from the center of Earth?), by common agreement all geographic heights and depths are expressed relative to sea level, an arbitrary reference with a defined elevation of "zero" meters or feet. Similarly, chemists have agreed on an arbitrary reference point for enthalpy.

The "sea level" reference point for all enthalpy expressions is called the ***standard enthalpy of formation*** **(ΔH_f°).** Substances are said to be in the ***standard state*** at 1 atm,[†] hence the term "standard enthalpy." The superscript "°" represents standard-state

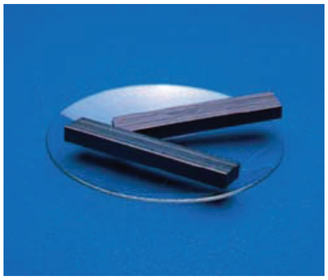
---

[†] In thermodynamics, the standard pressure is defined as 1 bar, where 1 bar = 10^5 Pa = 0.987 atm. Because 1 bar differs from 1 atm by only 1.3 percent, we will continue to use 1 atm as the standard pressure. Note that the normal melting point and boiling point of a substance are defined in terms of 1 atm.

conditions (1 atm), and the subscript "f" stands for formation. By convention, *the standard enthalpy of formation of any element in its most stable form is zero.* Take the element oxygen as an example. Molecular oxygen (O_2) is more stable than the other allotropic form of oxygen, ozone (O_3), at 1 atm and 25°C. Thus, we can write $\Delta H_f^\circ(O_2) = 0$, but $\Delta H_f^\circ(O_3) = 142.2$ kJ/mol. Similarly, graphite is a more stable allotropic form of carbon than diamond at 1 atm and 25°C, so we have $\Delta H_f^\circ(\text{C, graphite}) = 0$ and $\Delta H_f^\circ(\text{C, diamond}) = 1.90$ kJ/mol. Based on this reference for elements, we can now define the standard enthalpy of formation of a compound as *the heat change that results when 1 mole of the compound is formed from its elements at a pressure of 1 atm.* Table 6.4 lists the standard enthalpies of formation for a number of elements and compounds. (For a more complete list of ΔH_f° values, see Appendix 2.) Note that although the standard state does not specify a temperature, we will always use ΔH_f° values measured at 25°C for our discussion because most of the thermodynamic data are collected at this temperature.

The importance of the standard enthalpies of formation is that once we know their values, we can readily calculate the ***standard enthalpy of reaction, ΔH_{rxn}°,*** defined as *the enthalpy of a reaction carried out at 1 atm.* For example, consider the hypothetical reaction

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$



Graphite (top) and diamond (bottom).

TABLE 6.4 **Standard Enthalpies of Formation of Some Inorganic Substances at 25°C**

Substance	ΔH_f°(kJ/mol)	Substance	ΔH_f°(kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.0	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	$HI(g)$	25.9
$Br_2(l)$	0	$Mg(s)$	0
$HBr(g)$	−36.2	$MgO(s)$	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
$CO(g)$	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	$NO(g)$	90.4
$Ca(s)$	0	$NO_2(g)$	33.85
$CaO(s)$	−635.6	$N_2O(g)$	81.56
$CaCO_3(s)$	−1206.9	$N_2O_4(g)$	9.66
$Cl_2(g)$	0	$O(g)$	249.4
$HCl(g)$	−92.3	$O_2(g)$	0
$Cu(s)$	0	$O_3(g)$	142.2
$CuO(s)$	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
$HF(g)$	−271.6	$SO_2(g)$	−296.1
$H(g)$	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	$Zn(s)$	0
$H_2O(l)$	−285.8	$ZnO(s)$	−348.0

where a, b, c, and d are stoichiometric coefficients. For this reaction ΔH°_{rxn} is given by

$$\Delta H^\circ_{rxn} = [c\Delta H^\circ_f(C) + d\Delta H^\circ_f(D)] - [a\Delta H^\circ_f(A) + b\Delta H^\circ_f(B)] \qquad (6.17)$$

We can generalize Equation (6.17) as

$$\Delta H^\circ_{rxn} = \Sigma n\Delta H^\circ_f(\text{products}) - \Sigma m\Delta H^\circ_f(\text{reactants}) \qquad (6.18)$$

where m and n denote the stoichiometric coefficients for the reactants and products, and Σ (sigma) means "the sum of." Note that in calculations, the stoichiometric coefficients are just numbers without units.

To use Equation (6.18) to calculate ΔH°_{rxn}, we must know the ΔH°_f values of the compounds that take part in the reaction. These values can be determined by applying the direct method or the indirect method.

The Direct Method

This method of measuring ΔH°_f works for compounds that can be readily synthesized from their elements. Suppose we want to know the enthalpy of formation of carbon dioxide. We must measure the enthalpy of the reaction when carbon (graphite) and molecular oxygen in their standard states are converted to carbon dioxide in its standard state:

$$\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \qquad \Delta H^\circ_{rxn} = -393.5 \text{ kJ/mol}$$

We know from experience that this combustion easily goes to completion. Thus, from Equation (6.18) we can write

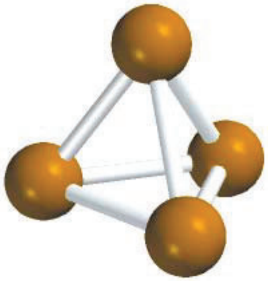
$$\begin{aligned}\Delta H^\circ_{rxn} &= \Delta H^\circ_f(\text{CO}_2, g) - [\Delta H^\circ_f(\text{C, graphite}) + \Delta H^\circ_f(\text{O}_2, g)] \\ &= -393.5 \text{ kJ/mol}\end{aligned}$$

Because both graphite and O_2 are stable allotropic forms of the elements, it follows that $\Delta H^\circ_f(\text{C, graphite})$ and $\Delta H^\circ_f(\text{O}_2, g)$ are zero. Therefore,

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f(\text{CO}_2, g) = -393.5 \text{ kJ/mol}$$

or

$$\Delta H^\circ_f(\text{CO}_2, g) = -393.5 \text{ kJ/mol}$$



P_4

Note that arbitrarily assigning zero ΔH°_f for each element in its most stable form at the standard state does not affect our calculations in any way. Remember, in thermochemistry we are interested only in enthalpy *changes* because they can be determined experimentally whereas the absolute enthalpy values cannot. The choice of a zero "reference level" for enthalpy makes calculations easier to handle. Again referring to the terrestrial altitude analogy, we find that Mt. Everest is 8708 ft higher than Mt. McKinley. This difference in altitude is unaffected by the decision to set sea level at 0 ft or at 1000 ft.

White phosphorus burns in air to form P_4O_{10}.

Other compounds that can be studied by the direct method are SF_6, P_4O_{10}, and CS_2. The equations representing their syntheses are

$$\begin{aligned}\text{S(rhombic)} + 3\text{F}_2(g) &\longrightarrow \text{SF}_6(g) \\ \text{P}_4\text{(white)} + 5\text{O}_2(g) &\longrightarrow \text{P}_4\text{O}_{10}(s) \\ \text{C(graphite)} + 2\text{S(rhombic)} &\longrightarrow \text{CS}_2(l)\end{aligned}$$

Note that S(rhombic) and P(white) are the most stable allotropes of sulfur and phosphorus, respectively, at 1 atm and 25°C, so their ΔH°_f values are zero.

The Indirect Method

Many compounds cannot be directly synthesized from their elements. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases, ΔH_f° can be determined by an indirect approach, which is based on Hess's law of heat summation, or simply Hess's law, named after the Swiss chemist Germain Hess.[†] ***Hess's law*** can be stated as follows: *When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.* In other words, if we can break down the reaction of interest into a series of reactions for which $\Delta H_{\text{rxn}}^\circ$ can be measured, we can calculate $\Delta H_{\text{rxn}}^\circ$ for the overall reaction. Hess's law is based on the fact that because H is a state function, ΔH depends only on the initial and final state (that is, only on the nature of reactants and products). The enthalpy change would be the same whether the overall reaction takes place in one step or many steps.

An analogy for Hess's law is as follows. Suppose you go from the first floor to the sixth floor of a building by elevator. The gain in your gravitational potential energy (which corresponds to the enthalpy change for the overall process) is the same whether you go directly there or stop at each floor on your way up (breaking the trip into a series of steps).

Let's say we are interested in the standard enthalpy of formation of carbon monoxide (CO). We might represent the reaction as

$$\text{C(graphite)} + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g)$$

However, burning graphite also produces some carbon dioxide (CO_2), so we cannot measure the enthalpy change for CO directly as shown. Instead, we must employ an indirect route, based on Hess's law. It is possible to carry out the following two separate reactions, which do go to completion:

$$\begin{array}{lrcll}
\text{(a)} & \text{C(graphite)} + \text{O}_2(g) & \longrightarrow & \text{CO}_2(g) & \Delta H_{\text{rxn}}^\circ = -393.5\text{ kJ/mol} \\
\text{(b)} & \text{CO}(g) + \tfrac{1}{2}\text{O}_2(g) & \longrightarrow & \text{CO}_2(g) & \Delta H_{\text{rxn}}^\circ = -283.0\text{ kJ/mol}
\end{array}$$

Remember to reverse the sign of ΔH when you reverse an equation.

First, we reverse Equation (b) to get

$$\text{(c)} \qquad \text{CO}_2(g) \longrightarrow \text{CO}(g) + \tfrac{1}{2}\text{O}_2(g) \qquad \Delta H_{\text{rxn}}^\circ = +283.0\text{ kJ/mol}$$

Because chemical equations can be added and subtracted just like algebraic equations, we carry out the operation (a) + (c) and obtain

$$\begin{array}{lrcll}
\text{(a)} & \text{C(graphite)} + \text{O}_2(g) & \longrightarrow & \text{CO}_2(g) & \Delta H_{\text{rxn}}^\circ = -393.5\text{ kJ/mol} \\
\text{(c)} & \text{CO}_2(g) & \longrightarrow & \text{CO}(g) + \tfrac{1}{2}\text{O}_2(g) & \Delta H_{\text{rxn}}^\circ = +283.0\text{ kJ/mol} \\
\hline
\text{(d)} & \text{C(graphite)} + \tfrac{1}{2}\text{O}_2(g) & \longrightarrow & \text{CO}(g) & \Delta H_{\text{rxn}}^\circ = -110.5\text{ kJ/mol}
\end{array}$$

Thus, $\Delta H_f^\circ(\text{CO}) = -110.5$ kJ/mol. Looking back, we see that the overall reaction is the formation of CO_2 [Equation (a)], which can be broken down into two parts [Equations (d) and (b)]. Figure 6.10 shows the overall scheme of our procedure.

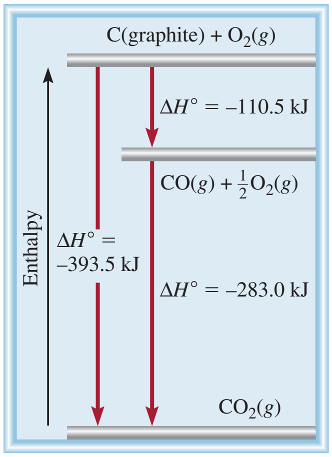


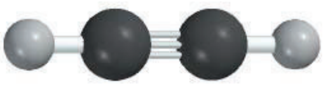
Figure 6.10 *The enthalpy change for the formation of 1 mole of CO_2 from graphite and O_2 can be broken down into two steps according to Hess's law.*

The general rule in applying Hess's law is to arrange a series of chemical equations (corresponding to a series of steps) in such a way that, when added together, all species will cancel except for the reactants and products that appear in the overall reaction. This means that we want the elements on the left and the

---

[†] Germain Henri Hess (1802–1850). Swiss chemist. Hess was born in Switzerland but spent most of his life in Russia. For formulating Hess's law, he is called the father of thermochemistry.

compound of interest on the right of the arrow. Further, we often need to multiply some or all of the equations representing the individual steps by the appropriate coefficients.



C_2H_2

An oxyacetylene torch has a high flame temperature (3000°C) and is used to weld metals.

EXAMPLE 6.9

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:

$$2\text{C(graphite)} + \text{H}_2(g) \longrightarrow \text{C}_2\text{H}_2(g)$$

The equations for each step and the corresponding enthalpy changes are

$$\begin{array}{llll}
\text{(a)} & \text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g) & \Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ/mol} \\
\text{(b)} & \text{H}_2(g) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l) & \Delta H^\circ_{\text{rxn}} = -285.8 \text{ kJ/mol} \\
\text{(c)} & 2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l) & \Delta H^\circ_{\text{rxn}} = -2598.8 \text{ kJ/mol}
\end{array}$$

Strategy Our goal here is to calculate the enthalpy change for the formation of C_2H_2 from its elements C and H_2. The reaction does not occur directly, however, so we must use an indirect route using the information given by Equations (a), (b), and (c).

Solution Looking at the synthesis of C_2H_2, we need 2 moles of graphite as reactant. So we multiply Equation (a) by 2 to get

$$\begin{array}{lll}
\text{(d)} & 2\text{C(graphite)} + 2\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) & \Delta H^\circ_{\text{rxn}} = 2(-393.5 \text{ kJ/mol}) \\
& & \phantom{\Delta H^\circ_{\text{rxn}}} = -787.0 \text{ kJ/mol}
\end{array}$$

Next, we need 1 mole of H_2 as a reactant and this is provided by Equation (b). Last, we need 1 mole of C_2H_2 as a product. Equation (c) has 2 moles of C_2H_2 as a reactant so we need to reverse the equation and divide it by 2:

$$\begin{array}{lll}
\text{(e)} & 2\text{CO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{C}_2\text{H}_2(g) + \tfrac{5}{2}\text{O}_2(g) & \Delta H^\circ_{\text{rxn}} = \tfrac{1}{2}(2598.8 \text{ kJ/mol}) \\
& & \phantom{\Delta H^\circ_{\text{rxn}}} = 1299.4 \text{ kJ/mol}
\end{array}$$

Adding Equations (d), (b), and (e) together, we get

$$\begin{array}{ll}
2\text{C(graphite)} + 2\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) & \Delta H^\circ_{\text{rxn}} = -787.0 \text{ kJ/mol} \\
\text{H}_2(g) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l) & \Delta H^\circ_{\text{rxn}} = -285.8 \text{ kJ/mol} \\
2\text{CO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{C}_2\text{H}_2(g) + \tfrac{5}{2}\text{O}_2(g) & \Delta H^\circ_{\text{rxn}} = 1299.4 \text{ kJ/mol} \\
\hline
2\text{C(graphite)} + \text{H}_2(g) \longrightarrow \text{C}_2\text{H}_2(g) & \Delta H^\circ_{\text{rxn}} = 226.6 \text{ kJ/mol}
\end{array}$$

Therefore, $\Delta H^\circ_f = \Delta H^\circ_{\text{rxn}} = 226.6$ kJ/mol. The ΔH°_f value means that when 1 mole of C_2H_2 is synthesized from 2 moles of C(graphite) and 1 mole of H_2, 226.6 kJ of heat are absorbed by the reacting system from the surroundings. Thus, this is an endothermic process.

Similar problems: 6.62, 6.63.

Practice Exercise Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that

$$\begin{array}{ll}
\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g) & \Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ/mol} \\
\text{S(rhombic)} + \text{O}_2(g) \longrightarrow \text{SO}_2(g) & \Delta H^\circ_{\text{rxn}} = -296.4 \text{ kJ/mol} \\
\text{CS}_2(l) + 3\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{SO}_2(g) & \Delta H^\circ_{\text{rxn}} = -1073.6 \text{ kJ/mol}
\end{array}$$

We can calculate the enthalpy of reactions from the values of ΔH°_f, as shown in Example 6.10

The molten iron formed in a thermite reaction is run down into a mold between the ends of two railroad rails. On cooling, the rails are welded together.

EXAMPLE 6.10

The thermite reaction involves aluminum and iron(III) oxide

$$2\text{Al}(s) + \text{Fe}_2\text{O}_3(s) \longrightarrow \text{Al}_2\text{O}_3(s) + 2\text{Fe}(l)$$

This reaction is highly exothermic and the liquid iron formed is used to weld metals. Calculate the heat released in kilojoules per gram of Al reacted with Fe_2O_3. The $\Delta H°$ for Fe(l) is 12.40 kJ/mol.

Strategy The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by its stoichiometric coefficient times the standard enthalpy of formation of the species.

Solution Using the given ΔH_f° value for Fe(l) and other ΔH_f° values in Appendix 3 and Equation (6.18), we write

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= [\Delta H_f^\circ(\text{Al}_2\text{O}_3) + 2\Delta H_f^\circ(\text{Fe})] - [2\Delta H_f^\circ(\text{Al}) + \Delta H_f^\circ(\text{Fe}_2\text{O}_3)]\\ &= [(-1669.8\text{ kJ/mol}) + 2(12.40\text{ kJ/mol})] - [2(0) + (-822.2\text{ kJ/mol})]\\ &= -822.8\text{ kJ/mol}\end{aligned}$$

This is the amount of heat released for two moles of Al reacted. We use the following ratio

$$\frac{-822.8\text{ kJ}}{2\text{ mol Al}}$$

to convert to kJ/g Al. The molar mass of Al is 26.98 g, so

$$\begin{aligned}\text{heat released per gram of Al} &= \frac{-822.8\text{ kJ}}{2\text{ mol Al}} \times \frac{1\text{ mol Al}}{26.98\text{ g Al}}\\ &= -15.25\text{ kJ/g}\end{aligned}$$

Check Is the negative sign consistent with the exothermic nature of the reaction? As a quick check, we see that 2 moles of Al weigh about 54 g and give off about 823 kJ of heat when reacted with Fe_2O_3. Therefore, the heat given off per gram of Al reacted is approximately −830 kJ/54 g or −15.4 kJ/g.

Practice Exercise Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. The standard enthalpy of formation of benzene is 49.04 kJ/mol.

when a certain amount of solute dissolves in a certain amount of solvent. The quantity ΔH_{soln} represents the difference between the enthalpy of the final solution and the enthalpies of its original components (that is, solute and solvent) before they are mixed. Thus,

ΔH_{soln}, can be read-ily determined in a constant-pressure calorimeter. Like other enthalpy changes, $\Delta H_{soln}$is positive for endothermic (heat-absorbing) processes and negative for exothermic (heat-generating) processes.

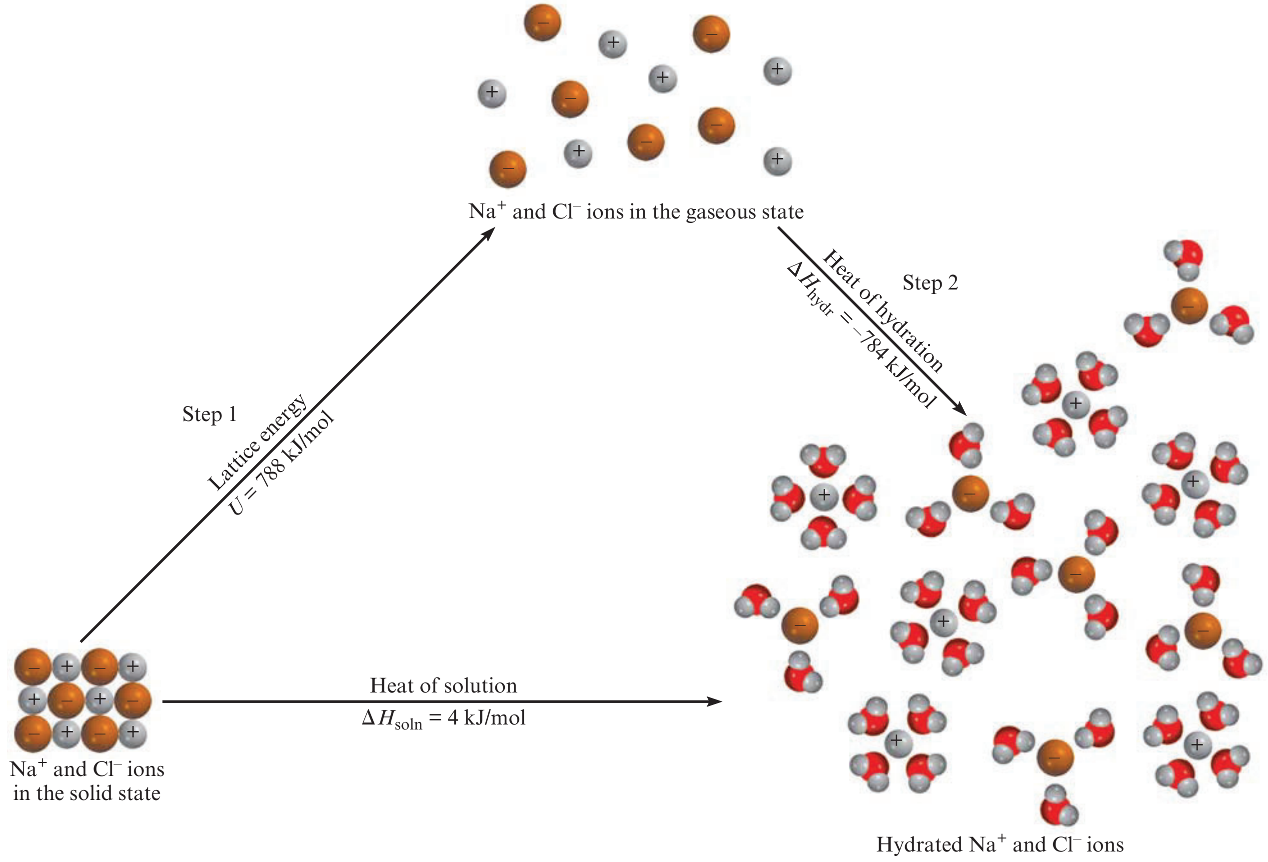


Figure 6.11 *The solution process for NaCl. The process can be considered to occur in two separate steps: (1) separation of ions from the crystal state to the gaseous state and (2) hydration of the gaseous ions. The heat of solution is equal to the energy changes for these two steps,* $\Delta H_{soln} = U + \Delta H_{hydr}$.

Thus, when 1 mole of NaCl dissolves in water, 4 kJ of heat will be absorbed from the surroundings. We would observe this effect by noting that the beaker containing the solution becomes slightly colder. Table 6.5 lists the ΔH_{soln} of several ionic compounds. Depending on the nature of the cation and anion involved, ΔH_{soln} for an ionic compound may be either negative (exothermic) or positive (endothermic).

TABLE 6.5

Heats of Solution of Some Ionic Compounds

Compound	ΔH_{soln} (kJ/mol)
LiCl	−37.1
$CaCl_2$	−82.8
NaCl	4.0
KCl	17.2
NH_4Cl	15.2
NH_4NO_3	26.2

Heat of Dilution

When a previously prepared solution is *diluted,* that is, when more solvent is added to lower the overall concentration of the solute, additional heat is usually given off or absorbed. The ***heat of dilution*** is *the heat change associated with the dilution process.* If a certain solution process is endothermic and the solution is subsequently diluted, *more* heat will be absorbed by the same solution from the surroundings. The converse holds true for an exothermic solution process—more heat will be liberated if additional solvent is added to dilute the solution. Therefore, always be cautious when working on a dilution procedure in the laboratory. Because of its highly exothermic heat of dilution, concentrated sulfuric acid (H_2SO_4) poses a particularly hazardous problem if its concentration must be reduced by mixing it with additional water. Concentrated H_2SO_4 is composed of 98 percent acid and

2 percent water by mass. Diluting it with water releases considerable amount of heat to the surroundings. This process is so exothermic that you must *never* attempt to dilute the concentrated acid by adding water to it. The heat generated could cause the acid solution to boil and splatter. The recommended procedure is to add the concentrated acid slowly to the water (while constantly stirring).

Generations of chemistry students have been reminded of the safe procedure for diluting acids by the venerable saying, "Do as you oughter, add acid to water."

Summary of Facts and Concepts

1. Energy is the capacity to do work. There are many forms of energy and they are interconvertible. The law of conservation of energy states that the total amount of energy in the universe is constant.
2. A process that gives off heat to the surroundings is exothermic; a process that absorbs heat from the surroundings is endothermic.
3. The state of a system is defined by properties such as composition, volume, temperature, and pressure. These properties are called state functions.
4. The change in a state function for a system depends only on the initial and final states of the system, and not on the path by which the change is accomplished. Energy is a state function; work and heat are not.
5. Energy can be converted from one form to another, but it cannot be created or destroyed (first law of thermodynamics). In chemistry we are concerned mainly with thermal energy, electrical energy, and mechanical energy, which is usually associated with pressure-volume work.
6. Enthalpy is a state function. A change in enthalpy ΔH is equal to $\Delta E + P\Delta V$ for a constant-pressure process.
7. The change in enthalpy (ΔH, usually given in kilojoules) is a measure of the heat of reaction (or any other process) at constant pressure.
8. Constant-volume and constant-pressure calorimeters are used to measure heat changes that occur in physical and chemical processes.
9. Hess's law states that the overall enthalpy change in a reaction is equal to the sum of enthalpy changes for individual steps in the overall reaction.
10. The standard enthalpy of a reaction can be calculated from the standard enthalpies of formation of reactants and products.
11. The heat of solution of an ionic compound in water is the sum of the lattice energy of the compound and the heat of hydration. The relative magnitudes of these two quantities determine whether the solution process is endothermic or exothermic. The heat of dilution is the heat absorbed or evolved when a solution is diluted.

Key Words

Calorimetry, p. 245
Chemical energy, p. 230
Closed system, p. 231
Endothermic process, p. 232
Energy, p. 230
Enthalpy (H), p. 240
Enthalpy of reaction (ΔH_{rxn}), p. 241
Enthalpy of solution (ΔH_{soln}), p. 258
Exothermic process, p. 232
First law of thermodynamics, p. 233
Heat, p. 231
Heat capacity (C), p. 246
Heat of dilution, p. 260
Heat of hydration (ΔH_{hydr}), p. 259
Heat of solution (ΔH_{soln}), p. 258
Hess's law, p. 255
Isolated system, p. 231
Lattice energy (U), p. 259
Law of conservation of energy, p. 230
Open system, p. 231
Potential energy, p. 230
Radiant energy, p. 230
Specific heat (s), p. 246
Standard enthalpy of formation ($\Delta H_{\text{f}}^{\circ}$), p. 252
Standard enthalpy of reaction ($\Delta H_{\text{rxn}}^{\circ}$), p. 253
Standard state, p. 252
State function, p. 233
State of a system, p. 233
Surroundings, p. 231
System, p. 231
Thermal energy, p. 230
Thermochemical equation, p. 242
Thermochemistry, p. 231
Thermodynamics, p. 233
Work, p. 230

Answers to Practice Exercises

6.1 (a) 0, (b) −286 J. **6.2** −63 J. **6.3** -6.47×10^3 kJ. **6.4** −111.7 kJ/mol. **6.5** −34.3 kJ. **6.6** −728 kJ/mol. **6.7** 21.19°C. **6.8** 22.49°C. **6.9** 87.3 kJ/mol. **6.10** −41.83 kJ/g.