

Energy Changes in Chemical Reactions

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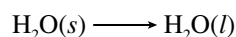
FOSSIL FUELS are a nonrenewable source of energy. According to some estimates, the world's supply of petroleum fuels will be exhausted within the next 50 years—prompting chemists to begin the search for alternative fuels. Of particular interest are biofuels—fuels derived from renewable sources such as corn, soybeans, rapeseeds, and even algae (shown here). Biodiesel is one such biofuel that is readily produced from a variety of oils and fats, and that may have potential as an alternative to petroleum for use in automobiles.

Before You Begin, Review These Skills

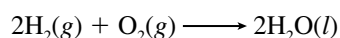
- Tracking units [◀ Section 1.6]
- Balancing chemical equations [◀ Section 8.1]
- Drawing Lewis structures [◀ Section 6.3]

10.1 ENERGY AND ENERGY CHANGES

You have already learned that matter can undergo physical changes and chemical changes [◀ Section 1.3]. The melting of ice, for example, is a physical change that can be represented by the following equation:



The formation of water from its constituent elements, represented by the following equation, is an example of a chemical change:



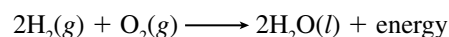
In each case, there is energy involved in the change. Energy (in the form of heat) must be *supplied* to melt ice, whereas energy (in the form of heat and light) is *produced* by the explosive combination of hydrogen and oxygen gases. In fact, every change that matter undergoes is accompanied by either the absorption or the release of energy [◀ Section 3.1]. In this chapter, we will focus on the energy changes associated with physical and chemical processes.

To analyze energy changes associated with physical processes and chemical reactions, we must first define the **system**, the specific part of the universe that is of interest to us. For chemists, systems usually include the substances involved in physical and chemical changes. In an experiment involving the melting of an ice cube, for example, the system would be the ice, and the surroundings would be the rest of the universe. In an acid-base neutralization experiment, the system may be the reactants HCl and NaOH; and the rest of the universe, including the container itself and the water in which the reactants are dissolved, may constitute the **surroundings**.

Many chemical reactions are carried out for the purpose of exploiting the associated energy change, rather than for the purpose of obtaining the products of the reactions. For example, combustion reactions involving fossil fuels are carried out for the thermal energy they produce, not for their products, which are carbon dioxide and water.

It is important to distinguish between thermal energy and heat. **Heat** is the transfer of thermal energy between two bodies that are at different temperatures. Although the term *heat* by itself implies the transfer of energy, we customarily talk of “heat flow,” meaning “energy absorbed” or “energy released,” when describing the energy changes that occur during a process. **Thermochemistry** is the study of the heat (the transfer of thermal energy) associated with chemical reactions.

The combustion of hydrogen gas in oxygen is one of many chemical reactions that release considerable quantities of energy (Figure 10.1):



In this case, we label the mixture of reactants and product (hydrogen, oxygen, and water molecules) the **system**. Because energy cannot be created or destroyed, any energy released 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 *from* the system *to* the surroundings. Figure 10.2 shows the energy change for the combustion of hydrogen gas.

Next, consider the decomposition of mercury(II) oxide (HgO) at high temperatures:

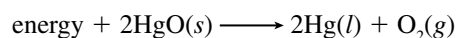
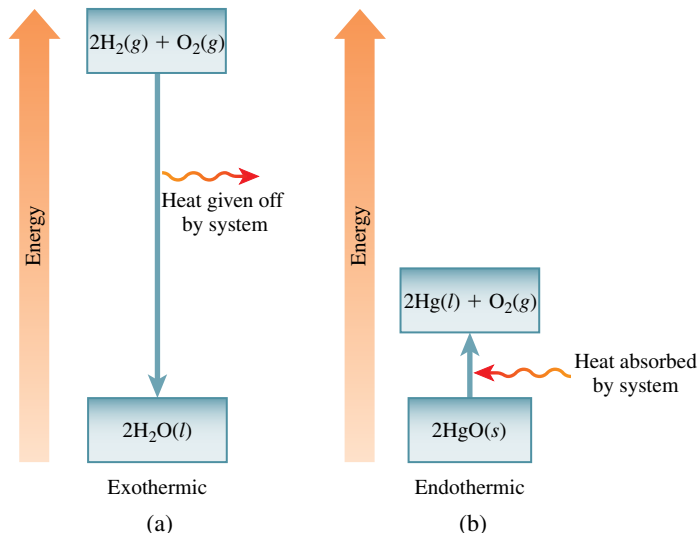


Figure 10.1 The Hindenburg, a German airship filled with hydrogen gas, was destroyed in a horrific fire as it landed at Lakehurst, New Jersey, in 1937.

Student Annotation: Although “surroundings” includes everything in the universe apart from the system, when chemists refer to the *surroundings* they generally mean the *immediate* surroundings—the part of the universe that is closest to the system.

Student Annotation: Emission of a photon from an atom when an electron falls from an excited state to a lower state [◀ Section 3.4] and most first electron affinities [◀ Section 4.4] are examples of exothermic processes that we have encountered in previous chapters.

Figure 10.2 (a) An exothermic reaction. Heat is given off by the system. (b) An endothermic reaction. Heat is absorbed by the system.



Multi 10.1

Thermochemistry—heat flow in endothermic and exothermic reactions

Student Annotation: In these examples, all the energy released or absorbed by the system is *thermal energy*, which is commonly referred to as heat. In Section 10.2, we will consider examples in which some of the energy is in the form of *work*.

Student Annotation: The triple equal sign is used to denote a definition. Recall that numbers with defined values are exact numbers, which do not limit the number of significant figures in a calculation [Section 1.5].

This reaction is an **endothermic process** because heat has to be supplied to the system (i.e., to HgO) by the surroundings [Figure 10.2(b)] in order for the reaction to occur. Thus, thermal energy is transferred *from* the surroundings *to* the system in an endothermic process.

According to Figure 10.2, the energy of the products of an exothermic reaction is lower than the energy of the reactants. The difference in energy between the reactants H_2 and O_2 and the product H_2O is the heat released by the system to the surroundings. In an endothermic reaction, on the other hand, the energy of the products is higher than the energy of the reactants. Here, the difference between the energy of the reactant HgO and the products Hg and O_2 is the heat absorbed by the system from the surroundings.

Recall that the SI unit for energy is the joule, which is the amount of energy possessed by a 2 kg object moving at 1 m/s [Section 3.1]. Another unit used to express energy is the calorie (cal), which was originally defined as the amount of energy required to raise the temperature of one gram of water by one degree ($^{\circ}\text{C}$). Although the calorie is not an SI unit, its use is still quite common. The calorie is now defined in terms of the joule:

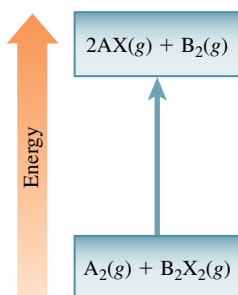
$$1 \text{ cal} \equiv 4.184 \text{ J}$$

Because this is a definition, the number 4.184 is an *exact* number, which does not limit the number of significant figures in a calculation [Section 1.5]. You may be familiar with the term *calorie* from nutrition labels. In fact, the “calories” listed on food packaging are really *kilocalories*. Often the distinction is made by capitalizing the “C” in “calorie” when it refers to the energy content of food:

$$1 \text{ Cal} \equiv 1000 \text{ cal}$$

and

$$1 \text{ Cal} \equiv 4184 \text{ J}$$



Section 10.1 Review

Energy and Energy Changes

- 10.1.1** Calculate the number of calories in 723.01 J.
- 10.1.2** The label on packaged food indicates that it contains 215 Cal per serving. Convert this amount of energy to joules.
- 10.1.3** Use the figure shown here to write (a) a chemical equation representing an exothermic process, and (b) a chemical equation representing an endothermic process.

10.2 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 introduce the first law of thermodynamics, which is particularly relevant to the study of thermochemistry. We will continue our discussion of thermodynamics in Chapter 14.

We have defined a system as the part of the universe we are studying. There are three types of systems. An *open system* can exchange mass and energy with its surroundings. For example, an open system may consist of a quantity of water in an open container, as shown in Figure 10.3(a). If we close the flask, as in Figure 10.3(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 but not mass. By placing the water in an insulated container, as shown in Figure 10.3(c), we can construct an *isolated system*, which does not exchange either mass or energy with its surroundings.

Student Annotation: The energy exchanged between open systems or closed systems and their surrounding is usually in the form of heat.

States and State Functions

In thermodynamics, we study changes in the *state of a system*, which is defined by the values of all relevant macroscopic properties, such as 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.

Consider, for example, your position in a six-story building. Your elevation depends upon which floor you are on. If you change your elevation by taking the stairs from the ground floor up to the fourth floor, the change in your elevation depends only upon your initial state (the ground floor—the floor you started on) and your final state (the fourth floor—the floor you went to). It does not depend on whether you went directly to the fourth floor or up to the sixth and then down to the fourth floor. Your overall change in elevation is the same either way because it depends only on your initial and final elevations. Thus, elevation is a state function.

The amount of effort it takes to get from the ground floor to the fourth floor, on the other hand, depends on how you get there. More effort has to be exerted to go from the ground floor to the sixth floor and back down to the fourth floor than to go from the ground floor to the fourth floor directly. The effort required for this change in elevation is *not* a state function. Furthermore, if you subsequently return to the ground floor, your overall change in elevation will be zero, because your initial and final states are the same, but the amount of effort you exerted going from the ground floor to the fourth floor and back to the ground floor is *not* zero. Even though your initial and final states are the same, you do not get back the effort that went into climbing up and down the stairs.

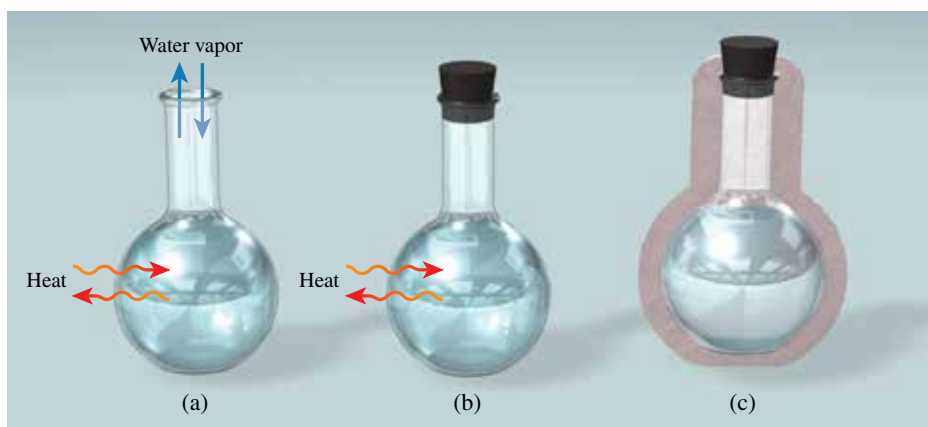


Figure 10.3 (a) An open system allows exchange of both energy and matter with the surroundings. (b) A closed system allows exchange of energy but not matter. (c) An isolated system does not allow exchange of energy or matter. (This flask is enclosed by an insulating vacuum jacket.)

Figure 10.4 The change in elevation that occurs when a person goes from the ground floor to the fourth floor in a building does not depend on the path taken.



Energy is a state function, too. Using potential energy as an example, your net increase in gravitational potential energy is always the same, regardless of how you get from the ground floor to the fourth floor of a building (Figure 10.4).

The First Law of Thermodynamics

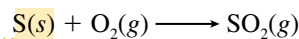
The *first law of thermodynamics*, which is based on the law of conservation of energy, states that energy can be converted from one form to another but cannot be created or destroyed. It would be impossible to demonstrate this by measuring the total amount of energy in the universe; in fact, just determining the total energy content of a small sample of matter would be extremely difficult. Fortunately, because energy is a state function, we can demonstrate the first law by measuring the change in the energy of a system between its initial state and its final state in a process. The change in internal energy, ΔU , is given by

$$\Delta U = U_f - U_i$$

where U_i and U_f are the internal energies of the system in the initial and final states, respectively; and the symbol Δ means *final minus initial*.

The internal energy of a system has two components: kinetic energy and potential energy. The kinetic energy component consists of various types of molecular motion and the movement of electrons within molecules. Potential energy is determined by the attractive interactions between electrons and nuclei and by repulsive interactions between electrons and between nuclei in individual molecules, as well as by interactions between molecules. It is impossible to measure all these contributions accurately, so we cannot calculate the total energy of a system with any certainty. *Changes* in energy, on the other hand, can be determined experimentally.

Consider the reaction between 1 mole of sulfur and 1 mole of oxygen gas to produce 1 mole of sulfur dioxide:



In this case our system is composed of the reactant molecules and the product molecules. We do not know the internal energy content of either the reactants or the product, but we can accurately measure the *change* in energy content ΔU given by

$$\begin{aligned} \Delta U &= U(\text{products}) - U(\text{reactants}) \\ &= \text{energy content of 1 mol SO}_2(g) - \text{energy content of 1 mol S}(s) \text{ and 1 mol O}_2(g) \end{aligned}$$

This reaction gives off heat: 296.4 kJ, to be exact. Therefore, the energy of the product is less than that of the reactants, and ΔU is negative (−296.4 kJ/mol).

The release of heat that accompanies this reaction indicates that some of the chemical energy contained in the system has been converted to thermal energy. Furthermore, the thermal energy released by the system is absorbed by the surroundings. The transfer of energy from the system to the surroundings does not change the total energy of the universe. That is, the sum of the energy changes is zero:

$$\Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0$$

Student Annotation: The symbol U is used to denote the internal energy of a system, as opposed to the symbol E , which is used to denote the energy possessed by a particle or associated with a particular process.

Student Annotation: Recall that the symbol Δ is commonly used to mean *final minus initial*.

Student Annotation: Elemental sulfur exists as S_8 molecules but we typically represent it simply as S to simplify chemical equations [see Section 8.1].

Student Annotation: Later in this chapter, we will learn about the experimental techniques used to measure energy changes [see Section 10.4].

where the subscripts “sys” and “surr” denote system and surroundings, respectively. Thus, if a system undergoes an energy change ΔU_{sys} , the rest of the universe, or the surroundings, must undergo a change in energy that is equal in magnitude but opposite in sign:

$$\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$$

Energy released in one place must be gained somewhere else. Furthermore, because energy can be changed from one form to another, the energy lost by one system can be gained by another system in a different form. For example, the energy released by burning coal in a power plant may ultimately turn up in our homes as electric energy, heat, light, and so on.

Work and Heat

Recall from Section 3.1 that energy is defined as the capacity to do work or transfer heat. When a system releases or absorbs heat, its internal energy changes. Likewise, when a system does work on its surroundings, or when the surroundings do work on the system, the system’s internal energy also changes. The overall change in the system’s internal energy is given by

$$\Delta U = q + w \quad \text{Equation 10.1}$$

where q is heat (released or absorbed by the system) and w is work (done on the system or done by the system). Note that it is possible for the heat and work components to cancel each other out and for there to be no change in the system’s internal energy.

In chemistry, we are normally interested in the energy changes associated with the system rather than the surroundings. Therefore, unless otherwise indicated, ΔU will refer specifically to ΔU_{sys} . The sign conventions for q and w are as follows: q is positive for an endothermic process and negative for an exothermic process, and w is positive for work done on the system by the surroundings and negative for work done by the system on the surroundings. Table 10.1 summarizes the sign conventions for q and w .

The drawings in Figure 10.5 illustrate the logic behind the sign conventions for q and w . If a system releases heat to the surroundings or does work on the surroundings [Figure 10.5(a)], we would expect its internal energy to decrease because they are energy-depleting processes. For this reason, both q and w are negative. Conversely, if heat is added to the system or if work is done on the system [Figure 10.5(b)] then the internal energy of the system increases. In this case, both q and w are positive.

Student Annotation: The units for heat and work are the same as those for energy: joules, kilojoules, or calories.

Student Annotation: Interestingly, although neither q nor w is a state function (each depends on the path between the initial and final states of the system), their sum, ΔU , does not depend on the path between initial and final states because U is a state function.

TABLE 10.1 Sign Conventions for Heat (q) and Work (w)

Process	Sign
Heat absorbed by the system (endothermic process)	q is positive
Heat released by the system (exothermic process)	q is negative
Work done on the system by the surroundings (for example, a volume decrease)	w is positive
Work done by the system on the surroundings (for example, a volume increase)	w is negative

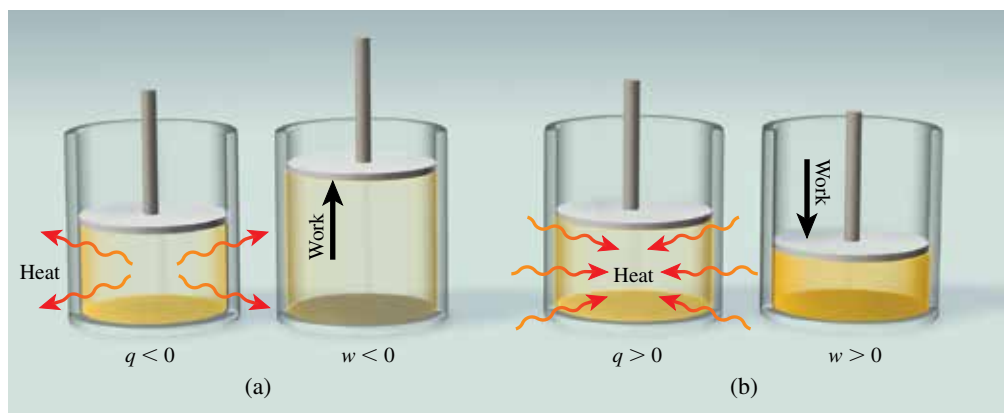


Figure 10.5 (a) When heat is released by the system (to the surroundings), q is negative. When work is done by the system (on the surroundings), w is negative. (b) When heat is absorbed by the system (from the surroundings), q is positive. When work is done on the system (by the surroundings), w is positive.

Worked Example 10.1 shows how to determine the overall change in the internal energy of a system.

Worked Example 10.1

Calculate the overall change in internal energy, ΔU , (in joules) for a system that absorbs 188 J of heat and does 141 J of work on its surroundings.

Strategy Combine the two contributions to internal energy using Equation 10.1 and the sign conventions for q and w .

Setup The system absorbs heat, so q is *positive*. The system does work on the surroundings, so w is *negative*.

Solution

$$\Delta U = q + w = 188 \text{ J} + (-141 \text{ J}) = 47 \text{ J}$$

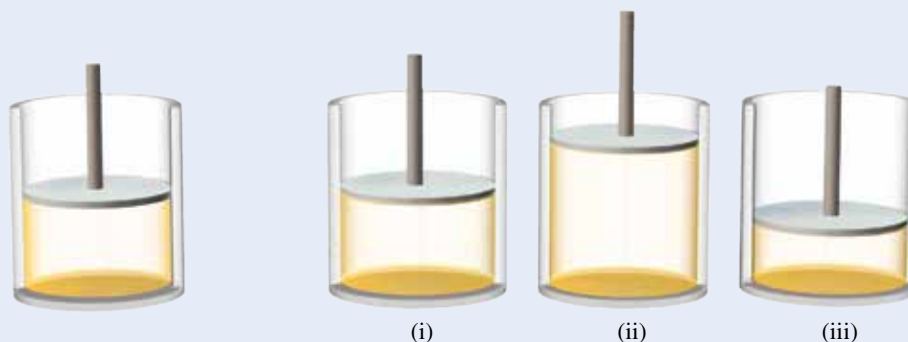
Think About It

Consult Table 10.1 to make sure you have used the proper sign conventions for q and w .

Practice Problem A TTEMPT Calculate the change in total internal energy for a system that releases 1.34×10^4 kJ of heat and does 2.98×10^4 kJ of work on the surroundings.

Practice Problem B UILD Calculate the magnitude of q for a system that does 7.05×10^5 kJ of work on its surroundings and for which the change in total internal energy is -9.55×10^3 kJ. Indicate whether heat is absorbed or released by the system.

Practice Problem C ONCEPTUALIZE The diagram on the left shows a system before a process. Which of the diagrams on the right could represent the system after it undergoes a process in which the system absorbs heat and ΔU is positive?



Section 10.2 Review

Introduction to Thermodynamics

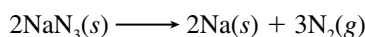
- 10.2.1** Calculate the overall change in internal energy for a system that releases 43 J in heat in a process in which no work is done.
- 10.2.2** Calculate w , and determine whether work is done by the system or on the system when 928 kJ of heat is released and $\Delta U = -1.47 \times 10^3$ kJ.

10.3 ENTHALPY

To calculate ΔU , we must know the values and signs of both q and w . As we will see in Section 10.4, we determine q by measuring temperature changes. To determine w , we need to know whether the reaction occurs under constant-volume conditions, or under constant-pressure conditions.

Reactions Carried Out at Constant Volume or at Constant Pressure

Imagine carrying out the decomposition of sodium azide (NaN_3) in two different experiments. In the first experiment, the reactant is placed in a metal cylinder with a fixed volume. When detonated, the NaN_3 reacts, generating a large quantity of N_2 gas inside the closed, fixed-volume container.



The effect of this reaction will be an increase in the pressure inside the container, similar to what happens if you shake a bottle of soda vigorously prior to opening it. (The concept of pressure will be examined in detail in Chapter 11. However, if you have ever put air in the tire of an automobile or a bicycle, you are familiar with the concept.)

Now imagine carrying out the same reaction in a metal cylinder with a movable piston. As this explosive decomposition proceeds, the piston in the metal cylinder will move. The gas produced in the reaction pushes the cylinder upward, thereby increasing the volume of the container and preventing any increase in pressure. This is a simple example of mechanical work done by a chemical reaction. Specifically, this type of work is known as *pressure-volume*, or *PV*, work. The amount of work done by such a process is given by

$$w = -P\Delta V$$

Equation 10.2

where P is the external, opposing pressure and ΔV is the change in the volume of the container as the result of the piston being pushed upward. In keeping with the sign conventions in Table 10.1, an increase in volume results in a negative value for w , whereas a decrease in volume results in a positive value for w . Figure 10.6 illustrates this reaction (a) being carried out at a constant volume, and (b) at a constant pressure.

Worked Example 10.2 shows how to calculate the work associated with a volume change.

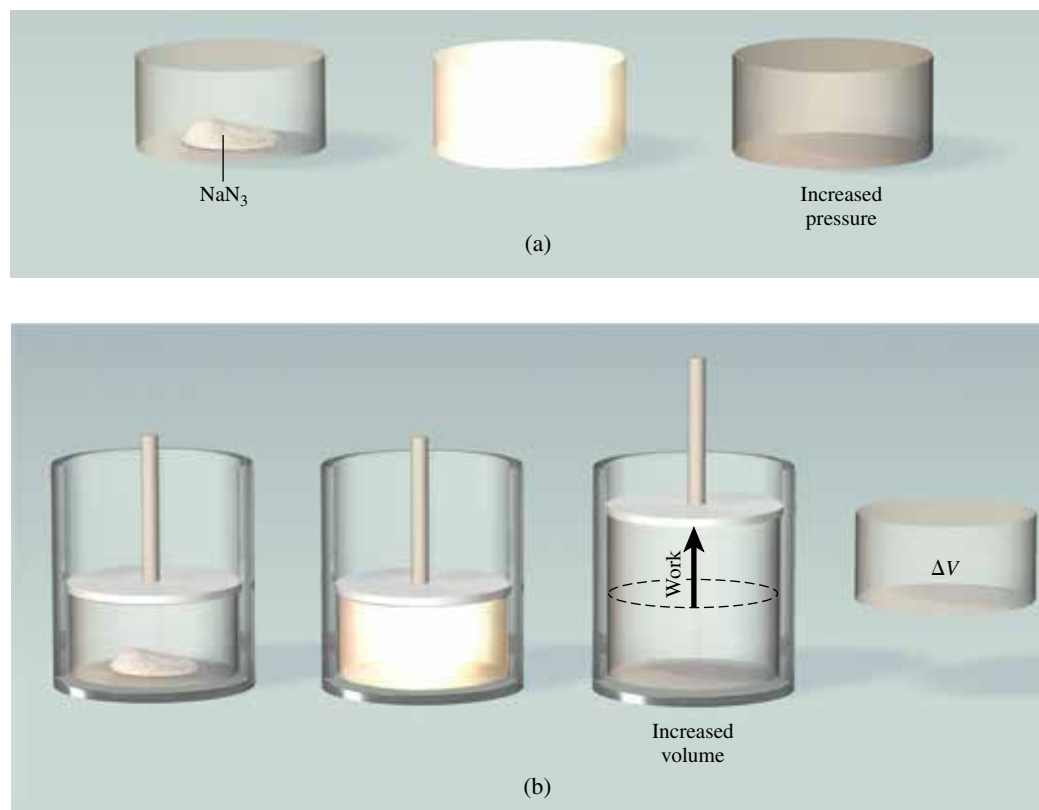


Figure 10.6 (a) The explosive decomposition of NaN_3 at constant volume results in an increase in pressure inside the vessel. (b) The decomposition at constant pressure, in a vessel with a movable piston, results in an increase in volume. The resulting change in volume, ΔV , can be used to calculate the work done by the system.

Student Annotation: The explosive decomposition of NaN_3 is the reaction that inflates air bags in cars.

Student Annotation: Pressure-volume work and electrical work are two important types of work done by chemical reactions. Electrical work will be discussed in detail in Chapter 18.

Student Annotation: The SI unit of pressure is the *pascal* (Pa), which, in SI base units is $1 \text{ kg}/(\text{m} \cdot \text{s}^2)$. Volume, in SI base units is cubic meters (m^3). Therefore, multiplying units of *pressure* by units of *volume* gives $[1 \text{ kg}/(\text{m} \cdot \text{s}^2)] \times (\text{m}^3) = 1 (\text{kg} \cdot \text{m}^2)/\text{s}^2$, which is the definition of the *joule* (J). Thus, $P\Delta V$ has units of *energy*.

Another commonly used unit of pressure is the *atmosphere* (atm) (►► Section 11.3). Worked Example 10.2 uses atmospheres to express pressure.

Worked Example 10.2

Determine the work done (in joules) when a sample of gas expands from 552 mL to 891 mL at constant temperature (a) against a constant pressure of 1.25 atm, (b) against a constant pressure of 1.00 atm, and (c) against a vacuum ($1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$).

Strategy Determine change in volume (ΔV), identify the external pressure (P), and use Equation 10.2 to calculate w . The result of Equation 10.2 will be in $\text{L} \cdot \text{atm}$; use the equality $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$ to convert to joules.

Setup $\Delta V = (891 - 552) \text{ mL} = 339 \text{ mL}$. (a) $P = 1.25 \text{ atm}$, (b) $P = 1.00 \text{ atm}$, (c) $P = 0 \text{ atm}$.

Solution

$$(a) w = -(1.25 \text{ atm})(339 \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = -42.9 \text{ J}$$

$$(b) w = -(1.00 \text{ atm})(339 \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = -34.3 \text{ J}$$

$$(c) w = -(0 \text{ atm})(339 \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = 0 \text{ J}$$

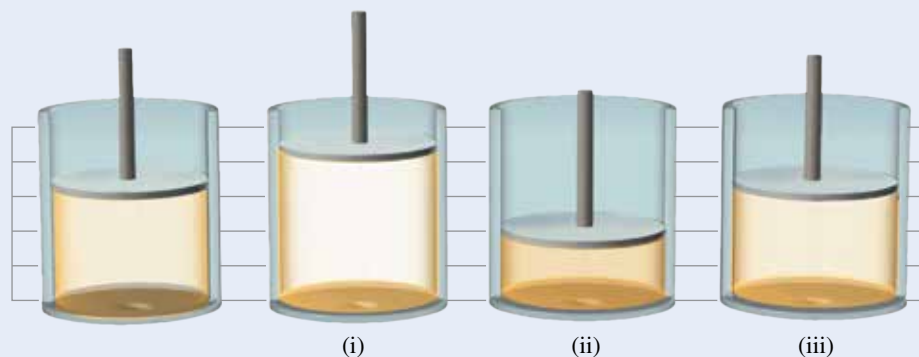
Think About It

Remember that the negative sign in the answers to parts (a) and (b) indicate that the system does work on the surroundings. When an expansion happens against a vacuum, no work is done. This example illustrates that work is *not* a state function. For an equivalent change in volume, the work varies depending on the external pressure against which the expansion must occur.

Practice Problem A **TEMPT** Calculate the work done by or on the system during the following processes: (a) A sample of gas expands from 1.2 L to 3.8 L against an external pressure of 1.01 atm; (b) A sample of gas is compressed from 87.5 mL to 72.9 mL by a pressure of 2.72 atm; (c) The volume of a 2.00-L gas sample increases by a factor of 2 against an external pressure of 0.998 atm.

Practice Problem B **UILD** (a) Against what external pressure must a gas sample expand from 50.0 mL to 219 mL to do 8.34 J of work? (b) To what volume will a 200.0-mL gas sample be compressed by an external pressure of 7.8 atm if 100.0 J of work are done on the system? (c) To what volume must a 200.0-mL gas sample expand against an external pressure of 7.8 atm to do 100.0 J of work?

Practice Problem C **ONCEPTUALIZE** The diagram on the left shows a sample of gas contained in a cylinder with a movable piston. Diagrams (i), (ii), and (iii) show the sample after a process has occurred. Fill in the table with the sign of w for each instance.



w (positive, negative, or zero)

External $P = 5 \text{ atm}$			
External $P = 0 \text{ atm}$			
	(i)	(ii)	(iii)

When a chemical reaction is carried out at constant volume, then no PV work can be done because $\Delta V = 0$ in Equation 10.2. From Equation 10.1 it follows that

$$\text{Equation 10.3} \quad \Delta U = q - P\Delta V$$

and, because $P\Delta V = 0$ at constant volume,

$$q_v = \Delta U \quad \text{Equation 10.4}$$

We add the subscript “V” to indicate that this is a constant-volume process. This equality may seem strange at first. We said earlier that q is *not* a state function. However, for a process carried out under constant-volume conditions, q can have only one specific value, which is equal to ΔU . In other words, although q is *not* a state function, q_v *is* one.

Constant-volume conditions are often inconvenient and sometimes impossible to achieve. Most reactions occur in open containers, under conditions of constant pressure (usually at whatever the atmospheric pressure happens to be where the experiments are conducted). In general, for a constant-pressure process, we write

$$\begin{aligned} \Delta U &= q + w \\ &= q_p - P\Delta V \end{aligned}$$

or

$$q_p = \Delta U + P\Delta V \quad \text{Equation 10.5}$$

where the subscript “P” denotes constant pressure.

Enthalpy and Enthalpy Changes

There is a thermodynamic function of a system called *enthalpy* (H), which is defined by Equation 10.6:

$$H = U + PV \quad \text{Equation 10.6}$$

where U is the internal energy of the system and P and V are the pressure and volume of the system, respectively. Because U and PV have energy units, enthalpy also has energy units. Furthermore, U , P , and V are all state functions—that is, the changes in $(U + PV)$ depend only on the initial and final states. It follows, therefore, that the change in H , or ΔH , also depends only on the initial and final states. Thus, H is a state function.

For any process, the *change* in enthalpy is given by

$$\Delta H = \Delta U + \Delta(PV) \quad \text{Equation 10.7}$$

If the pressure is held constant, then

$$\Delta H = \Delta U + P\Delta V \quad \text{Equation 10.8}$$

If we solve Equation 10.8 for ΔU ,

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

Then, substituting the result for ΔU into Equation 10.5, we obtain

$$q_p = (\Delta H - P\Delta V) + P\Delta V$$

The $P\Delta V$ terms cancel, and for a constant-pressure process, the heat exchanged between the system and the surroundings is equal to the enthalpy change:

$$q_p = \Delta H \quad \text{Equation 10.9}$$

Again, q is *not* a state function, but q_p *is* one; that is, the heat change at constant pressure can have only one specific value and is equal to ΔH .

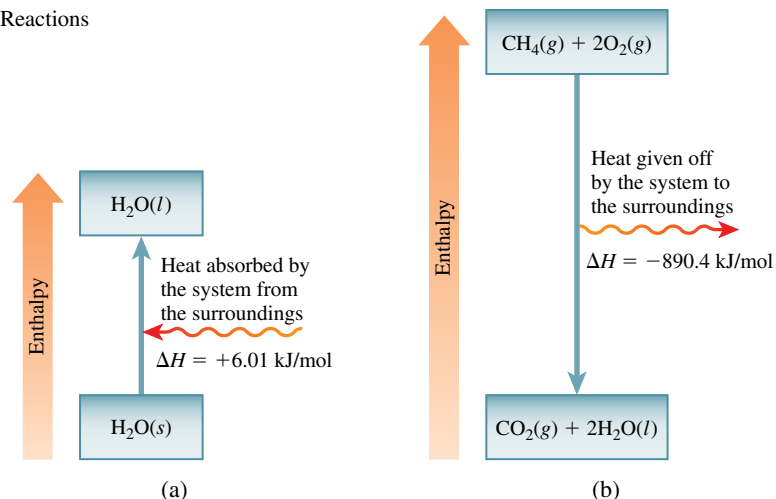
We now have two quantities— ΔU and ΔH —that can be associated with a reaction. If the reaction occurs under constant-volume conditions, then the heat change, q_v , is equal to ΔU . If the reaction is carried out at constant pressure, on the other hand, the heat change, q_p , is equal to ΔH .

Because most laboratory reactions are constant-pressure processes, the heat exchanged between the system and surroundings is equal to the change in enthalpy for the process. For any reaction, 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:

$$\Delta H = H(\text{products}) - H(\text{reactants}) \quad \text{Equation 10.10}$$

Student Annotation: The enthalpy of reaction is often symbolized by ΔH_{rxn} . The subscript can be changed to denote a specific type of reaction or physical process: ΔH_{vap} can be used for the enthalpy of vaporization, for example.

Figure 10.7 (a) Melting 1 mole of ice at 0°C, an endothermic process, results in an enthalpy increase of 6.01 kJ ($\Delta H = +6.01$ kJ/mol). (b) The burning of 1 mole of methane in oxygen gas, an exothermic process, results in an enthalpy decrease in the system of 890.4 kJ ($\Delta H = -890.4$ kJ/mol). The enthalpy diagrams of these two processes are not shown to the same scale.



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

We will now apply the idea of enthalpy changes to two common processes, the first involving a physical change and the second involving a chemical change.

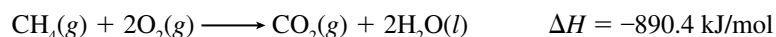
Thermochemical Equations

Under ordinary atmospheric conditions at sea level, ice melts to form liquid water at temperatures above 0°C. Measurements show that for every mole of ice converted to liquid water under these conditions, 6.01 kJ of heat energy is absorbed by the system (the ice). Because the pressure is constant, the heat change is equal to the enthalpy change, ΔH . This is an *endothermic* process ($\Delta H > 0$), because heat is absorbed by the ice from its surroundings (Figure 10.7a). The equation for this physical change is



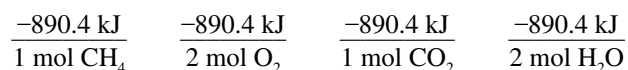
The “per mole” in the unit for ΔH means that this is the enthalpy change *per mole of the reaction (or process) as it is written*—that is, when 1 mole of ice is converted to 1 mole of liquid water.

Now consider the combustion of methane (CH_4), the principal component of natural gas:



From experience we know that burning natural gas releases heat to the surroundings, so it is an exothermic process. Under constant-pressure conditions, this heat change is equal to the enthalpy change and ΔH must have a negative sign [Figure 10.7(b)]. Again, the “per mole” in the units for ΔH means that when 1 mole of CH_4 reacts with 2 moles of O_2 to yield 1 mole of CO_2 and 2 moles of liquid H_2O , 890.4 kJ of heat is **released** to the surroundings.

It is important to keep in mind that the ΔH value in kJ/mol does not mean *per mole* of a particular reactant or product. It refers to all the species in a reaction in the molar amounts specified by the coefficients in the balanced equation. Thus, for the combustion of methane, the ΔH value of -890.4 kJ/mol can be expressed in any of the following ways:



Although the importance of expressing ΔH in units of kJ/mol (rather than just kilojoules) will become apparent when we study thermodynamics in greater detail [► Chapter 14], you should learn and become comfortable with this convention now.

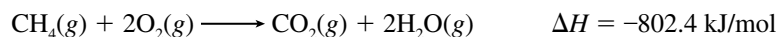
The equations for the melting of ice and the combustion of methane are examples of **thermochemical equations**, which are chemical equations that show the enthalpy changes as well as the mass relationships. It is essential to specify a balanced chemical equation when quoting the enthalpy change of a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

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. In the

Student Annotation: Although, strictly speaking, it is unnecessary to include the sign of a positive number, we will include the sign of all positive ΔH values to emphasize the thermochemical sign convention.

Student Annotation: When you specify that a particular amount of heat is released, it is not necessary to include a negative sign.

equation for the combustion of methane, for example, changing the liquid water product to water vapor changes the value of ΔH :



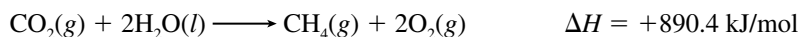
The enthalpy change is -802.4 kJ rather than -890.4 kJ (see page 388) because 88.0 kJ are needed to convert 2 moles of liquid water to 2 moles of water vapor; that is,



2. If we multiply both sides of a thermochemical equation by a factor n , then ΔH must also be multiplied by the same factor. Thus, for the melting of ice, if $n = 2$, we have



3. When we reverse a chemical 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 (i.e., if it is endothermic), then the reverse reaction must release thermal energy back to its surroundings (i.e., 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



What was an endothermic process becomes an exothermic process when reversed, and vice versa.

Worked Example 10.3 illustrates the use of a thermochemical equation to relate the mass of a product to the energy consumed in the reaction.

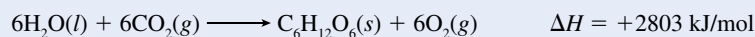
Student Annotation: Remember that the “per mole” in this context refers to per mole of *reaction*—not, in this case, per mole of water.

Student Annotation: A convenient way to summarize this concept is:

$$\Delta H_{\text{forward}} = -\Delta H_{\text{reverse}}$$

Worked Example 10.3

Given the thermochemical equation for photosynthesis,



calculate the solar energy required to produce 75.0 g of $\text{C}_6\text{H}_{12}\text{O}_6$.

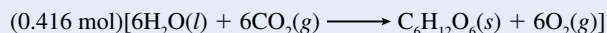
Strategy The thermochemical equation shows that for every mole of $\text{C}_6\text{H}_{12}\text{O}_6$ produced, 2803 kJ is absorbed. We need to find out how much energy is absorbed for the production of 75.0 g of $\text{C}_6\text{H}_{12}\text{O}_6$. We must first find out how many moles there are in 75.0 g of $\text{C}_6\text{H}_{12}\text{O}_6$.

Setup The molar mass of $\text{C}_6\text{H}_{12}\text{O}_6$ is 180.2 g/mol , so 75.0 g of $\text{C}_6\text{H}_{12}\text{O}_6$ is

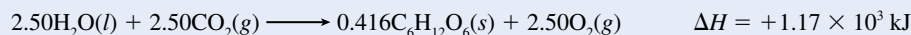
$$75.0 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.416 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

We will multiply the thermochemical equation, including the enthalpy change, by 0.416 , in order to write the equation in terms of the appropriate amount of $\text{C}_6\text{H}_{12}\text{O}_6$.

Solution



and $(0.416 \text{ mol})(\Delta H) = (0.416 \text{ mol})(2803 \text{ kJ/mol})$ gives



Therefore, $1.17 \times 10^3 \text{ kJ}$ of energy in the form of sunlight is consumed in the production of 75.0 g of $\text{C}_6\text{H}_{12}\text{O}_6$. Note that the “per mole” units in ΔH are canceled when we multiply the thermochemical equation by the number of moles of $\text{C}_6\text{H}_{12}\text{O}_6$.

Think About It

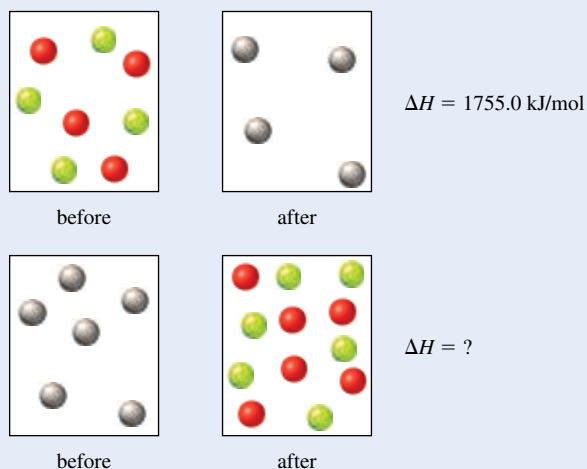
The specified amount of $\text{C}_6\text{H}_{12}\text{O}_6$ is less than half a mole. Therefore, we should expect the associated enthalpy change to be less than half that specified in the thermochemical equation for the production of 1 mole of $\text{C}_6\text{H}_{12}\text{O}_6$.

(Continued on next page)

Practice Problem A TTEMPT Calculate the solar energy required to produce 5255 g of $C_6H_{12}O_6$.

Practice Problem B UILD Calculate the mass (in grams) of O_2 that is produced by photosynthesis when 2.49×10^4 kJ of solar energy is consumed.

Practice Problem C ONCEPTUALIZE The diagrams represent systems before and after reaction for two related chemical processes. ΔH for the first reaction is 1755.0 kJ/mol. Determine the value of ΔH for the second reaction.



Section 10.3 Review

Enthalpy

- 10.3.1** Given the thermochemical equation: $H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$, $\Delta H = -72.4$ kJ/mol, calculate the amount of heat released when a kilogram of $Br_2(l)$ is consumed in this reaction.
- 10.3.2** Given the thermochemical equation: $2Cu_2O(s) \longrightarrow 4Cu(s) + O_2(g)$, $\Delta H = +333.8$ kJ/mol, calculate the mass of copper produced when 1.47×10^4 kJ is consumed in this reaction.

10.4 CALORIMETRY

In the study of thermochemistry, heat changes that accompany physical and chemical processes are measured with a *calorimeter*, a closed container designed specifically for this purpose. We begin our discussion of *calorimetry*, the measurement of heat changes, by defining two important terms: *specific heat* and *heat capacity*.

Specific Heat and Heat Capacity

The *specific heat* (s) of a substance is the amount of heat required to raise the temperature of 1 g of the substance by $1^\circ C$. The *heat capacity* (C) is the amount of heat required to raise the temperature of an *object* by $1^\circ C$. We can use the specific heat of a substance to determine the heat capacity of a specified quantity of that substance. For example, we can use the specific heat of water, 4.184 J/(g \cdot $^\circ C$), to determine the heat capacity of a kilogram of water:

$$\text{Heat capacity of 1 kg of water} = \frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ C} \times 1000 \text{ g} = 4184 \text{ or } 4.184 \times 10^3 \text{ J}/^\circ C$$

Note that specific heat has the units J/(g \cdot $^\circ C$) and heat capacity has the units J/ $^\circ C$. Table 10.2 shows the specific heat values of some common substances. If we know the specific heat and the

Student Annotation: Although heat capacity is typically given for an object rather than for a substance—the “object” may be a given quantity of a particular substance.

TABLE 10.2 Specific Heat Values of Some Common Substances

Substance	Specific heat (J/g · °C)
Al(<i>s</i>)	0.900
Au(<i>s</i>)	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu(<i>s</i>)	0.385
Fe(<i>s</i>)	0.444
Hg(<i>l</i>)	0.139
H ₂ O(<i>l</i>)	4.184
C ₂ H ₅ OH(<i>l</i>) (ethanol)	2.46

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. One equation for calculating the heat associated with a temperature change is given by

$$q = sm\Delta T \quad \text{Equation 10.11}$$

where s is the specific heat, m is the mass of the substance undergoing the temperature change, and ΔT is the temperature change: $\Delta T = T_{\text{final}} - T_{\text{initial}}$. Another equation for calculating the heat associated with a temperature change is given by

$$q = C\Delta T \quad \text{Equation 10.12}$$

where C is the heat capacity and ΔT is the temperature change: The sign convention for q is the same as that for an enthalpy change: q is positive for endothermic processes and negative for exothermic processes. Worked Example 10.4 shows how to use the specific heat of a substance to calculate the amount of heat needed to raise the temperature of the substance by a particular amount.

Student Annotation: Note that $C = sm$. Although specific heat is a property of substances, and heat capacity is a property of objects, we can define a specified quantity of a substance as an "object" and determine its heat capacity using its mass and its specific heat.

Worked Example 10.4

Calculate the amount of heat (in kJ) required to heat 255 g of water from 25.2°C to 90.5°C.

Strategy Use Equation 10.11 ($q = sm\Delta T$) to calculate q .

Setup $s = 4.184 \text{ J/g} \cdot ^\circ\text{C}$, $m = 255 \text{ g}$, and $\Delta T = 90.5^\circ\text{C} - 25.2^\circ\text{C} = 65.3^\circ\text{C}$.

Solution

$$q = \frac{4.184 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times 255 \text{ g} \times 65.3^\circ\text{C} = 6.97 \times 10^4 \text{ J or } 69.7 \text{ kJ}$$

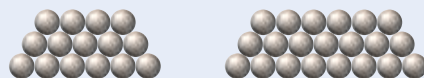
Think About It

Look carefully at the cancellation of units and make sure that the number of kilojoules is smaller than the number of joules. It is a common error to multiply by 1000 instead of dividing in conversions of this kind.

Practice Problem A TTEMPT Calculate the amount of heat (in kJ) required to heat 1.01 kg of water from 0.05°C to 35.81°C.

Practice Problem B UILD What will be the final temperature of a 514-g sample of water, initially at 10.0°C, after the addition of 90.8 kJ?

Practice Problem C ONCEPTUALIZE Shown here are two samples of the same substance. When equal amounts of heat are added to both samples, the temperature of the sample on the left increases by 15.3°C. Determine the increase in temperature of the sample on the right.



Constant-Pressure Calorimetry

A crude constant-pressure calorimeter can be constructed from two Styrofoam coffee cups, as shown in Figure 10.8. This device, called a coffee-cup calorimeter, can be used to measure the heat exchanged between the system and surroundings for a variety of reactions, such as acid-base neutralization, heat of solution, and heat of dilution. Because the pressure is constant, the heat change for the process (q) is equal to the enthalpy change (ΔH). In such experiments, we consider the reactants and products to be the system, and the water in the calorimeter to be the surroundings. We neglect the small heat capacity of the Styrofoam cups in our calculations. In the case of an exothermic reaction, the heat released by the system is absorbed by the water (surroundings), thereby increasing its temperature. Knowing the mass of the water in the calorimeter, the specific heat of water, and the change in temperature, we can calculate q_p of the system using the equation

$$\text{Equation 10.13} \quad q_{\text{sys}} = -sm\Delta T$$

Note that the minus sign makes q_{sys} a negative number if ΔT is a positive number (i.e., if the temperature goes up). This is in keeping with the sign conventions listed in Table 10.1. A negative ΔH or a negative q indicates an exothermic process, whereas a positive ΔH or a positive q indicates an endothermic process. Table 10.3 lists some of the reactions that can be studied with a constant-pressure calorimeter. Figure 10.9 (pages 394–395) shows how constant-pressure calorimetry can be used to determine ΔH for a reaction.

Constant-pressure calorimetry can also be used to determine the heat capacity of an object or the specific heat of a substance. Suppose, for example, that we have a lead pellet with a mass of 26.47 g originally at 89.98°C. We drop the pellet into a constant-pressure calorimeter containing 100.0 g of water at 22.50°C. The temperature of the water increases to 23.17°C. In this case, we consider the pellet to be the system and the water to be the surroundings. Because it is the temperature of the surroundings that we measure, and because $q_{\text{sys}} = -q_{\text{surr}}$, we calculate q_p of the surroundings as

$$\text{Equation 10.14} \quad q_{\text{surr}} = sm\Delta T$$

Thus, q_{water} of the water is

$$q = \frac{4.184 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times 100.0 \text{ g} \times (23.17^\circ\text{C} - 22.50^\circ\text{C}) = 280 \text{ J}$$

and q_{pellet} is -280 J . The negative sign indicates that heat is *released* by the pellet. Dividing q_{pellet} by the temperature change (ΔT) gives us the heat capacity of the pellet (C_{pellet}).

$$C_{\text{pellet}} = \frac{-280 \text{ J}}{23.17^\circ\text{C} - 89.98^\circ\text{C}} = 4.19 \text{ J/}^\circ\text{C}$$

Furthermore, because we know the *mass* of the pellet, we can determine the specific heat of lead (s_{Pb}):

$$s_{\text{Pb}} = \frac{C_{\text{pellet}}}{m_{\text{pellet}}} = \frac{4.19 \text{ J/}^\circ\text{C}}{26.47 \text{ g}} = 0.158 \text{ J/g} \cdot ^\circ\text{C} \text{ or } 0.16 \text{ J/g} \cdot ^\circ\text{C}$$

Worked Example 10.5 shows how to use constant-pressure calorimetry to calculate the heat capacity (C) of a substance. Figure 10.10 (pages 396–397) illustrates the process of determining the specific heat of a metal using constant-pressure calorimetry.



Multi 10.2

Figure 10.9 Determination of $\Delta H_{\text{rxn}}^\circ$ by Constant-Pressure Calorimetry

Student Annotation: The temperature of the water stops changing when it and the temperature of the lead pellet are equal. Therefore, the final temperature of the pellet is also 23.17°C.



Multi 10.3

Figure 10.10 Determination of Specific Heat by Constant-Pressure Calorimetry

TABLE 10.3

Heats of Some Typical Reactions and Physical Processes Measured at Constant Pressure

Type of reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{NaCl}(aq)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	+56.2
Heat of fusion	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$	+6.01
Heat of vaporization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	+44.0*

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

Worked Example 10.5

A metal pellet with a mass of 100.0 g, originally at 88.4°C, is dropped into 125 g of water originally at 25.1°C. The final temperature of both the pellet and the water is 31.3°C. Calculate the heat capacity C (in J/°C) of the pellet.

Strategy Water constitutes the *surroundings*; the pellet is the *system*. Use Equation 10.14 ($q_{\text{surr}} = sm\Delta T$) to determine the heat absorbed by the water; then use Equation 10.12 ($q = C\Delta T$) to determine the heat capacity of the metal pellet.

Setup $m_{\text{water}} = 125 \text{ g}$, $s_{\text{water}} = 4.184 \text{ J/g} \cdot ^\circ\text{C}$, and $\Delta T_{\text{water}} = 31.3^\circ\text{C} - 25.1^\circ\text{C} = 6.2^\circ\text{C}$. The heat absorbed by the water must be released by the pellet: $q_{\text{water}} = -q_{\text{pellet}}$, $m_{\text{pellet}} = 100.0 \text{ g}$, and $\Delta T_{\text{pellet}} = 31.3^\circ\text{C} - 88.4^\circ\text{C} = -57.1^\circ\text{C}$.

Solution From Equation 10.14, we have

$$q_{\text{water}} = \frac{4.184 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times 125 \text{ g} \times 6.2^\circ\text{C} = 3242.6 \text{ J}$$

Thus,

$$q_{\text{pellet}} = -3242.6 \text{ J}$$

From Equation 10.12, we have

$$-3242.6 \text{ J} = C_{\text{pellet}} \times (-57.1^\circ\text{C})$$

Thus,

$$C_{\text{pellet}} = 57 \text{ J/}^\circ\text{C}$$

Think About It

The units cancel properly to give appropriate units for heat capacity. Moreover, ΔT_{pellet} is a negative number because the temperature of the pellet decreases.

Practice Problem A **TEMPT** What would the final temperature be if the pellet from Worked Example 10.5, initially at 95°C, were dropped into a 218-g sample of water, initially at 23.8°C?

Practice Problem B **UILD** What mass of water could be warmed from 23.8°C to 46.3°C by the pellet in Worked Example 10.5 initially at 116°C?

Practice Problem C **ONCEPTUALIZE** Two samples of the same substance are shown. The temperatures of the two samples are indicated on the thermometer. Which of the final temperatures shown [(i), (ii), or (iii)] best represents the final temperature when the two samples are combined?

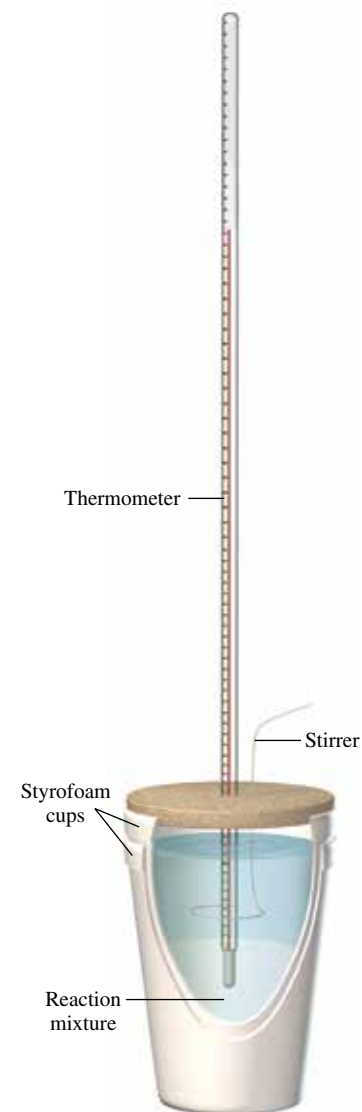
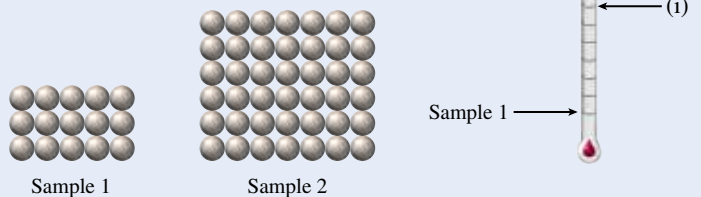


Figure 10.8 A constant-pressure coffee-cup calorimeter made of two Styrofoam cups. The nested cups help to insulate the reaction mixture from the surroundings. Two solutions of known volume containing the reactants at the same temperature are carefully mixed in the calorimeter. The heat produced or absorbed by the reaction can be determined by measuring the temperature change.

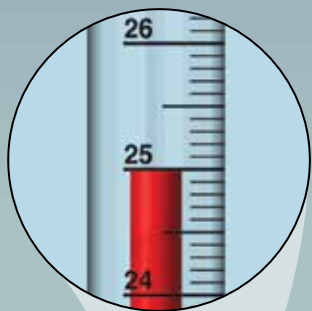
Constant-Volume Calorimetry

The heat of combustion is usually measured using constant-volume calorimetry. Typically, a known mass of the compound to be analyzed is placed in a steel container called a *constant-volume bomb*, or simply a *bomb*, which is pressurized with oxygen. The closed bomb is then immersed in a known amount of water in an insulated container, as shown in Figure 10.11 (page 398). (Together, the steel bomb and the water in which it is submerged constitute the *calorimeter*.) The sample is ignited electrically, and the heat released by the combustion of the sample is absorbed by the bomb and the water and can be determined by measuring the increase in temperature of the water. The special design of this type of calorimeter allows us to assume that no heat (or mass) is lost to the surroundings during the time it takes to carry out the reaction and measure the temperature change. 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 during the process, the heat change of the system overall (q_{system}) is zero and we can write

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

Figure 10.9

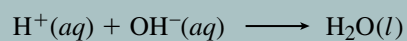
Determination of $\Delta H_{\text{rxn}}^{\circ}$ by Constant-Pressure Calorimetry



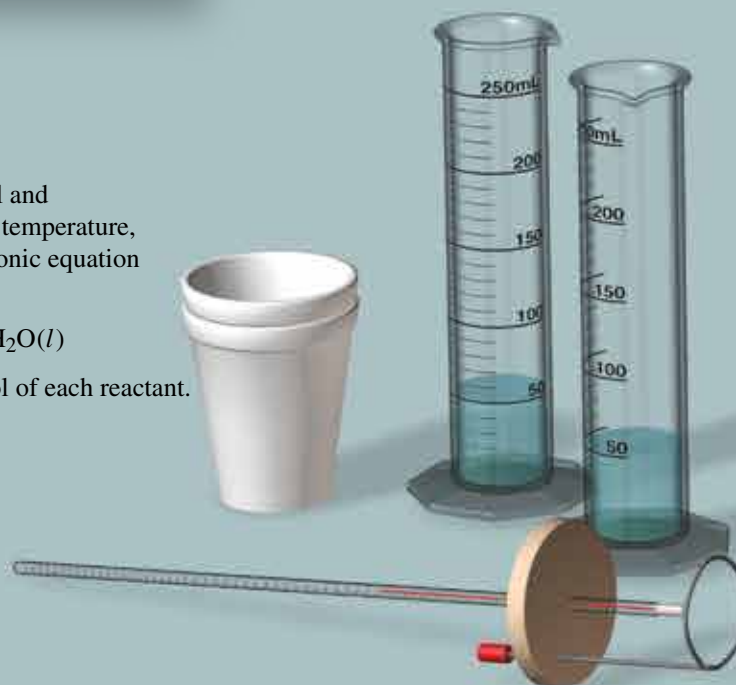
We pour the solutions into the calorimeter one at a time.



We start with 50.0 mL each of 1.00 M HCl and 1.00 M NaOH. Both solutions are at room temperature, which in this example is 25.0°C. The net ionic equation that represents the reaction is

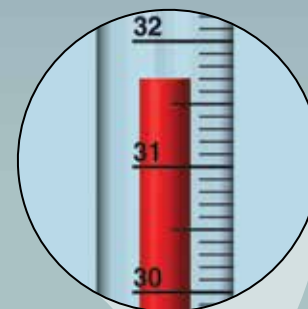


We have $0.0500 \text{ L} \times 1.00 \text{ M} = 0.0500 \text{ mol}$ of each reactant.





When both solutions have been added, we cap the calorimeter to prevent loss of energy to the environment and use the stirrer to ensure that the solutions are mixed thoroughly.



As the reaction proceeds, the temperature of the water increases as it absorbs the energy given off by the reaction. We record the maximum water temperature as 31.7°C.



Assuming the density and specific heat of the solution to be the same as those of water (1 g/mL, 4.184 J/g · °C), we calculate q_{soln} as follows:

$$q_{\text{soln}} = \text{specific heat of water} \times \text{mass of water} \times \text{temperature change}$$

$$= \frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} \times 100.0 \text{ g} \times (31.7 - 25.0)^\circ\text{C} = 2803 \text{ J}$$

Assuming that the heat capacity of the calorimeter is negligible, we know that $q_{\text{soln}} = -q_{\text{rxn}}$, and we can write

$$q_{\text{rxn}} = -2803 \text{ J}$$

This is the heat of reaction when 0.0500 mol H^+ reacts with 0.0500 mol OH^- . To determine ΔH_{rxn} , we divide q_{rxn} by the number of moles. (These reactants are present in stoichiometric amounts. If there were a *limiting* reactant, we would divide by the number of moles of limiting reactant.)

$$\Delta H_{\text{rxn}} = \frac{-2803 \text{ J}}{0.0500 \text{ mol}} = -5.61 \times 10^4 \text{ J/mol or } -56.1 \text{ kJ/mol}$$

This result is very close to the number we get using Equation 10.18 [► Section 10.6] and the data in Appendix 2.

What's the point?

Constant-pressure calorimetry can be used to determine ΔH_{rxn} —the heat of reaction for the reactant quantities specified by the balanced equation. However, when we carry out calorimetry experiments in the laboratory, we typically use much smaller quantities of reactants than those represented in a chemical equation. By measuring the temperature change of the surroundings (a known quantity of water in which the reactants are dissolved), we can determine q_{rxn} for the reactant quantities in the experiment. We can then divide q_{rxn} by the number of moles of reactant to determine ΔH_{rxn} .

Figure 10.10

Determination of Specific Heat by Constant-Pressure Calorimetry

We add metal shot (125.0 g at 100.0°C) to the water, and we cap the calorimeter to prevent loss of energy to the environment.



We place 100.0 mL (100.0 g) of water in the calorimeter. The temperature of this water is 25.0°C.

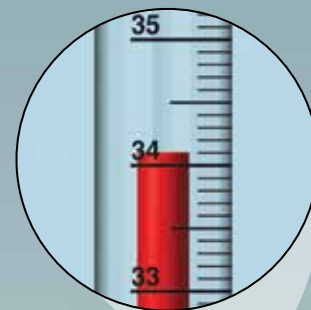


We place 125.0 g of metal shot in a test tube and immerse it in boiling water long enough to heat all of the metal to the boiling point of water (100.0°C).





As energy is transferred from the metal shot to the water, the temperature of the water increases and the temperature of the metal shot decreases. We use the stirrer to ensure thorough mixing. The thermometer measures the temperature of the water.



When the temperature of the metal shot and the water are equal, the temperature of the water has reached a maximum value. We record this temperature as 34.1°C.



We know that $q_{\text{water}} = -q_{\text{metal}}$.

Substituting in the information given we write:

$$q_{\text{water}} = \text{specific heat of water} \times \text{mass of water} \times \text{temperature change}$$

$$= \frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} \times 100.0 \text{ g} \times (34.1 - 25.0)^\circ\text{C} = 3807 \text{ J}$$

$$q_{\text{metal}} = \text{specific heat of metal} \times \text{mass of metal} \times \text{temperature change}$$

$$= x \times 125.0 \text{ g} \times (34.1 - 100.0)^\circ\text{C} = -8238 x \text{ g} \cdot ^\circ\text{C}$$

and

$$3807 \text{ J} = -(-8238 x) \text{ g} \cdot ^\circ\text{C}$$

$$x = \frac{3807 \text{ J}}{8238 \text{ g} \cdot ^\circ\text{C}} = 0.46 \text{ J/g} \cdot ^\circ\text{C}$$

The specific heat of the metal is therefore 0.46 J/g · °C.

What's the point?

We can determine the specific heat of a metal by combining a known mass of the metal at a known temperature with a known mass of water at a known temperature. Assuming the calorimeter has a negligible heat capacity, the amount of energy lost by the hotter metal is equal to the amount of energy gained by the cooler water.

Thinking Outside the Box



Heat Capacity of Calorimeters

Although we usually assume that no heat is absorbed by the Styrofoam cups we use in the laboratory for constant-pressure calorimetry, in reality, the calorimeter generally does absorb a small portion of the heat produced by a chemical reaction. We can determine the heat capacity of a coffee-cup calorimeter by combining reactant solutions with precisely known concentrations and masses. Once we have determined the heat capacity, we can correct for the heat absorbed by the calorimeter when we carry out other experiments.

Consider an experiment in which we combine 50.0 mL of 0.250 M HCl(aq) with 50.0 mL of 0.250 M NaOH. The calorimeter and both solutions are initially at 23.50°C, and the density and specific heat of the combined solution are the same as that of water (1.000 g/mL and 4.184 J/g · °C, respectively). We can determine the amount of heat the reaction will generate using moles of reactants and the heat of neutralization value from Table 10.3. We have 0.0500 L × 0.250 M = 0.0125 mole of each reactant. According to Table 10.3, the heat of neutralization is −56.2 kJ/mol. Thus, we expect the enthalpy change of the system to be 0.0125 mol × (−56.2 kJ/mol) = −0.703 kJ. Converting this to joules and using Equation 10.13, we calculate the temperature change we expect from the combination of these reactants.

$$q_{\text{sys}} = -703 \text{ J} = -\frac{4.184 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times 100.0 \text{ g} \times \Delta T$$

$$\Delta T = \frac{-703 \text{ J}}{-(4.184 \text{ J/g} \cdot ^\circ\text{C})(100.0 \text{ g})} = 1.68^\circ\text{C}$$

Thus, we expect the temperature to increase by 1.68°C. However, the measured final temperature is 25.09°C, an increase of only 1.59°C. The water temperature increased by less than expected because the calorimeter absorbed part of the heat produced by the neutralization reaction. We can determine how much heat the calorimeter absorbed using Equation 10.14. This time, we use the measured temperature change to calculate the amount of heat absorbed by the water.

$$q_{\text{surr}} = \frac{4.184 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times 100.0 \text{ g} \times 1.59^\circ\text{C} = 665 \text{ J}$$

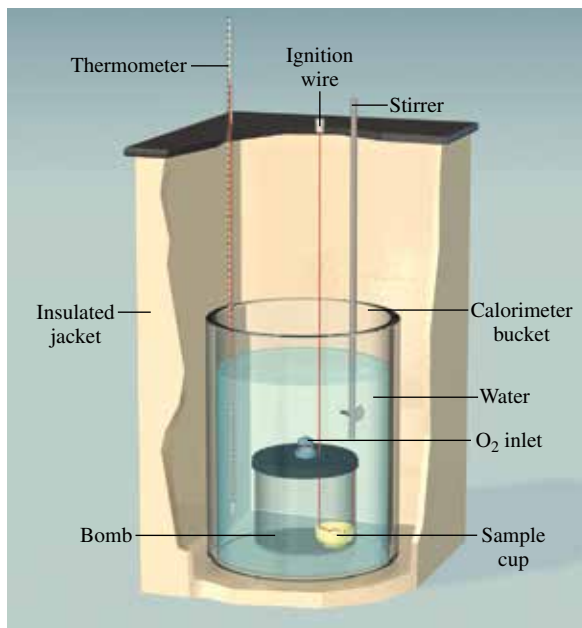
We know that the reaction produced 703 J but the water absorbed only 665 J. The remaining energy, 703 − 665 = 38 J, is $q_{\text{calorimeter}}$, the heat absorbed by the calorimeter itself. We use Equation 10.12 to calculate the heat capacity of the calorimeter.

$$38 \text{ J} = C_{\text{calorimeter}} \times 1.59^\circ\text{C}$$

$$C_{\text{calorimeter}} = 23.9 \text{ J/}^\circ\text{C}$$

Student Annotation: The calorimeter had the same initial temperature and the same final temperature as the solutions.

Figure 10.11 A constant-volume bomb calorimeter. The calorimeter is filled with oxygen gas at high pressure before it is placed in the bucket. The sample is ignited electrically, and the heat produced by the reaction is determined by measuring the temperature increase in the known amount of water surrounding the bomb.



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

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

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

$$q_{\text{cal}} = C_{\text{cal}}\Delta T \quad \text{Equation 10.15}$$

And, because $q_{\text{rxn}} = -q_{\text{cal}}$,

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T \quad \text{Equation 10.16}$$

The heat capacity of the calorimeter (C_{cal}) is determined by burning a substance with an accurately known heat of combustion. For example, it is known that the combustion of a 1.000-g sample of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) releases 26.38 kJ of heat. If the measured temperature increase is 4.673°C , then the heat capacity of the calorimeter is given by

$$C_{\text{cal}} = \frac{q_{\text{cal}}}{\Delta T} = \frac{26.38 \text{ kJ}}{4.673^\circ\text{C}} = 5.645 \text{ kJ}/^\circ\text{C}$$

Once C_{cal} has been determined, the calorimeter can be used to measure the heat of combustion of other substances. Because a reaction in a bomb calorimeter occurs under constant-volume rather than constant-pressure conditions, the measured heat change corresponds to the *internal energy* change (ΔU) rather than to the *enthalpy* change (ΔH) (see Equations 10.4 and 10.9). 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.

Worked Example 10.6 shows how to use constant-volume calorimetry to determine the energy content per gram of a substance.

Worked Example 10.6

A Famous Amos bite-sized chocolate chip cookie weighing 7.25 g is burned in a bomb calorimeter to determine its energy content. The heat capacity of the calorimeter is $39.97 \text{ kJ}/^\circ\text{C}$. During the combustion, the temperature of the water in the calorimeter increases by 3.90°C . Calculate the energy content (in kJ/g) of the cookie.

Strategy Use Equation 10.16 ($q_{\text{rxn}} = -C_{\text{cal}}\Delta T$) to calculate the heat released by the combustion of the cookie. Divide the heat released by the mass of the cookie to determine its energy content per gram.

Setup $C_{\text{cal}} = 39.97 \text{ kJ}/^\circ\text{C}$ and $\Delta T = 3.90^\circ\text{C}$.

Solution From Equation 10.16 we have

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T = -(39.97 \text{ kJ}/^\circ\text{C})(3.90^\circ\text{C}) = -1.559 \times 10^2 \text{ kJ}$$

Because energy content is a positive quantity, we write

$$\text{energy content per gram} = \frac{1.559 \times 10^2 \text{ kJ}}{7.25 \text{ g}} = 21.5 \text{ kJ/g}$$

Think About It

According to the label on the cookie package, a serving size is four cookies, or 29 g, and each serving contains 150 Cal. Convert the energy per gram to Calories per serving to verify the result.

$$\frac{21.5 \text{ kJ}}{\text{g}} \times \frac{1 \text{ Cal}}{4.184 \text{ kJ}} \times \frac{29 \text{ g}}{\text{serving}} = 1.5 \times 10^2 \text{ Cal/serving}$$

Practice Problem A **TEMPT** A serving of Grape-Nuts cereal (5.80 g) is burned in a bomb calorimeter with a heat capacity of $43.7 \text{ kJ}/^\circ\text{C}$. During the combustion, the temperature of the water in the calorimeter increased by 1.92°C . Calculate the energy content (in kJ/g) of Grape-Nuts.

Practice Problem B **UILD** The energy content of raisin bread is 13.1 kJ/g . Calculate the temperature increase when a slice of raisin bread (32.0 g) is burned in the calorimeter in Worked Example 10.6.

Practice Problem C **ONCEPTUALIZE** Suppose an experiment to determine the energy content of food used a calorimeter that contained less water than it did when it was calibrated. Explain how this would affect the result of the experiment.

Student Annotation: The negative sign in the result indicates that heat is released by the combustion.

Section 10.4 Review

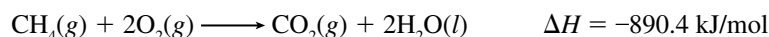
Calorimetry

- 10.4.1** A 1.000-g sample of benzoic acid is burned in a calorimeter to determine its heat capacity, C_{cal} . The reaction gives off 26.42 kJ of heat and the temperature of the water in the calorimeter increases from 23.40°C to 27.20°C. What is the heat capacity of the calorimeter?
- 10.4.2** In a constant-pressure calorimetry experiment, a reaction gives off 21.8 kJ of heat. The calorimeter contains 150 g of water, initially at 23.4°C. What is the final temperature of the water? The heat capacity of the calorimeter is negligibly small.
- 10.4.3** A reaction, carried out in a bomb calorimeter with $C_{\text{cal}} = 5.01 \text{ kJ/}^\circ\text{C}$, gives off 318 kJ of heat. The initial temperature of the water is 24.8°C. What is the final temperature of the water in the calorimeter?
- 10.4.4** Quantities of 50.0 mL of 1.00 M HCl and 50.0 mL of 1.00 M NaOH are combined in a constant-pressure calorimeter. Both solutions are initially at 24.4°C. Calculate the final temperature of the combined solutions. (Use the data from Table 10.3. Assume that the mass of the combined solutions is 100.0 g and that the solution's specific heat is the same as that for water, 4.184 J/g · °C.) The heat capacity of the calorimeter is negligibly small.

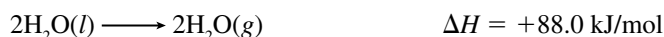
10.5 HESS'S LAW

Because enthalpy is a state function, the change in enthalpy that occurs when reactants are converted to products in a reaction is the same whether the reaction takes place in one step or in a series of steps. This observation is called **Hess's law**.¹ An analogy for Hess's law can be made to the floors in a building. Suppose, for example, that you take the elevator from the first floor to the sixth floor of the building. The net gain in your gravitational potential energy (which is analogous 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).

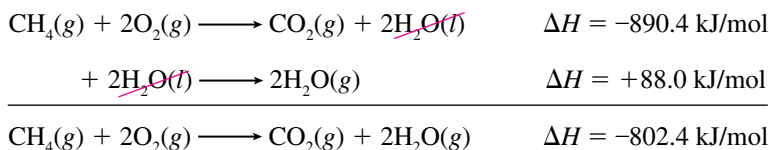
Recall from Section 10.3 that the enthalpy change for the combustion of a mole of methane depends on whether the product water is liquid or gas. More heat is given off by the reaction that produces liquid water. We can use this example to illustrate Hess's law by envisioning the first of these reactions happening in two steps. In step 1, methane and oxygen are converted to carbon dioxide and liquid water, releasing heat.



In step 2, the liquid water is vaporized, which requires an input of heat.



We can add balanced chemical equations just as we can add algebraic equalities, canceling identical items on opposite sides of the equation arrow:



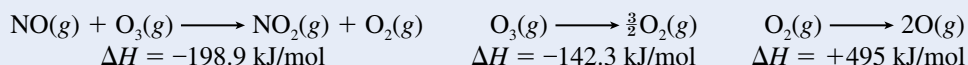
¹Germain Henri Hess (1802–1850), a Swiss chemist, was born in Switzerland but spent most of his life in Russia. For formulating Hess's law, he is called the father of thermochemistry.

When we add thermochemical equations, we add the ΔH values as well. This gives us the overall enthalpy change for the net reaction. Using this method, we can deduce the enthalpy changes for many reactions, some of which may not be possible to carry out directly. In general, we apply Hess's law by arranging a series of chemical equations (corresponding to a series of steps) in such a way that they sum to the desired overall equation. Often, in applying Hess's law, we must manipulate the equations involved, multiplying by appropriate coefficients, reversing equations, or both. It is important to follow the guidelines [Section 10.3] for the manipulation of thermochemical equations and to make the corresponding change to the enthalpy change of each step.

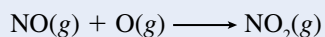
Worked Example 10.7 illustrates the use of this method for determining ΔH .

Worked Example 10.7

Given the following thermochemical equations,

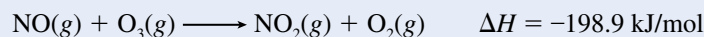


determine the enthalpy change for the reaction

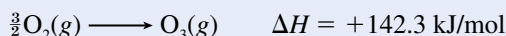


Strategy Arrange the given thermochemical equations so that they sum to the desired equation. Make the corresponding changes to the enthalpy changes, and add them to get the desired enthalpy change.

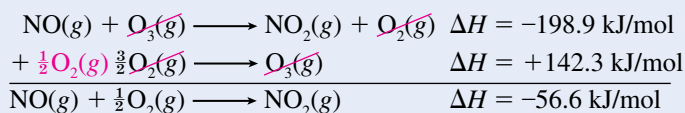
Setup The first equation has NO as a reactant with the correct coefficient, so we use it as is.



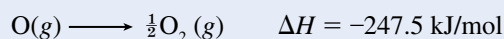
The second equation must be reversed so that the O_3 introduced by the first equation will cancel (O_3 is not part of the overall chemical equation). We also must change the sign on the corresponding ΔH value.



These two steps sum to give the following:

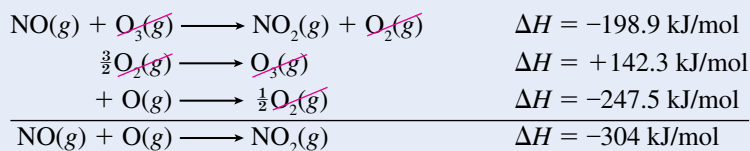


We then replace the $\frac{1}{2}\text{O}_2$ on the left with O by incorporating the last equation. To do so, we divide the third equation by 2 and reverse its direction. As a result, we must also divide its ΔH value by 2 and change its sign.



Finally, we sum all the steps and add their enthalpy changes.

Solution



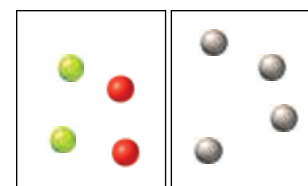
Think About It

Double-check the cancellation of identical items.

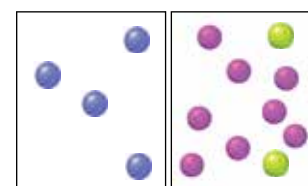
Practice Problem A **TEMPT** Use the thermochemical equations provided in Worked Example 10.7 to determine the enthalpy change for the reaction $2\text{NO}(g) + 4\text{O}(g) \longrightarrow 2\text{NO}_2(g) + \text{O}_2(g)$.

Practice Problem B **UILD** Use the thermochemical equations provided in Worked Example 10.7 to determine the enthalpy change for the reaction $2\text{NO}_2(g) \longrightarrow 2\text{NO}(g) + \text{O}_2(g)$.

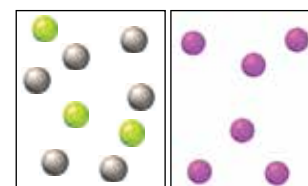
Practice Problem C **ONCEPTUALIZE** The diagrams shown are representations of four systems before and after reactions involving five different chemical species—each represented by a different color sphere. The ΔH values are given for the first three. Determine ΔH for the last reaction.



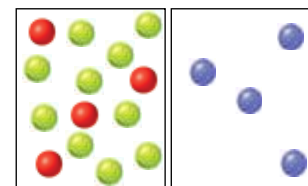
before after
 $\Delta H = 25 \text{ kJ/mol}$



before after
 $\Delta H = 100 \text{ kJ/mol}$



before after
 $\Delta H = -60 \text{ kJ/mol}$

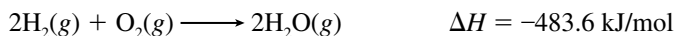


before after
 $\Delta H = ?$

Section 10.5 Review

Hess's Law

10.5.1 Given the following information, determine ΔH for $3\text{H}_2(\text{g}) + \text{O}_3(\text{g}) \longrightarrow 3\text{H}_2\text{O}(\text{g})$:



10.5.2 Given the following information, determine ΔH_{rxn} for $\text{P}_4\text{O}_6(\text{s}) + 2\text{O}_2(\text{g}) \longrightarrow \text{P}_4\text{O}_{10}(\text{s})$:



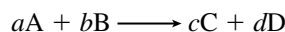
10.6 STANDARD ENTHALPIES OF FORMATION

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). According to Equation 10.10, ΔH can also be calculated if we know the enthalpies of all reactants and products. However, 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 the distance from the center of Earth), by common agreement all geographical 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°), which is defined as the heat change that results when 1 mole of a compound is formed from its constituent elements in their standard states. The superscript degree sign denotes standard-state conditions, and the subscript f stands for *formation*. The phrase “in their standard states” refers to the most stable form of an element under standard conditions, meaning at ordinary atmospheric pressure. The element oxygen, for example, can exist as atomic oxygen (O), diatomic oxygen (O_2), or ozone (O_3). By far the most stable form at ordinary atmospheric pressure, though, is diatomic oxygen. Thus, the standard state of oxygen is O_2 . Although the standard state does not specify a temperature, we will always use (ΔH_f°) values measured at 25°C .

Appendix 2 lists the standard enthalpies of formation for a number of elements and compounds. By convention, the standard enthalpy of formation of any element in its most stable form is zero. Again, using the element oxygen as an example, we can write $\Delta H_f^\circ(\text{O}_2) = 0$, but $\Delta H_f^\circ(\text{O}_3) \neq 0$ and $\Delta H_f^\circ(\text{O}) \neq 0$. Similarly, graphite is a more stable allotropic form of carbon than diamond under standard conditions and 25°C , so we have $\Delta H_f^\circ(\text{graphite}) = 0$ and $\Delta H_f^\circ(\text{diamond}) \neq 0$.

The importance of the standard enthalpies of formation is that once we know their values, we can readily calculate the *standard enthalpy of reaction* ($\Delta H_{\text{rxn}}^\circ$), defined as the enthalpy of a reaction carried out under standard conditions. For example, consider the hypothetical reaction



where a , b , c , and d are stoichiometric coefficients. For this reaction, $\Delta H_{\text{rxn}}^\circ$ is given by

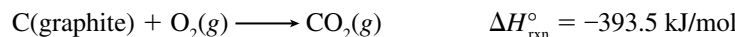
$$\text{Equation 10.17} \quad \Delta H_{\text{rxn}}^\circ = [c\Delta H_f^\circ(\text{C}) + d\Delta H_f^\circ(\text{D})] - [a\Delta H_f^\circ(\text{A}) + b\Delta H_f^\circ(\text{B})]$$

We can generalize Equation 10.17 as

$$\text{Equation 10.18} \quad \Delta H_{\text{rxn}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

where m and n are the stoichiometric coefficients for the reactants and products, respectively, and Σ (sigma) means “the sum of.” In these calculations, the stoichiometric coefficients are treated as numbers without units. Thus, the result has units of kJ/mol, where again, “per mole” means per mole of reaction as written. To use Equation 10.18 to calculate $\Delta H_{\text{rxn}}^\circ$, we must know the ΔH_f° values of the compounds that take part in the reaction. These values, tabulated in Appendix 2, are determined either by the direct method or the indirect method.

The *direct* method of measuring ΔH_f° works for compounds that can be synthesized from their elements easily and safely. 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:



We know from experience that this combustion goes to completion. Thus, from Equation 10.18 we can write

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{CO}_2) - [\Delta H_f^\circ(\text{graphite}) + \Delta H_f^\circ(\text{O}_2)] = -393.5 \text{ kJ/mol}$$

Because graphite and O_2 are the most stable allotropic forms of their respective elements, $\Delta H_f^\circ(\text{graphite})$ and $\Delta H_f^\circ(\text{O}_2)$ are both zero. Therefore,

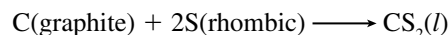
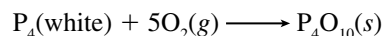
$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{CO}_2) = -393.5 \text{ kJ/mol}$$

or

$$\Delta H_f^\circ(\text{CO}_2) = -393.5 \text{ kJ/mol}$$

Arbitrarily assigning a value of zero to ΔH_f° for each element in its standard state does *not* affect the outcome of these calculations. 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 is intended to simplify the calculations. Referring again to the terrestrial altitude analogy, we find that Mt. Everest (the highest peak in the world) is 8708 ft higher than Mt. Denali (the highest peak in North America). This difference in altitude would be the same whether we had chosen sea level or the center of Earth as our reference elevation.

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



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.

Worked Example 10.8 shows how ΔH_f° values can be used to determine $\Delta H_{\text{rxn}}^\circ$.

Worked Example 10.8

Using data from Appendix 2, calculate $\Delta H_{\text{rxn}}^\circ$ for $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$.

Strategy Use Equation 10.18 [$\Delta H_{\text{rxn}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$] and ΔH_f° values from Appendix 2 to calculate $\Delta H_{\text{rxn}}^\circ$.

Setup The (ΔH_f°) values for $\text{Ag}^+(\text{aq})$, $\text{Cl}^-(\text{aq})$, and $\text{AgCl}(\text{s})$ are +105.9, -167.2, and -127.0 kJ/mol, respectively.

Solution Using Equation 10.18,

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Delta H_f^\circ(\text{AgCl}) - [\Delta H_f^\circ(\text{Ag}^+) + \Delta H_f^\circ(\text{Cl}^-)] \\ &= -127.0 \text{ kJ/mol} - [(+105.9 \text{ kJ/mol}) + (-167.2 \text{ kJ/mol})] \\ &= -127.0 \text{ kJ/mol} - (-61.3 \text{ kJ/mol}) = -65.7 \text{ kJ/mol} \end{aligned}$$

Think About It

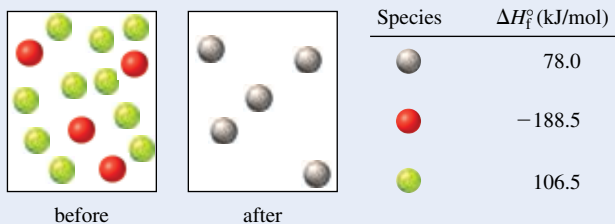
Watch out for misplaced or missing minus signs. This is an easy place to lose track of them.

Practice Problem A TTEMPT Using data from Appendix 2, calculate ($\Delta H_{\text{rxn}}^\circ$) for $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$.

Practice Problem B UILD Using data from Appendix 2, calculate ($\Delta H_{\text{rxn}}^\circ$) for $2\text{SO}(\text{g}) + \frac{2}{3}\text{O}_3(\text{g}) \longrightarrow 2\text{SO}_2(\text{g})$.

(Continued on next page)

Practice Problem **C** **CONCEPTUALIZE** The diagrams represent a system before and after a chemical reaction. Using the table of ΔH_f° values for the species involved in the reaction, determine $\Delta H_{\text{rxn}}^\circ$ for the process represented by the diagrams.

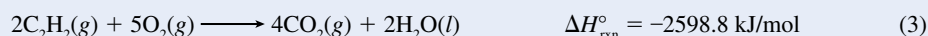
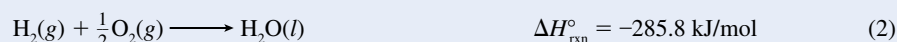
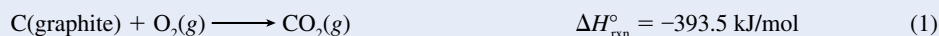


Many compounds cannot be synthesized from their elements directly. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases, ΔH_f° can be determined by an *indirect* approach, using Hess's law. If we know a series of reactions for which $\Delta H_{\text{rxn}}^\circ$ can be measured, and we can arrange them in such a way as to have them sum to the equation corresponding to the formation of the compound of interest, we can calculate ΔH_f° for the compound.

Worked Example 10.9 shows how to use Hess's law to calculate the ΔH_f° value by the indirect method for a compound that cannot be produced easily from its constituent elements.

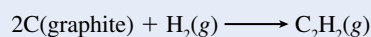
Worked Example 10.9

Given the following information, calculate the standard enthalpy of formation of acetylene (C_2H_2) from its constituent elements:

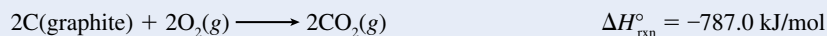


Strategy Arrange the equations that are provided so that they will sum to the desired equation. This may require reversing or multiplying one or more of the equations. For any such change, the corresponding change must also be made to the $\Delta H_{\text{rxn}}^\circ$ value.

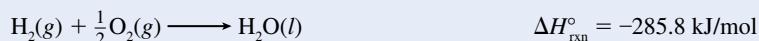
Setup The desired equation, corresponding to the standard enthalpy of formation of acetylene, is



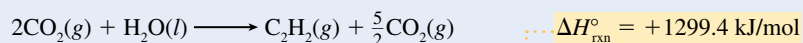
We multiply Equation (1) and its $\Delta H_{\text{rxn}}^\circ$ value by 2:



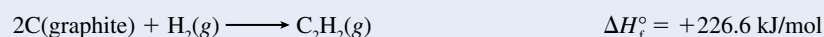
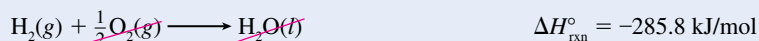
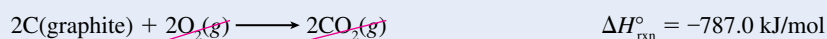
We include Equation (2) and its $\Delta H_{\text{rxn}}^\circ$ value as is:



We reverse Equation (3) and divide it by 2 (i.e., multiply through by 1/2):



Solution Summing the resulting equations and the corresponding $\Delta H_{\text{rxn}}^\circ$ values:

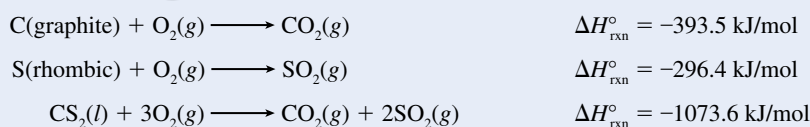


Student Annotation: The original $\Delta H_{\text{rxn}}^\circ$ value of Equation (3) has its sign reversed and it is divided by 2.

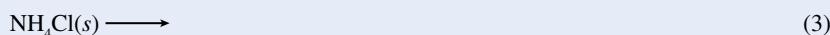
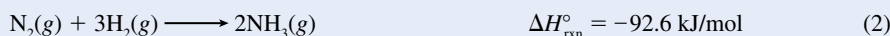
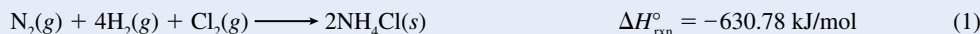
Think About It

Remember that a $\Delta H_{\text{rxn}}^\circ$ is only a ΔH_f° when there is just *one product*, just *one mole* is produced, and all the reactants are *elements in their standard states*.




Practice Problem A **TEMPT** Use the following data to calculate ΔH_f° for $\text{CS}_2(l)$:



Practice Problem B **UILD** ΔH_f° of hydrogen chloride [$\text{HCl}(g)$] is -92.3 kJ/mol . Given the following data, determine the identity of the two missing products and calculate $\Delta H_{\text{rxn}}^\circ$ for Equation (3). [*Hint*: Start by writing the chemical equation that corresponds to ΔH_f° for $\text{HCl}(g)$.]



Practice Problem C **ONCEPTUALIZE** The diagrams represent a system before and after a chemical reaction for which $\Delta H_{\text{rxn}}^\circ$ is -2624.9 kJ/mol . Use this information to complete the table of ΔH_f° values for the species involved in the reaction.

Species	ΔH_f° (kJ/mol)
	-148.7
	?
	255.1

before after

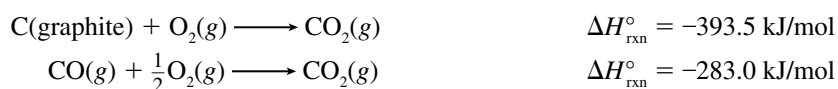
Section 10.6 Review

Standard Enthalpies of Formation

10.6.1 Using data from Appendix 2, calculate $\Delta H_{\text{rxn}}^\circ$ for $\text{H}_2(g) + \text{F}_2(g) \longrightarrow 2\text{HF}(g)$.

10.6.2 Using data from Appendix 2, calculate $\Delta H_{\text{rxn}}^\circ$ for $2\text{NO}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$.

10.6.3 Using the following data, calculate ΔH_f° for $\text{CO}(g)$:



10.7 BOND ENTHALPY AND THE STABILITY OF COVALENT MOLECULES

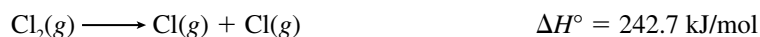
Why do covalent bonds form? According to valence bond theory, a covalent bond will form between two atoms if the potential energy of the resulting molecule is lower than that of the isolated atoms. Simply put, this means that the formation of covalent bonds is exothermic. While this fact may not seem intuitively obvious, you know that energy must be supplied to a molecule to *break* covalent bonds. Because the formation of a bond is the *reverse* process, we should expect energy to be given off when a bond forms.

One measure of the stability of a molecule is its **bond enthalpy**, which is the enthalpy change associated with breaking a particular bond in 1 mole of gaseous molecules. (Bond enthalpies in solids and liquids are affected by neighboring molecules.) The experimentally determined bond enthalpy of the diatomic hydrogen molecule, for example, is



Student Annotation: Recall that we previously used the term *bond energy* to refer to this property, before the term *enthalpy* had been introduced. [↩ Section 6.1]

According to this equation, breaking the covalent bonds in 1 mole of gaseous H_2 molecules requires 436.4 kJ of energy. For the less stable chlorine molecule,



Bond enthalpies can also be directly measured for heteronuclear diatomic molecules, such as HCl,



as well as for molecules containing multiple bonds:



Measuring the strength of covalent bonds in polyatomic molecules is more complicated. For example, measurements show that the energy needed to break the first O–H bond in H_2O is different from that needed to break the second O–H bond:



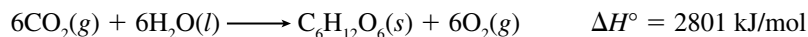
In each case, an O–H bond is broken, but the first step requires the input of more energy than the second. The difference between the two ΔH° values suggests that the second O–H bond itself undergoes change, because of the changes in its chemical environment.

We can now understand why the bond enthalpy of the same O–H bond in two different molecules, such as methanol (CH_3OH) and water (H_2O), will not be the same: their environments are different. For polyatomic molecules, therefore, we speak of the *average* bond enthalpy of a particular bond. For example, we can measure the enthalpy of the O–H bond in 10 different polyatomic molecules and obtain the average O–H bond enthalpy by dividing the sum of the bond enthalpies by 10. Table 10.4 lists the average bond enthalpies of a number of diatomic and polyatomic molecules. As we noted earlier, triple bonds are stronger than double bonds, and double bonds are stronger than single bonds.

A comparison of the thermochemical changes that take place during a number of reactions reveals a strikingly wide variation in the enthalpies of different reactions. For example, the combustion of hydrogen gas in oxygen gas is fairly *exothermic*:



The formation of glucose from carbon dioxide and water, on the other hand, best achieved by photosynthesis, is highly *endothermic*:



We can account for such variations by looking at the stability of individual reactant and product molecules. After all, most chemical reactions involve the making and breaking of bonds. Therefore, knowing the bond enthalpies and hence the stability of molecules reveals something about the thermochemical nature of the reactions that molecules undergo.

In many cases, it is possible to predict the approximate enthalpy of a reaction by using the average bond enthalpies. Because energy is always required to break chemical bonds and chemical bond formation is always accompanied by a release of energy, we can estimate the enthalpy of a reaction by counting the total number of bonds broken and formed in the reaction and recording all the corresponding enthalpy changes. The enthalpy of reaction in the gas phase is given by

$$\begin{aligned} \text{Equation 10.19} \quad \Delta H^\circ &= \sum \text{BE (reactants)} - \sum \text{BE (products)} \\ &= \text{total energy input} - \text{total energy released} \\ &\quad (\text{to break bonds}) \quad (\text{by bond formation}) \end{aligned}$$

where BE stands for average bond enthalpy and Σ is the summation sign. As written, Equation 10.19 takes care of the sign convention for ΔH° . Thus, if the total energy input needed to break bonds in the reactants is less than the total energy released when bonds are formed in the products, then ΔH° is negative and the reaction is exothermic [Figure 10.12(a)]. On the other hand, if less energy is released (bond making) than absorbed (bond breaking), ΔH° is positive and the reaction is endothermic [Figure 10.12(b)].

Student Annotation: To many students, Equation 10.19 appears to be backward. Ordinarily you calculate as *final minus initial*. Here we are determining the difference between the amount of heat we have to add to break reactant bonds and the amount of heat released when product bonds form. The sign of the final answer tells us if the process is endothermic (+) or exothermic (-).

TABLE 10.4		Bond Enthalpies	
Bond	Bond enthalpy (kJ/mol)	Bond	Bond enthalpy (kJ/mol)
H-H*	436.4	N-N	193
H-N	393	N=N	418
H-O	460	N≡N	941.4
H-S	368	N-O	176
H-P	326	N=O	607
H-F	568.2	N-F	272
H-Cl	431.9	N-Cl	200
H-Br	366.1	N-Br	243
H-I	298.3	N-I	159
C-H	414	O-O	142
C-C	347	O=O	498.7
C=C	620	O-P	502
C≡C	812	O=S	469
C-N	276	O-F	190
C=N	615	O-Cl	203
C≡N	891	O-Br	234
C-O	351	O-I	234
C=O†	745	P-P	197
C≡O	1070	P=P	489
C-P	263	S-S	268
C-S	255	S=S	352
C=S	477	F-F	156.9
C-F	453	Cl-Cl	242.7
C-Cl	339	Cl-F	193
C-Br	276	Br-Br	192.5
C-I	216	I-I	151.0

*Bond enthalpies shown in red are for diatomic molecules.

†The C=O bond enthalpy in CO₂ is 799 kJ/mol.

Student Annotation: Bond enthalpies for diatomic molecules have more significant figures than those for polyatomic molecules. Those for polyatomic molecules are average values based on the bonds in more than one compound.

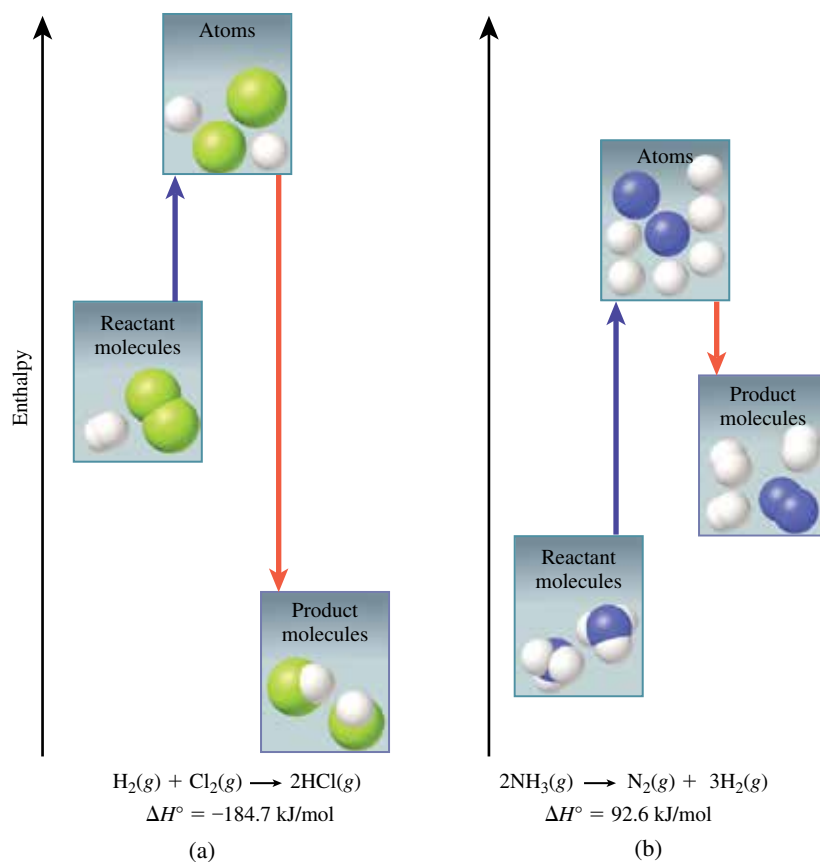


Figure 10.12 Enthalpy changes in (a) an exothermic reaction and (b) an endothermic reaction. The ΔH° values are calculated using Equation 10.18 and tabulated ΔH_f° values from Appendix 2.

If all the reactants and products are diatomic molecules, then the equation for the enthalpy of reaction will yield accurate results because the bond enthalpies of diatomic molecules are accurately known. If some or all of the reactants and products are polyatomic molecules, the equation will yield only approximate results because the bond enthalpies used will be averages.

Worked Example 10.10 shows how to estimate enthalpies of reaction using bond enthalpies.

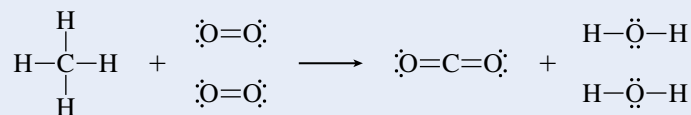
Worked Example 10.10

Use bond enthalpies from Table 10.4 to estimate the enthalpy of reaction for the combustion of methane:



Strategy Draw Lewis structures to determine what bonds are to be broken and what bonds are to be formed. (Don't skip the step of drawing Lewis structures. This is the only way to know for certain what types and numbers of bonds must be broken and formed.)

Setup



Bonds to break: 4 C–H and 2 O=O.

Bonds to form: 2 C=O and 4 H–O.

Bond enthalpies from Table 10.4: 414 kJ/mol (C–H), 498.7 kJ/mol (O=O), 799 kJ/mol (C=O in CO₂), and 460 kJ/mol (H–O).

Solution

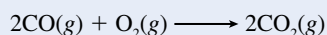
$$[4(414 \text{ kJ/mol}) + 2(498.7 \text{ kJ/mol})] - [2(799 \text{ kJ/mol}) + 4(460 \text{ kJ/mol})] = -785 \text{ kJ/mol.}$$

Remember that heats of reaction are expressed in kJ/mol, where the “per mole” refers to *per mole of reaction as written* [Section 10.3].

Think About It

Use Equation 10.18 [Section 10.6] and data from Appendix 2 to calculate this enthalpy of reaction again; then compare your results using the two approaches. The difference in this case is due to two things: Most tabulated bond enthalpies are averages and, by convention, we show the product of combustion as liquid water—but average bond enthalpies apply to species in the gas phase, where there is little or no influence exerted by neighboring molecules.

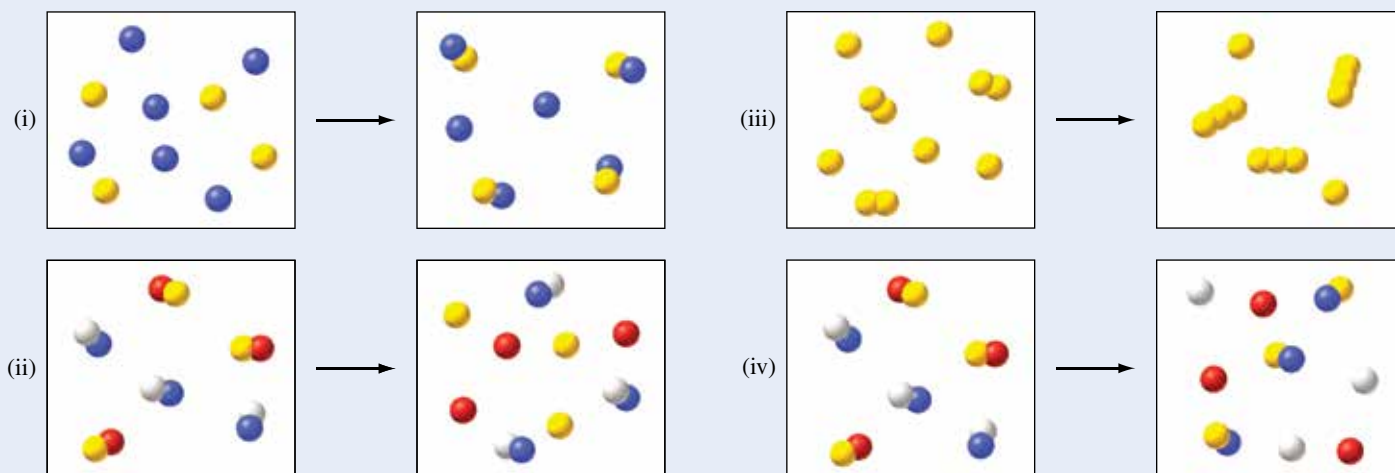
Practice Problem A **TEMPT** Use bond enthalpies from Table 10.4 to estimate the enthalpy of reaction for the combination of carbon monoxide and oxygen to produce carbon dioxide:



Practice Problem B **UILD** Using the following chemical equation, data from Table 10.4, and data from Appendix 2, determine the P–Cl bond enthalpy:



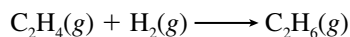
Practice Problem C **ONCEPTUALIZE** Four different chemical reactions are represented here. For each reaction, indicate whether it is endothermic or exothermic—or if there is not enough information to determine.



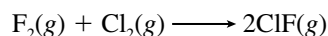
Section 10.7 Review

Bond Enthalpy and the Stability of Covalent Molecules

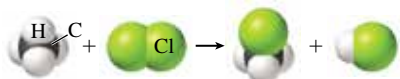
- 10.7.1** Use data from Table 10.4 to estimate ΔH_{rxn} for the reaction of ethylene with hydrogen to produce ethane.



- 10.7.2** Use data from Table 10.4 to estimate ΔH_{rxn} for the reaction of fluorine and chlorine to produce ClF.



- 10.7.3** Use bond enthalpies to determine ΔH_{rxn} for the reaction shown.



- 10.7.4** Use bond enthalpies to determine ΔH_{rxn} for the reaction shown

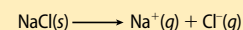


10.8 LATTICE ENERGY AND THE STABILITY OF IONIC SOLIDS

Unlike covalent compounds, ionic compounds consist of vast arrays of interspersed cations and anions, not discrete molecular units. For example, solid sodium chloride (NaCl) consists of equal numbers of Na^+ and Cl^- ions arranged in a three-dimensional network, the lattice, of alternating cations and anions (Figure 5.2, page 148).

We learned in Chapter 5 that the energy change associated with the formation of a lattice is the **lattice energy**. Although lattice energy is a useful measure of an ionic compound's stability, it is *not* a quantity that we can measure directly. Instead, we use various thermodynamic quantities that can be measured, and calculate lattice energy using Hess's law [Section 10.5].

Student Annotation: Recall that *lattice energy* is the amount of energy required to convert one mole of ionic solid to its constituent ions in the gas phase [Section 5.3]. For NaCl, the equation representing the process is:

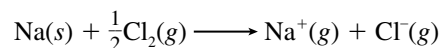


The Born-Haber Cycle

We have described the formation of an ionic compound as though it happens when gaseous ions coalesce into a solid. In fact, the reactions that produce ionic solids generally do not occur this way. Figure 10.13 illustrates the formation of sodium chloride (NaCl) from its constituent elements.

We can imagine the reaction of $\text{Na}(s)$ and $\text{Cl}_2(g)$ to form $\text{NaCl}(s)$ as taking place in a series of steps for which the energy changes can be measured. This method of determining the lattice energy is known as the **Born-Haber cycle**. Table 10.5 lists the energy changes associated with each step.

The net reaction resulting from the series of steps in Table 10.5 is



The final step in the formation of $\text{NaCl}(g)$ would be the coalescence of $\text{Na}^+(g) + \text{Cl}^-(g)$. This is the step for which we cannot measure the energy change directly. However, we *can* measure the standard heat of formation of $\text{NaCl}(s)$. (It is tabulated in Appendix 2 as -410.9 kJ/mol .) Although the formation of $\text{NaCl}(s)$ from its constituent elements is not actually a step in our imaginary process, knowing its value enables us to calculate the lattice energy of NaCl. Figure 10.14 (pages 412–413) illustrates how this is done using all of these thermodynamic data and Hess's law. The numbered steps correspond to the steps in Table 10.5. The Born-Haber cycle enables us to calculate the lattice energy, which we cannot measure directly, using the quantities that we can measure.

Worked Example 10.11 shows how to use the Born-Haber cycle to calculate the lattice energy.



Multi 10.4

Figure 10.14 Born-Haber Cycle

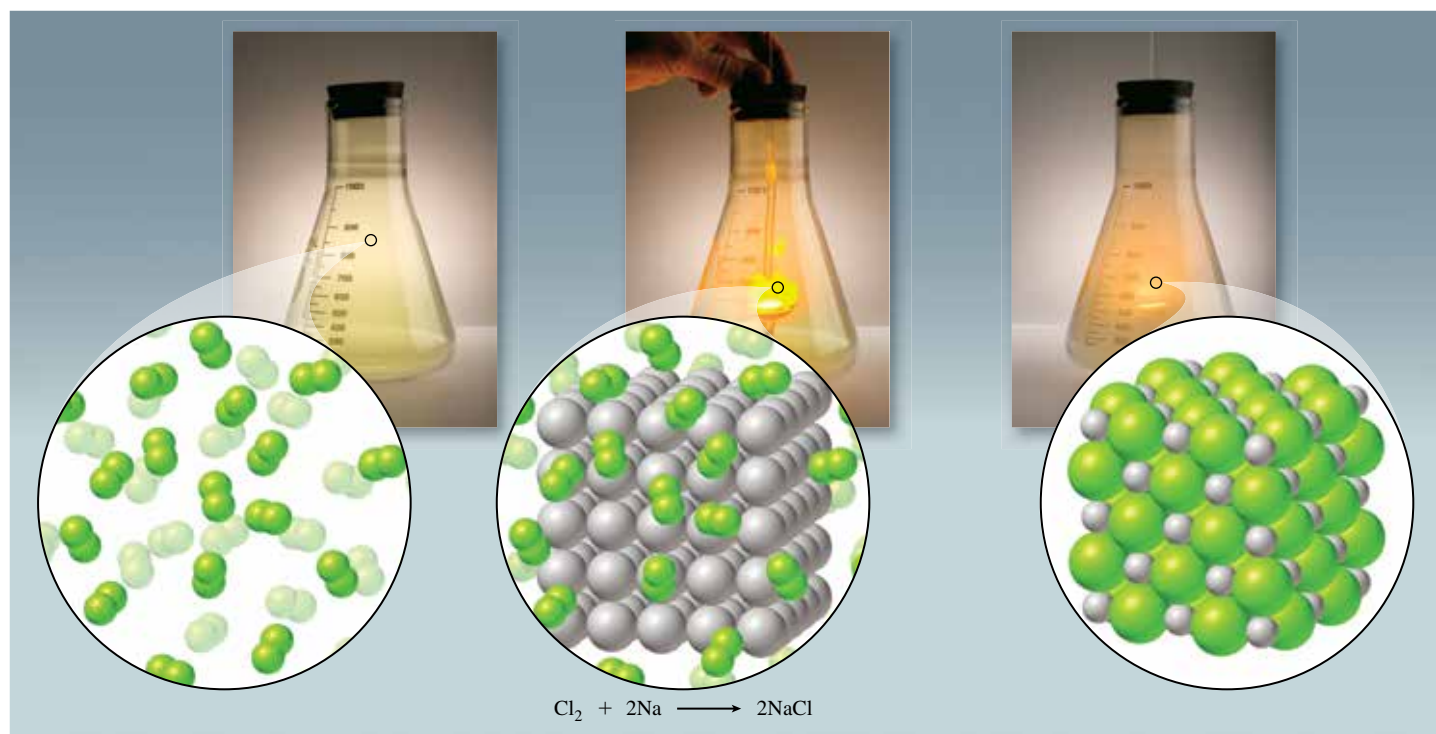


Figure 10.13 Sodium metal and chlorine gas combine to produce sodium chloride in a highly exothermic reaction.

TABLE 10.5

Hypothetical Steps in the Formation of $\text{Na}^+(\text{g})$ and $\text{Cl}^-(\text{g})$ from $\text{Na}(\text{s})$ and $\text{Cl}_2(\text{g})$

Chemical equation	Energy change (kJ/mol)
$\text{Na}(\text{s}) \longrightarrow \text{Na}(\text{g})$	107.7*
$\frac{1}{2}\text{Cl}_2(\text{g}) \longrightarrow \text{Cl}(\text{g})$	121.7†
$\text{Na}(\text{g}) \longrightarrow \text{Na}^+(\text{g}) + e^-$	495.9‡
$\text{Cl}(\text{g}) + e^- \longrightarrow \text{Cl}^-(\text{g})$	-349§

*Standard heat of formation (ΔH_f°) of $\text{Na}(\text{g})$ from Appendix 2.

†Standard heat of formation (ΔH_f°) of $\text{Cl}(\text{g})$ from Appendix 2.

‡First ionization energy (IE_1) of Na from Figure 4.8.

§ ΔH° for this process is negative. (Recall that by definition, EA is the amount of energy released [Section 4.4]. This ΔH is equal to $-EA$.)

Worked Example 10.11

Using data from Figures 4.8 and 4.10 and Appendix 2, calculate the lattice energy of cesium chloride (CsCl).

Strategy Using Figure 10.14 as a guide, combine the pertinent thermodynamic data and use Hess's law to calculate the lattice energy.

Setup From Figure 4.8, $IE_1(\text{Cs}) = 376 \text{ kJ/mol}$. From Figure 4.10, $EA_1(\text{Cl}) = 349.0 \text{ kJ/mol}$. From Appendix 2, $\Delta H_f^\circ[\text{Cs}(\text{g})] = 76.50 \text{ kJ/mol}$, $\Delta H_f^\circ[\text{Cl}(\text{g})] = 121.7 \text{ kJ/mol}$, $\Delta H_f^\circ[\text{CsCl}(\text{s})] = -442.8 \text{ kJ/mol}$. Because we are interested in magnitudes only, we can use the absolute values of the thermodynamic data. And, because only the standard heat of formation of $\text{CsCl}(\text{s})$ is a negative number, it is the only one for which the sign changes.

Solution

$$\begin{aligned} & [\Delta H_f^\circ[\text{Cs}(\text{g})] + \Delta H_f^\circ[\text{Cl}(\text{g})] + IE_1(\text{Cs}) + |\Delta H_f^\circ[\text{CsCl}(\text{s})|] - EA_1(\text{Cl}) = \text{lattice energy} \\ & = (76.50 \text{ kJ/mol} + 121.7 \text{ kJ/mol} + 376 \text{ kJ/mol} + 442.8 \text{ kJ/mol}) - 349.0 \text{ kJ/mol} \\ & = 668 \text{ kJ/mol} \end{aligned}$$

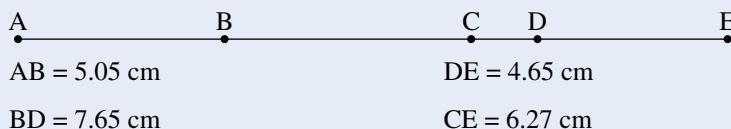
Think About It

Compare this value to that for NaCl in Figure 10.14 (787 kJ/mol). Both compounds contain the same anion (Cl^-) and both have cations with the same charge (+1), so the relative sizes of the cations will determine the relative strengths of their lattice energies. Because Cs^+ is larger than Na^+ , the lattice energy of CsCl is smaller than the lattice energy of NaCl.

Practice Problem A **TEMPT** Using data from Figures 4.8 and 4.10 and Appendix 2, calculate the lattice energy of rubidium iodide (RbI).

Practice Problem B **UILD** The lattice energy of MgO is 3890 kJ/mol, and the second ionization energy (IE_2) of Mg is 1450.6 kJ/mol. Using these data, as well as data from Figures 4.8 and 4.10 and Appendix 2, determine the second electron affinity for oxygen, $EA_2(\text{O})$.

Practice Problem C **ONCEPTUALIZE** Five points (A through E) lie along a line. The known distances between points are given. Determine the distance between points A and C.



Comparison of Ionic and Covalent Compounds

Ionic and covalent compounds differ markedly in their general physical properties because of differences in the nature of their bonds. There are two types of attractive forces in covalent compounds, the *intramolecular* bonding force that holds the atoms together in a molecule, and the *intermolecular* forces between molecules. Bond enthalpy can be used to quantify the intramolecular bonding force. Intermolecular forces are usually quite weak compared to the forces holding atoms together within a molecule, so molecules of a covalent compound are not held together tightly. As a result, covalent compounds are usually gases, liquids, or low-melting solids.

On the other hand, the electrostatic forces [Section 5.3] holding ions together in an ionic compound are usually very strong, so ionic compounds are solids at room temperature and have high melting points. Many ionic compounds are soluble in water, and the resulting aqueous solutions conduct electricity because the compounds are strong electrolytes [Section 9.1]. Most covalent compounds are insoluble in water, or if they do dissolve, their aqueous solutions generally do not conduct electricity because the compounds are nonelectrolytes. Molten ionic compounds conduct electricity because they contain mobile cations and anions; liquid or molten covalent compounds do *not* conduct electricity because no ions are present. Table 10.6 compares some of the properties of a typical ionic compound, sodium chloride (NaCl), with those of a covalent compound, carbon tetrachloride (CCl_4).

TABLE 10.6

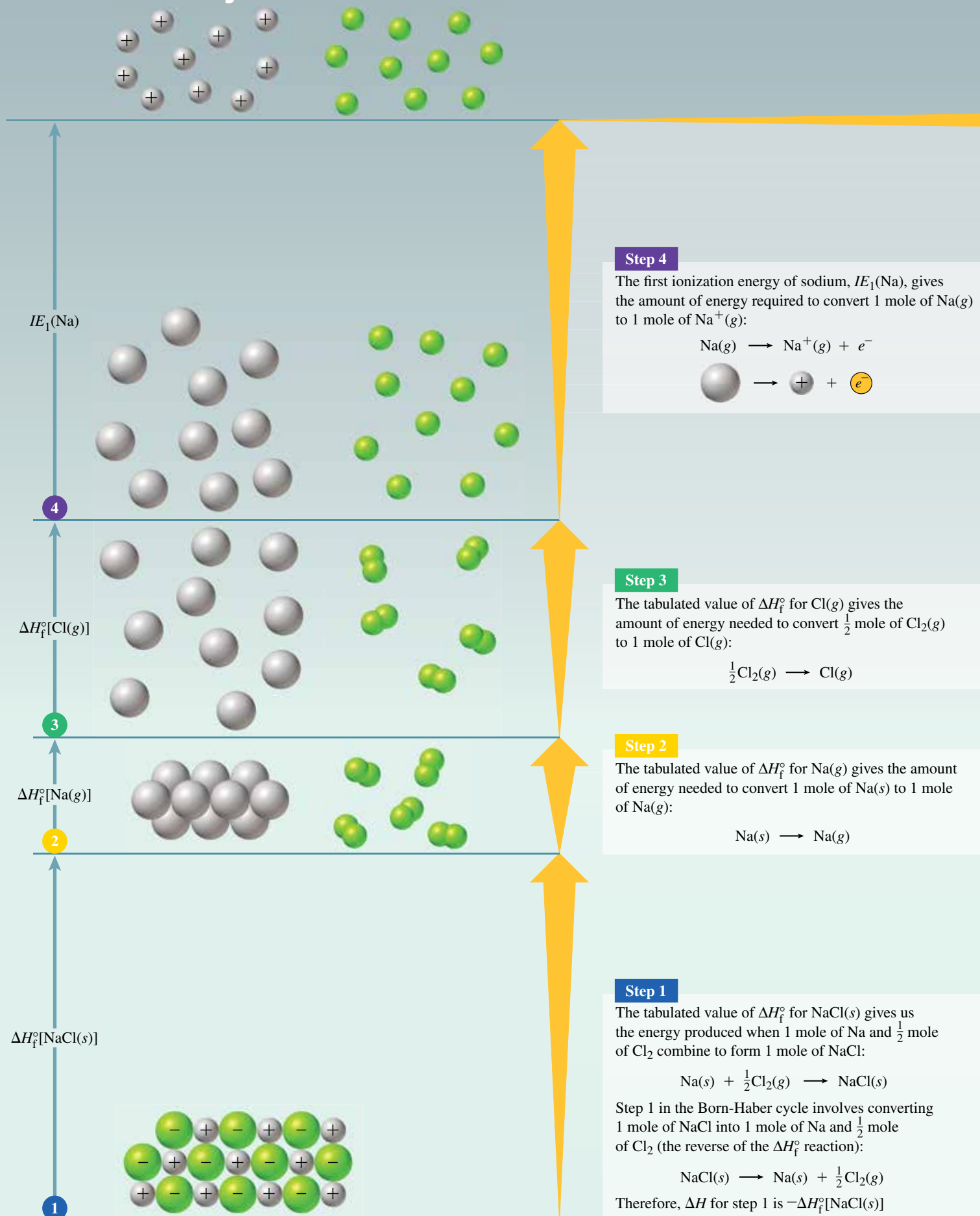
Comparison of Some Properties of an Ionic Compound (NaCl) and a Covalent Compound (CCl_4)

Property	NaCl	CCl_4
Appearance	White solid	Colorless liquid
Melting point ($^{\circ}\text{C}$)	801	-23
Molar heat of fusion* (kJ/mol)	30.2	2.5
Boiling point ($^{\circ}\text{C}$)	1413	76.5
Molar heat of vaporization* (kJ/mol)	600	30
Density (g/cm^3)	2.17	1.59
Solubility in water	High	Very low
Electrical conductivity		
Solid	Poor	Poor
Liquid	Good	Poor
Aqueous	Good	Poor

*The molar heat of fusion and molar heat of vaporization are the amounts of heat needed to melt 1 mole of the solid and to vaporize 1 mole of the liquid, respectively.

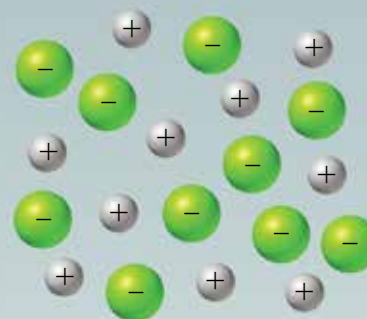
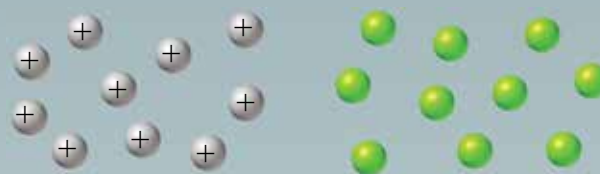
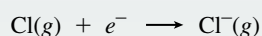
Figure 10.14

Born-Haber Cycle



Step 5

The electron affinity of chlorine, $EA(\text{Cl})$, gives the amount of energy produced when 1 mole of $\text{Cl}(g)$ is converted to 1 mole of $\text{Cl}^-(g)$:



5

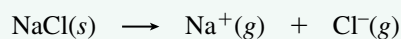
$EA(\text{Cl})$

$$\begin{array}{ccccccccc} \text{1} & & \text{2} & & \text{3} & & \text{4} & & \text{5} \\ \boxed{410.9 \text{ kJ/mol}} & + & \boxed{107.7 \text{ kJ/mol}} & + & \boxed{121.7 \text{ kJ/mol}} & + & \boxed{495.9 \text{ kJ/mol}} & - & \boxed{349 \text{ kJ/mol}} & = & \boxed{787 \text{ kJ/mol}} \end{array}$$

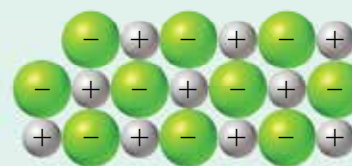
Lattice Energy

What's the point?

Lattice energy is the energy required to convert 1 mole of an ionic solid into its constituent ions in the gas phase. In the case of NaCl , the equation representing the process is



Lattice energy is not a quantity that we can measure directly. Rather, we determine lattice energy by combining tabulated values of a series of quantities that can be measured directly. Although the steps in the Born-Haber cycle are not necessarily the steps that actually take place, because they combine to give the correct overall process, the energy changes associated with them can be used (with Hess's law) to determine the overall energy change.



Section 10.8 Review

Lattice Energy and the Stability of Ionic Solids

10.8.1 Compare the lattice energy of KF with (a) the lattice energy of LiF, (b) the lattice energy of KCl, and (c) the lattice energy of KI.

10.8.2 Using the following data, calculate the lattice energy of KF:

$$\Delta H_f^\circ[\text{K}(g)] = 89.99 \text{ kJ/mol}, \Delta H_f^\circ[\text{F}(g)] = 80.0 \text{ kJ/mol},$$

$$IE_1(\text{K}) = 419 \text{ kJ/mol}, \Delta H_f^\circ[\text{KF}(s)] = -547 \text{ kJ/mol}, \text{ and } EA_1(\text{F}) = 328 \text{ kJ/mol}.$$

Learning Outcomes

- Identify the system and surroundings for a given experiment.
- Identify a process as endothermic or exothermic.
- Understand the various units used to measure energy including joules and calories.
- Identify a system as being open, closed, or isolated.
- Understand the concept of state functions and be able to identify state functions and nonstate functions.
- Define work and heat and understand the sign conventions associated with these terms.
- Understand the key differences between internal energy measurements using constant-pressure and constant-volume calorimetry.
- Understand enthalpy and enthalpy changes.
- Calculate the enthalpy change of a reaction and understand how it is dependent upon stoichiometric amounts of products and reactants.
- Perform calorimetric calculations involving specific heat or heat capacity.
- Apply Hess's law in the determination of the heat of reaction of a multistep process.
- Understand the nature of the standard state, particularly as it applies to standard heat of formation.
- Use the standard heats of formation of products and reactants to calculate the enthalpy change of a reaction.
- Use bond enthalpies to calculate an estimate of the enthalpy change of a reaction.
- Calculate the lattice energy of a compound using the Born-Haber cycle.

Chapter Summary

SECTION 10.1

- The **system** is the particular part of the universe that we are interested in studying—such as the reactants and products in a chemical reaction. The term **surroundings** refers to the rest of the universe. System + surroundings = universe.
- **Heat** refers to the flow of thermal energy between two bodies at different temperatures. **Thermochemistry** is the study of the heat associated with chemical reactions and physical processes.
- In an **exothermic process**, heat is released to the surroundings, so the energy of the system decreases. In an **endothermic process**, heat is absorbed from the surroundings, so the energy of the system increases.

SECTION 10.2

- **Thermodynamics** is the study of the conversions among different types of energy. Thermochemistry is a branch of thermodynamics.
- An **open system** is one that can exchange both matter and energy with its surroundings. A **closed system** is one that can exchange energy but not matter with its surroundings. An **isolated system** is one that cannot exchange either energy or matter with its surroundings.
- The **state of a system** is defined by the values of all relevant macroscopic properties, such as temperature, volume, and pressure. A **state function** is one whose value depends only on the state of the system and not on how that state was achieved. State functions include energy, pressure, volume, and temperature.
- The **first law of thermodynamics** states that energy cannot be created or destroyed, but it can be changed from one form to another. The first law of thermodynamics is based on the law of conservation of energy.

SECTION 10.3

- **Enthalpy** is the heat exchanged between the system and surroundings at constant pressure. It is a state function. **Enthalpy of reaction** (ΔH_{rxn}) is the heat exchanged at constant pressure for a specific reaction.
- A **thermochemical equation** is a balanced chemical equation for which the enthalpy change (ΔH_{rxn}) is given.

SECTION 10.4

- **Calorimetry** is the science of measuring temperature changes to determine heats associated with chemical reactions. Calorimetry may be carried out at constant pressure (in a coffee-cup calorimeter) or at constant volume (in a bomb calorimeter).
- The **specific heat** (s) of a substance is the amount of heat required to increase the temperature of 1 g of the substance by 1°C. The **heat capacity** of an object is the amount of heat required to increase the temperature of the object by 1°C.

SECTION 10.5

- **Hess's law** states that the enthalpy change for a reaction that occurs in a series of steps is equal to the sum of the enthalpy changes of the individual steps. Hess's law is valid because enthalpy is a state function.

SECTION 10.6

- The **standard enthalpy of formation** (ΔH_f°) is the enthalpy change associated with the formation of 1 mole of a substance from its constituent elements, each in its standard state. The **standard enthalpy of reaction** ($\Delta H_{\text{rxn}}^\circ$) can be calculated for any reaction using tabulated standard enthalpies of formation (ΔH_f°) of the products and reactants.

SECTION 10.7

- **Bond enthalpy** is the energy required to break 1 mole of a particular type of bond. Bond enthalpies are a measure of the stability of covalent bonds and can be used to estimate the enthalpy change for a reaction.

SECTION 10.8

- Lattice energy is the amount of energy required to convert a mole of ionic solid to its constituent ions in the gas phase. Lattice energy cannot be measured directly, but is determined using the **Born-Haber cycle** and thermodynamic quantities that can be measured directly.

Key Words

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Born-Haber cycle, 409

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Key Equations

10.1 $\Delta U = q + w$	The change in internal energy of a system (ΔU) is the sum of heat (q) and the work (w) associated with a process. Proper sign conventions must be used for heat and work (Table 10.1).
10.2 $w = -P\Delta V$	Pressure-volume work done by (or on) a system is calculated using the external pressure (P) and the change in volume (ΔV).
10.3 $\Delta U = q - P\Delta V$	The change in internal energy of a system (ΔU) is equal to heat (q) minus pressure-volume work ($P\Delta V$).
10.4 $q_v = \Delta U$	Heat given off (or absorbed) by a system at constant volume (q_v) is equal to the change in internal energy (ΔU).
10.5 $q_p = \Delta U + P\Delta V$	Heat given off (or absorbed) by a system at constant pressure (q_p) is equal to the sum of change in internal energy (ΔU) and pressure-volume work ($P\Delta V$).
10.6 $H = U + PV$	Enthalpy (H) is equal to the sum of internal energy (U) and pressure-volume work ($P\Delta V$).
10.7 $\Delta H = \Delta U + \Delta(PV)$	The change in enthalpy (ΔH) is equal to the sum of change in internal energy (ΔU) and change in the product of pressure and volume [$\Delta(PV)$].
10.8 $\Delta H = \Delta U + P\Delta V$	The change in enthalpy (ΔH) is equal to the sum of change in internal energy (ΔU) and the product of external pressure (P) and change volume (ΔV).
10.9 $q_p = \Delta H$	Heat given off (or absorbed) by a process at constant pressure (q_p) is equal to change in enthalpy (ΔH).
10.10 $\Delta H = H(\text{products}) - H(\text{reactants})$	Enthalpy change for a reaction (ΔH) is the difference between the enthalpy of products [$H(\text{products})$] and enthalpy of reactants [$H(\text{reactants})$], although this is not the equation generally used to calculate enthalpy changes because the absolute values of enthalpy are not known.
10.11 $q = sm\Delta T$	Heat given off (or absorbed) by a substance (q) is equal to the product of specific heat of the substance (s), mass of the substance (m), and the change in temperature (ΔT).
10.12 $q = C\Delta T$	Heat given off (or absorbed) by an object (q) is equal to the product of specific heat of the object (C) and the change in temperature (ΔT).
10.13 $q_{\text{sys}} = -sm\Delta T$	Heat given off (or absorbed) by a system (q_{sys}) is equal in magnitude and opposite in sign to the heat given off or absorbed by the surroundings.
10.14 $q_{\text{surr}} = sm\Delta T$	Heat given off (or absorbed) by the surroundings (q_{surr}) is equal in magnitude and opposite in sign to the heat given off or absorbed by the system.
10.15 $q_{\text{cal}} = C_{\text{cal}}\Delta T$	Heat given off (or absorbed) by a calorimeter (q_{cal}) is equal to the product of heat capacity of the calorimeter (C_{cal}) and change in temperature (ΔT).
10.16 $q_{\text{rxn}} = -C_{\text{cal}}\Delta T$	Heat of reaction (q_{rxn}) is equal in magnitude and opposite in sign to heat of calorimeter (q_{cal}).
10.17 $\Delta H_{\text{rxn}}^{\circ} = [c\Delta H_f^{\circ}(\text{C}) + d\Delta H_f^{\circ}(\text{D})] - [a\Delta H_f^{\circ}(\text{A}) + b\Delta H_f^{\circ}(\text{B})]$	Standard enthalpy change for a reaction ($\Delta H_{\text{rxn}}^{\circ}$) can be calculated by multiplying the coefficient of each species in the reaction by the corresponding standard enthalpy of formation (ΔH_f°).
10.18 $\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_f^{\circ}(\text{products}) - \sum m\Delta H_f^{\circ}(\text{reactants})$	Standard enthalpy change for a reaction ($\Delta H_{\text{rxn}}^{\circ}$) is the difference between the sum of standard enthalpies of formation of products $\sum \Delta H_f^{\circ}(\text{products})$ and the sum of standard enthalpies of formation of reactants $\sum \Delta H_f^{\circ}(\text{reactants})$.
10.19 $\Delta H^{\circ} = \sum \text{BE}(\text{reactants}) - \sum \text{BE}(\text{products})$	The enthalpy change of a reaction can be estimated by subtracting the sum of bond enthalpies in products from the sum of bond enthalpies in reactants.

Questions and Problems

SECTION 10.1: ENERGY AND ENERGY CHANGES

Review Questions

- Define these terms: *system*, *surroundings*, *thermal energy*, *chemical energy*.
- What is heat? How does heat differ from thermal energy? Under what condition is heat transferred from one system to another?
- These are various forms of energy: chemical, heat, light, mechanical, and electrical. Suggest several ways of converting one form of energy to another.
- Define these terms: *thermochemistry*, *exothermic process*, *endothermic process*.

Conceptual Problems

- Stoichiometry is based on the law of conservation of mass. On what law is thermochemistry based?
- Describe two exothermic processes and two endothermic processes.
- Decomposition reactions are usually endothermic, whereas combination reactions are usually exothermic. Give a qualitative explanation for this observation.

SECTION 10.2: INTRODUCTION TO THERMODYNAMICS

Review Questions

- On what law is the first law of thermodynamics based? Explain the sign conventions in the equation

$$\Delta U = q + w$$

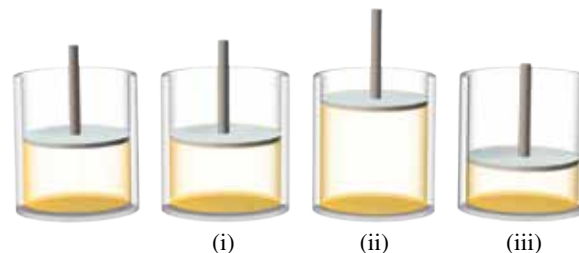
- Explain what is meant by a state function. Give two examples of quantities that are state functions and two that are not state functions.

Computational Problems

- In a gas expansion, 87 J of heat is absorbed from the surroundings and the energy of the system decreases by 128 J. Calculate the work done.
- The work done to compress a gas is 74 J. As a result, 26 J of heat is given off to the surroundings. Calculate the change in energy of the gas.
- Calculate q , and determine whether heat is absorbed or released when a system does work on the surroundings equal to 64 J and $\Delta U = -213$ J.
- Calculate w , and determine whether work is done *by* the system or *on* the system when 67 J of heat is released and $\Delta U = 510$ J.

Conceptual Problems

Use the following diagrams for Problems 10.14 and 10.15.



- The diagram on the left shows a system before a process. Determine which of the diagrams on the right could represent the system after it undergoes a process in which (a) the system absorbs heat and ΔU is negative; (b) the system absorbs heat and does work on the surroundings; (c) the system releases heat and does work on the surroundings.
- The diagram on the left shows a system before a process. Determine which of the diagrams on the right could represent the system after it undergoes a process in which (a) work is done on the system and ΔU is negative; (b) the system releases heat and ΔU is positive; (c) the system absorbs heat and ΔU is positive.

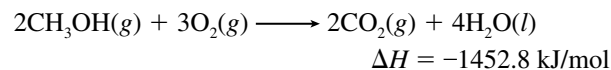
SECTION 10.3: ENTHALPY

Review Questions

- Consider these changes.
 - $\text{Hg}(l) \longrightarrow \text{Hg}(g)$
 - $3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
 - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \longrightarrow \text{CuSO}_4(s) + 5\text{H}_2\text{O}(g)$
 - $\text{H}_2(g) + \text{F}_2(g) \longrightarrow 2\text{HF}(g)$

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

- Define these terms: *enthalpy* and *enthalpy of reaction*. Under what condition is the heat of a reaction equal to the enthalpy change of the same reaction?
- In writing thermochemical equations, why is it important to indicate the physical state (i.e., gaseous, liquid, solid, or aqueous) of each substance?
- Consider the reaction:



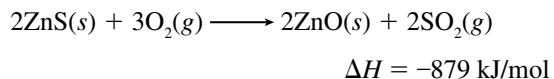
What is the value of ΔH if (a) the equation is multiplied throughout by 2; (b) the direction of the reaction is reversed so that the products become the reactants, and vice versa; (c) water vapor instead of liquid water is formed as the product?

Computational Problems

- A sample of nitrogen gas expands in volume from 1.6 to 5.4 L at constant temperature. Calculate the work done in joules if the gas expands (a) against a vacuum,

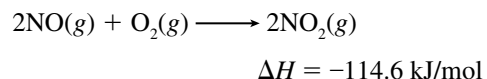
(b) against a constant pressure of 0.80 atm, and (c) against a constant pressure of 3.7 atm. (See Equation 10.2.)

- 10.21** A gas expands in volume from 26.7 to 89.3 mL at constant temperature. Calculate the work done (in joules) if the gas expands (a) against a vacuum, (b) against a constant pressure of 1.5 atm, and (c) against a constant pressure of 2.8 atm. (See Equation 10.2.)
- 10.22 A gas expands and does PV work on the surroundings equal to 325 J. At the same time, it absorbs 127 J of heat from the surroundings. Calculate the change in energy of the gas.
- 10.23** The first step in the industrial recovery of zinc from the zinc sulfide ore is roasting, that is, the conversion of ZnS to ZnO by heating:

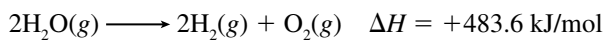


Calculate the heat evolved (in kJ) per gram of ZnS roasted.

- 10.24 Determine the amount of heat (in kJ) given off when 1.26×10^4 g of NO_2 are produced according to the equation

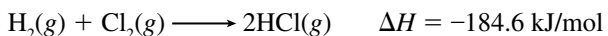


- 10.25** Consider the reaction



at a certain temperature. If the increase in volume is 32.7 L against an external pressure of 1.00 atm, calculate ΔU for this reaction. (The conversion factor is $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$.)

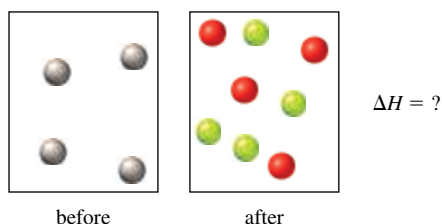
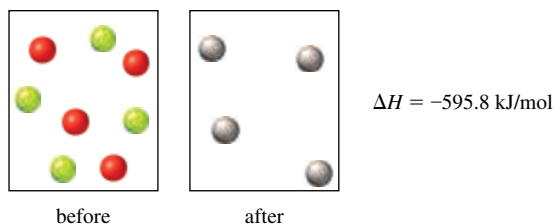
- 10.26 Consider the reaction



If 3 moles of H_2 react with 3 moles of Cl_2 to form HCl, calculate the work done (in joules) against a pressure of 1.0 atm. What is ΔU for this reaction? Assume the reaction goes to completion and that $\Delta V = 0$. (The conversion factor is $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$.)

Conceptual Problems

- 10.27** The diagrams represent systems before and after reaction for two related chemical processes. ΔH for the first reaction is -595.8 kJ/mol . Determine the value of ΔH for the second reaction.



- 10.28 For most biological processes, the changes in internal energy are approximately equal to the changes in enthalpy. Explain.

SECTION 10.4: CALORIMETRY



Visualizing Chemistry

Figure 10.9 and Figure 10.10

- VC 10.1 Referring to Figure 10.9, which of the following would result in the calculated value of ΔH_{rxn} being too high?
- Spilling some of one of the reactant solutions before adding it to the calorimeter.
 - Reading the final temperature before it reached its maximum value.
 - Misreading the thermometer at the beginning of the experiment and recording too low an initial temperature.
- VC 10.2 How would the ΔH_{rxn} calculated in Figure 10.9 be affected if the concentration of one of the reactant solutions were twice as high as it was supposed to be?
- The calculated ΔH_{rxn} would not be affected.
 - The calculated ΔH_{rxn} would be too low.
 - The calculated ΔH_{rxn} would be too high.
- VC 10.3 For an exothermic reaction like the one depicted in Figure 10.9, if the heat capacity of the calorimeter is not negligibly small, the heat absorbed by the water will be _____ the heat given off by the reaction.
- greater than
 - less than
 - equal to
- VC 10.4 Referring to Figure 10.9, how would the results of the experiment have been different if the reaction had been endothermic?
- The results would have been the same.
 - There would have been a smaller temperature increase.
 - There would have been a temperature decrease.
- VC 10.5 What would happen to the specific heat calculated in Figure 10.10 if some of the warm metal shot were lost during the transfer to the calorimeter?
- It would not affect the calculated value of specific heat.
 - It would cause the calculated value of specific heat to be too high.
 - It would cause the calculated value of specific heat to be too low.
- VC 10.6 What would happen to the specific heat calculated in Figure 10.10 if the test tube containing the metal shot were left in the boiling water for longer than the recommended time?
- It would not affect the calculated value of specific heat.
 - It would cause the calculated value of specific heat to be too high.
 - It would cause the calculated value of specific heat to be too low.

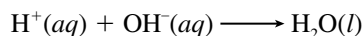
- VC 10.7 What would happen to the specific heat calculated in Figure 10.10 if some of the water were spilled prior to being added to the calorimeter?
- It would not affect the calculated value of specific heat.
 - It would cause the calculated value of specific heat to be too high.
 - It would cause the calculated value of specific heat to be too low.
- VC 10.8 Referring to the process depicted in Figure 10.10, which of the following must be known precisely for the calculated specific heat to be accurate.
- The mass of the boiling water.
 - The temperature of the metal shot before it is immersed in the boiling water.
 - The mass of the water that is added to the calorimeter.

Review Questions

- 10.29 What is the difference between specific heat and heat capacity? What are the units for these two quantities? Which is the *intensive* property and which is the *extensive* property?
- 10.30 Define *calorimetry* and describe two commonly used calorimeters. In a calorimetric measurement, why is it important that we know the heat capacity of the calorimeter? How is this value determined?

Computational Problems

- 10.31 A 6.22-kg piece of copper metal is heated from 20.5°C to 324.3°C. Calculate the heat absorbed (in kJ) by the metal.
- 10.32 Calculate the amount of heat liberated (in kJ) from 366 g of mercury when it cools from 77.0°C to 12.0°C.
- 10.33 A sheet of gold weighing 10.0 g and at a temperature of 18.0°C is placed flat on a sheet of iron weighing 20.0 g and at a temperature of 55.6°C. What is the final temperature of the combined metals? Assume that no heat is lost to the surroundings. (*Hint:* The heat gained by the gold must be equal to the heat lost by the iron. The specific heats of the metals are given in Table 10.2.)
- 10.34 A 0.1375-g sample of solid magnesium is burned in a constant-volume bomb calorimeter that has a heat capacity of 3024 J/°C. The temperature increases by 1.126°C. Calculate the heat given off by the burning Mg, in kJ/g and in kJ/mol.
- 10.35 A quantity of 2.00×10^2 mL of 0.862 M HCl is mixed with 2.00×10^2 mL of 0.431 M Ba(OH)₂ in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and Ba(OH)₂ solutions is the same at 20.48°C. For the process




the heat of neutralization is -56.2 kJ/mol. What is the final temperature of the mixed solution? Assume the specific heat of the solution is the same as that for pure water.


- 10.36 The fuel value of hamburger is approximately 3.6 kcal/g. If a man eats 1 lb of hamburger for lunch and if none of

the energy is stored in his body, estimate the amount of water that would have to be lost in perspiration to keep his body temperature constant. The heat of vaporization of water may be taken as 2.41 kJ/g (1 lb = 453.6 g).

- 10.37 Metabolic activity in the human body releases approximately 1.0×10^4 kJ of heat per day. Assuming the body contains 50 kg of water, how fast would the body temperature rise if it were an isolated system? How much water must the body eliminate as perspiration to maintain the normal body temperature (98.6°F)? The heat of vaporization of water may be taken as 2.41 kJ/g. Comment on your results.

- 10.38 A piece of silver with a mass 362 g has a heat capacity of 85.7 J/°C. What is the specific heat of silver?

-  10.39 A 25.95-g sample of methanol at 35.6°C is added to a 38.65-g sample of ethanol at 24.7°C in a constant-pressure calorimeter. If the final temperature of the combined liquids is 28.5°C and the heat capacity of the calorimeter is 19.3 J/°C, determine the specific heat of methanol.

-  10.40 A 50.75-g sample of water at 75.6°C is added to a sample of water at 24.1°C in a constant-pressure calorimeter. If the final temperature of the combined water is 39.4°C and the heat capacity of the calorimeter is 26.3 J/°C, calculate the mass of the water originally in the calorimeter.

Conceptual Problems

- 10.41 Consider the following data:

Metal	Al	Cu
Mass (g)	10	30
Specific heat [J/(g · °C)]	0.900	0.385
Temperature (°C)	40	60

When these two metals are placed in contact, which of the following will take place?

- Heat will flow from Al to Cu because Al has a larger specific heat.
 - Heat will flow from Cu to Al because Cu has a larger mass.
 - Heat will flow from Cu to Al because Cu has a larger heat capacity.
 - Heat will flow from Cu to Al because Cu is at a higher temperature.
 - No heat will flow in either direction.
- 10.42 Consider two metals A and B, each having a mass of 100 g and an initial temperature of 20°C. The specific heat of A is larger than that of B. Under the same heating conditions, which metal would take longer to reach a temperature of 21°C?

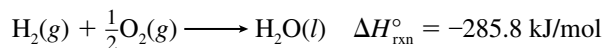
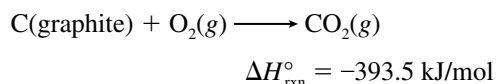
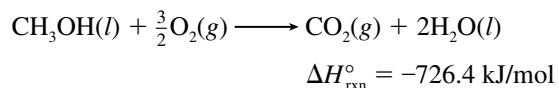
SECTION 10.5: HESS'S LAW

Review Questions

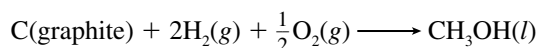
- 10.43 State Hess's law. Explain, with one example, the usefulness of Hess's law in thermochemistry.
- 10.44 Describe how chemists use Hess's law to determine the ΔH_f° of a compound by measuring its heat (enthalpy) of combustion.

Computational Problems

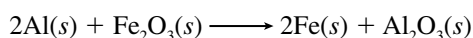
10.45 From the following heats of combustion,



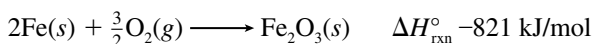
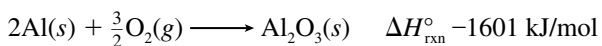
calculate the enthalpy of formation of methanol (CH_3OH) from its elements:



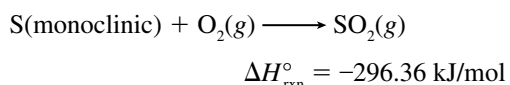
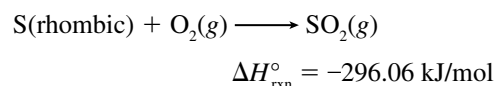
10.46 Calculate the standard enthalpy change for the reaction



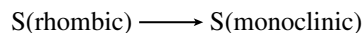
given that



10.47 From these data,

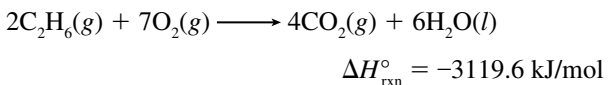
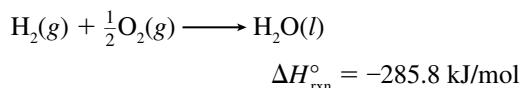
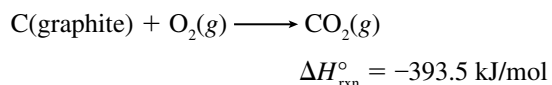


calculate the enthalpy change for the transformation



(Monoclinic and rhombic are different allotropic forms of elemental sulfur.)

10.48 From the following data,

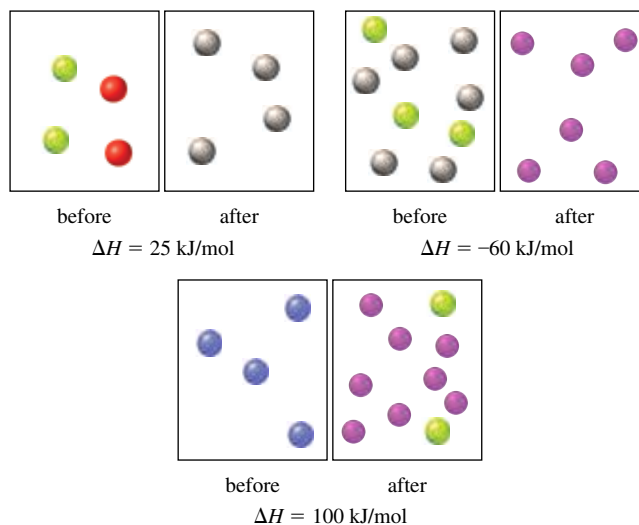


calculate the enthalpy change for the reaction

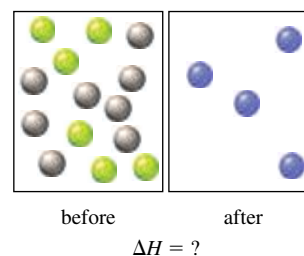


Conceptual Problems

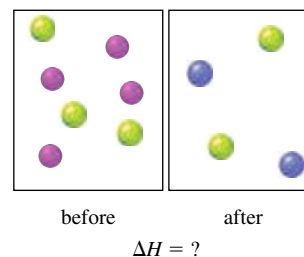
The following diagrams depict three chemical reactions involving five different chemical species—each represented by a different color sphere. Use this information to solve Problems 10.49 and 10.50.



10.49 Determine the value of ΔH for the following reaction:



10.50 Determine the value of ΔH for the following reaction:



SECTION 10.6: STANDARD ENTHALPIES OF FORMATION

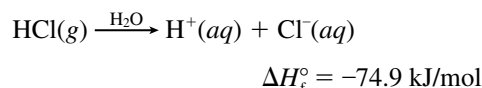
Review Questions

- 10.51 What is meant by the standard-state condition?
- 10.52 How are the standard enthalpies of an element and of a compound determined?
- 10.53 What is meant by the standard enthalpy of a reaction?
- 10.54 Write the equation for calculating the enthalpy of a reaction. Define all the terms.

Computational Problems

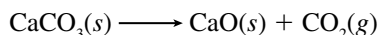
- 10.55 The ΔH_f° values of the two allotropes of oxygen, O_2 and O_3 , are 0 kJ/mol and 142.2 kJ/mol , respectively, at 25°C . Which is the more stable form at this temperature?
- 10.56 The standard enthalpies of formation of ions in aqueous solutions are obtained by arbitrarily assigning a value

of zero to H^+ ions; that is, $\Delta H_f^\circ = [\text{H}^+(\text{aq})] = 0$. (a) For the following reaction



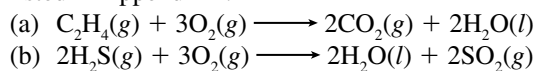
calculate ΔH_f° for the Cl^- ion. (b) Given that ΔH_f° for OH^- ion is -229.6 kJ/mol , calculate the enthalpy of neutralization when 1 mole of a strong monoprotic acid (such as HCl) is titrated by 1 mole of a strong base (such as KOH) at 25°C .

- 10.57** Calculate the heat of decomposition for this process at constant pressure and 25°C :

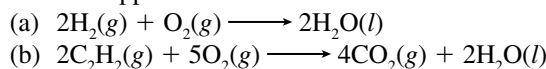


(Look up the standard enthalpy of formation of the reactant and products in Appendix 2.)

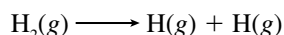
- 10.58** Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 2:



- 10.59** Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 2:

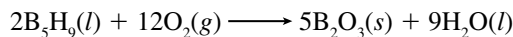


- 10.60** The standard enthalpy change for the following reaction is 436.4 kJ/mol :



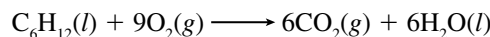
Calculate the standard enthalpy of formation of atomic hydrogen (H).

- 10.61** Methanol, ethanol, and *n*-propanol are three common alcohols. When 1.00 g of each of these alcohols is burned in air, heat is liberated as follows: (a) methanol (CH_3OH), -22.6 kJ ; (b) ethanol ($\text{C}_2\text{H}_5\text{OH}$), -29.7 kJ ; (c) *n*-propanol ($\text{C}_3\text{H}_7\text{OH}$), -33.4 kJ . Calculate the heats of combustion of these alcohols in kJ/mol .
- 10.62** Pentaborane-9 (B_5H_9) is a colorless, highly reactive liquid that will burst into flames when exposed to oxygen. The reaction is



Calculate the kilojoules of heat released per gram of the compound reacted with oxygen. The standard enthalpy of formation of B_5H_9 is 73.2 kJ/mol .

- 10.63** From the standard enthalpies of formation, calculate $\Delta H_{\text{rxn}}^\circ$ for the reaction



For $\text{C}_6\text{H}_{12}(\text{l})$, $\Delta H_f^\circ = -151.9 \text{ kJ/mol}$.

- 10.64** At 850°C , CaCO_3 undergoes substantial decomposition to yield CaO and CO_2 . Assuming that the ΔH_f° values of the reactant and products are the same at 850°C as they are at 25°C , calculate the enthalpy change (in kJ) if 66.8 g of CO_2 is produced in one reaction.

- 10.65** Determine the amount of heat (in kJ) given off when $1.26 \times 10^4 \text{ g}$ of ammonia is produced according to the equation

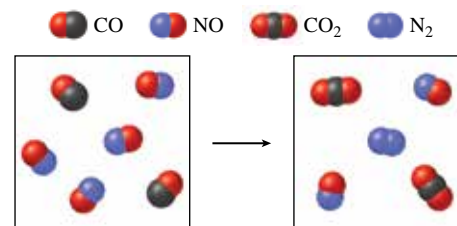


Assume that the reaction takes place under standard-state conditions at 25°C .

- 10.66** Which of the following standard enthalpy of formation values is not zero at 25°C : $\text{Na}(\text{monoclinic})$, $\text{Ne}(\text{g})$, $\text{CH}_4(\text{g})$, $\text{S}_8(\text{monoclinic})$, $\text{Hg}(\text{l})$, $\text{H}(\text{g})$?
- 10.67** Which is the more negative quantity at 25°C : ΔH_f° for $\text{H}_2\text{O}(\text{l})$ or ΔH_f° for $\text{H}_2\text{O}(\text{g})$?

Conceptual Problems

- 10.68** Predict the value of ΔH_f° (greater than, less than, or equal to zero) for these elements at 25°C : (a) $\text{Br}_2(\text{g})$, $\text{Br}_2(\text{l})$; (b) $\text{I}_2(\text{g})$, $\text{I}_2(\text{s})$.
- 10.69** In general, compounds with negative ΔH_f° values are more stable than those with positive ΔH_f° values. $\text{H}_2\text{O}_2(\text{l})$ has a negative ΔH_f° (see Appendix 2). Why, then, does $\text{H}_2\text{O}_2(\text{l})$ have a tendency to decompose to $\text{H}_2\text{O}(\text{l})$ and $\text{O}_2(\text{g})$?
- 10.70** Suggest ways (with appropriate equations) that would allow you to measure the ΔH_f° values of $\text{Ag}_2\text{O}(\text{s})$ and $\text{CaCl}_2(\text{s})$ from their elements. No calculations are necessary.
- 10.71** Using the data in Appendix 2, calculate the enthalpy change for the gaseous reaction shown here. (*Hint*: First determine the limiting reactant.)



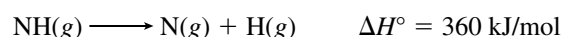
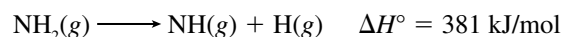
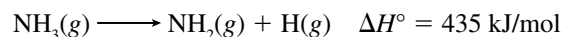
SECTION 10.7: BOND ENTHALPY AND THE STABILITY OF COVALENT MOLECULES

Review Questions

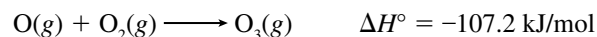
- 10.72** What is *bond enthalpy*? Bond enthalpies of polyatomic molecules are average values, whereas those of diatomic molecules can be accurately determined. Why?
- 10.73** Explain why the bond enthalpy of a molecule is usually defined in terms of a gas-phase reaction. Why are bond-breaking processes always endothermic and bond-forming processes always exothermic?

Computational Problems

- 10.74** From the following data, calculate the average bond enthalpy for the $\text{N}-\text{H}$ bond:



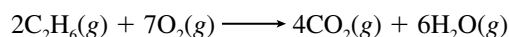
- 10.75** For the reaction



Calculate the average bond enthalpy in O_3 .

- 10.76** The bond enthalpy of $\text{F}_2(\text{g})$ is 156.9 kJ/mol . Calculate ΔH_f° for $\text{F}(\text{g})$.

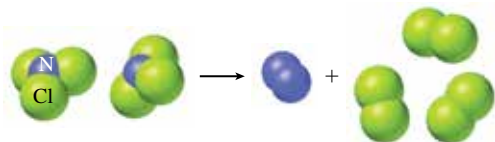
10.77 For the reaction



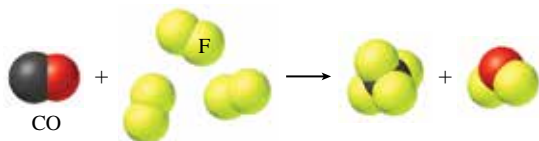
- Predict the enthalpy of reaction from the average bond enthalpies in Table 10.4.
- Calculate the enthalpy of reaction from the standard enthalpies of formation (see Appendix 2) of the reactant and product molecules, and compare the result with your answer for part (a).

Conceptual Problems

10.78 Use average bond enthalpies from Table 10.4 to estimate ΔH_{rxn} for the following reaction.



10.79 Use average bond enthalpies from Table 10.4 to estimate ΔH_{rxn} for the following reaction.



SECTION 10.8: LATTICE ENERGY AND THE STABILITY OF IONIC SOLIDS



Visualizing Chemistry

Figure 10.14

VC 10.9 What additional information would you need to calculate the lattice energy for a compound if the charges on the cation and anion were +2 and -1, respectively, rather than +1 and -1?

- No additional information is needed.
- IE_2 of the cation.
- IE_2 of the cation and EA_2 of the anion.

VC 10.10 What additional information would you need to calculate the lattice energy for a compound if the charges on the cation and anion were +2 and -2, respectively, rather than +1 and -1?

- No additional information is needed.
- IE_2 of the cation.
- IE_2 of the cation and EA_2 of the anion.

VC 10.11 How would the magnitude of the lattice energy calculated using the Born-Haber cycle change if the charges on the cation and anion were +2 and -2, respectively, rather than +1 and -1?

- Lattice energy would increase.
- Lattice energy would decrease.
- Whether lattice energy would increase or decrease depends on the relative magnitudes of IE_2 of the cation and EA_2 of the anion.

VC 10.12 What law enables us to use the Born-Haber cycle to calculate lattice energy?

- Coulomb's law
- Hess's law
- law of multiple proportions

Review Questions

- 10.80 Explain how the lattice energy of an ionic compound such as KCl can be determined using the Born-Haber cycle. On what law is this procedure based?
- 10.81 Specify which compound in each of the following pairs of ionic compounds should have the higher lattice energy: (a) KCl or MgO, (b) LiF or LiBr, (c) Mg_3N_2 or NaCl, (d) AlN or CaO, (e) NaF or CsF, (f) MgCl_2 or MgF_2 . Explain your choice.

Computational Problems

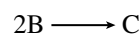
- 10.82 Calculate the lattice energy of LiCl. Use data from Figures 4.8 and 4.10 and Appendix 2.
- 10.83 Use the Born-Haber cycle outlined in Section 10.8 for NaCl to calculate the lattice energy of CaCl_2 . Use data from Figures 4.8 and 4.10 and Appendix 2. (The second ionization energy of Ca, IE_2 , is 1145 kJ/mol.)

ADDITIONAL PROBLEMS

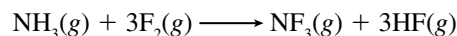
10.84 Consider the following two reactions:



Determine the enthalpy change for the process



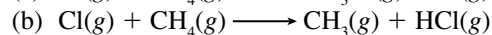
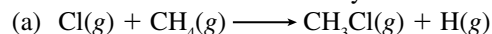
10.85 Consider the reaction



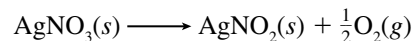
$$\Delta H_{\text{rxn}}^\circ = -881.2 \text{ kJ/mol}$$

Using data from Appendix 2, determine the standard enthalpy of formation of NF_3 .

10.86 Based on changes in enthalpy, which of the following reactions will occur more readily?

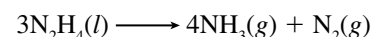


10.87 The standard enthalpy change ΔH° for the thermal decomposition of silver nitrate according to the following equation is +78.67 kJ:



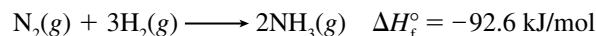
The standard enthalpy of formation of $\text{AgNO}_3(s)$ is -123.02 kJ/mol. Calculate the standard enthalpy of formation of $\text{AgNO}_2(s)$.

10.88 Hydrazine (N_2H_4) decomposes according to the following reaction:



(a) Given that the standard enthalpy of formation of hydrazine is 50.42 kJ/mol, calculate ΔH° for its decomposition. (b) Both hydrazine and ammonia burn in oxygen to produce $\text{H}_2\text{O}(l)$ and $\text{N}_2(g)$. Write balanced equations for each of these processes, and calculate ΔH° for each of them. On a mass basis (per kg), which would be the better fuel: hydrazine or ammonia?

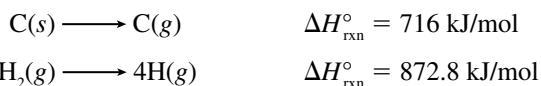
10.89 Consider the reaction



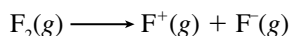
When 2 moles of N_2 react with 6 moles of H_2 to form 4 moles of NH_3 at 1 atm and a certain temperature,

there is a decrease in volume equal to 98 L. Calculate ΔU for this reaction. (The conversion factor is $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$.)

- 10.90 Calculate the heat released when 2.00 L of $\text{Cl}_2(\text{g})$ with a density of 1.88 g/L reacts with an excess of sodium metal at 25°C and 1 atm to form sodium chloride.
- 10.91 Using the following information and the fact that the average C–H bond enthalpy is 414 kJ/mol, estimate the standard enthalpy of formation of methane (CH_4).

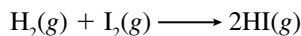


- 10.92 Compare the bond enthalpy of F_2 with the overall energy change for the following process:



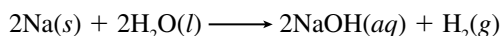
Which is the preferred dissociation for F_2 , energetically speaking? (*Hint*: You will need data from Figures 4.8 and 4.10.)

- 10.93 Calculate ΔH° for the reaction



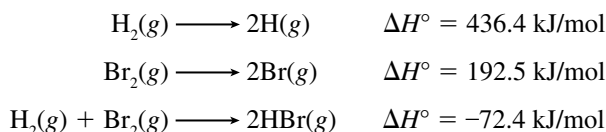
(a) using Equation 10.18, given that ΔH_f° for $\text{I}_2(\text{g})$ is 61.0 kJ/mol, and (b) using Equation 10.19.

- 10.94 Consider the reaction

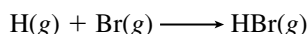


When 2 moles of Na react with water at 25°C and 1 atm, the volume of H_2 formed is 24.5 L. Calculate the work done in joules when 0.34 g of Na reacts with water under the same conditions. (The conversion factor is $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$.)

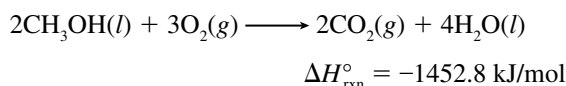
- 10.95 You are given the following data:



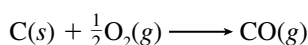
Calculate ΔH° for the reaction



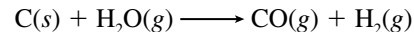
- 10.96 Methanol (CH_3OH) is an organic solvent and is also used as a fuel in some automobile engines. From the following data, calculate the standard enthalpy of formation of methanol:



- 10.97 A 44.0-g sample of an unknown metal at 99.0°C was placed in a constant-pressure calorimeter containing 80.0 g of water at 24.0°C . The final temperature of the system was found to be 28.4°C . Calculate the specific heat of the metal. (The heat capacity of the calorimeter is $12.4 \text{ J}^\circ\text{C}$.)
- 10.98 A student mixes 88.6 g of water at 74.3°C with 57.9 g of water at 24.8°C in an insulated flask. What is the final temperature of the combined water?
- 10.99 Producer gas (carbon monoxide) is prepared by passing air over red-hot coke:

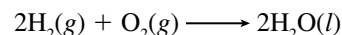


Water gas (a mixture of carbon monoxide and hydrogen) is prepared by passing steam over red-hot coke:



For many years, both producer gas and water gas were used as fuels in industry and for domestic cooking. The large-scale preparation of these gases was carried out alternately, that is, first producer gas, then water gas, and so on. Using thermochemical reasoning, explain why this procedure was chosen.

- 10.100 Compare the heat produced by the complete combustion of 1 mole of methane (CH_4) with a mole of water gas (0.50 mole H_2 and 0.50 mole CO) under the same conditions. On the basis of your answer, would you prefer methane over water gas as a fuel? Can you suggest two other reasons why methane is preferable to water gas as a fuel?
- 10.101 The so-called hydrogen economy is based on hydrogen produced from water using solar energy. The gas is then burned as a fuel:



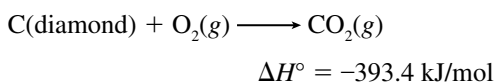
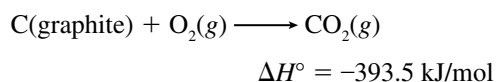
A primary advantage of hydrogen as a fuel is that it is nonpolluting. A major disadvantage is that it is a gas and therefore is harder to store than liquids or solids. Calculate the number of moles of H_2 required to produce an amount of energy equivalent to that produced by the combustion of a gallon of octane (C_8H_{18}). The density of octane is 2.66 kg/gal, and its standard enthalpy of formation is -249.9 kJ/mol .

- 10.102 Ethanol ($\text{C}_2\text{H}_5\text{OH}$) and gasoline (assumed to be all octane, C_8H_{18}) are both used as automobile fuel. If gasoline is selling for $\$2.79/\text{gal}$, what would the price of ethanol have to be to provide the same amount of heat per dollar? The density and ΔH_f° of octane are 0.7025 g/mL and -249.9 kJ/mol , respectively, and of ethanol are 0.7894 g/mL and -277.0 kJ/mol , respectively (1 gal = 3.785 L).
- 10.103 How many moles of ethane (C_2H_6) would have to be burned for the combustion to heat 855 g of water from 25.0°C to 98.0°C ?
- 10.104 Calculate the heat of reaction for the following process:
- $$2\text{NF}_3(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{ONF}_3(\text{g})$$
- 10.105 The heat of vaporization of a liquid (ΔH_{vap}) is the energy required to vaporize 1.00 g of the liquid at its boiling point. In one experiment, 60.0 g of liquid nitrogen (boiling point = -196°C) is poured into a Styrofoam cup containing $2.00 \times 10^2 \text{ g}$ of water at 55.3°C . Calculate the molar heat of vaporization of liquid nitrogen if the final temperature of the water is 41.0°C .
- 10.106 Explain the cooling effect experienced when ethanol is rubbed on your skin, given that
- $$\text{C}_2\text{H}_5\text{OH}(\text{l}) \longrightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) \quad \Delta H^\circ = 42.2 \text{ kJ/mol}$$
- 10.107 For which of the following reactions does $\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ$?
- $\text{H}_2(\text{g}) + \text{S}(\text{rhombic}) \longrightarrow \text{H}_2\text{S}(\text{g})$
 - $\text{C}(\text{diamond}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
 - $\text{H}_2(\text{g}) + \text{CuO}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{Cu}(\text{s})$
 - $\text{O}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{O}_3(\text{g})$

10.108 Calculate the work done (in joules) when 1.0 mole of water is frozen at 0°C and 1.0 atm. The volumes of 1 mole of water and ice at 0°C are 0.0180 and 0.0196 L, respectively. (The conversion factor is 1 L · atm = 101.3 J.)

10.109 A certain gas initially at 0.050 L undergoes expansion until its volume is 0.50 L. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 0.20 atm. (The conversion factor is 1 L · atm = 101.3 J.)

10.110 Calculate the standard enthalpy of formation for diamond, given that



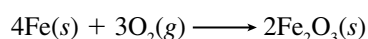
10.111 The first step in the industrial recovery of zinc from zinc sulfide ore is known as *roasting*. Roasting is the conversion of ZnS to ZnO by heating according to the following *unbalanced* equation:



Determine the amount of heat involved when 1.26×10^4 g of SO₂ are produced in the roasting process.

10.112 Calculate the standard enthalpy change for the fermentation process, in which glucose (C₆H₁₂O₆) is converted to ethanol (C₂H₅OH) and carbon dioxide.

10.113 Portable hot packs are available for skiers and people engaged in other outdoor activities in a cold climate. The air-permeable paper packet contains a mixture of powdered iron, sodium chloride, and other components, all moistened by a little water. The exothermic reaction that produces the heat is a very common one—the rusting of iron:



When the outside plastic envelope is removed, O₂ molecules penetrate the paper, causing the reaction to begin. A typical packet contains 250 g of iron to warm your hands or feet for up to 4 hours. Using data from Appendix 2, determine how much heat (in kJ) is produced by this reaction.

10.114 The bond enthalpy of the C–N bond in the amide group of proteins (see Problem 6.60) can be treated as an average of C–N and C=N bonds. Calculate the maximum wavelength of light needed to break the bond.

10.115 The total volume of the Pacific Ocean is estimated to be $7.2 \times 10^8 \text{ km}^3$. A medium-sized atomic bomb produces $1.0 \times 10^{15} \text{ J}$ of energy upon explosion. Calculate the number of atomic bombs needed to release enough energy to raise the temperature of the water in the Pacific Ocean by 1°C.

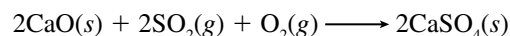
10.116 A woman expends 95 kJ of energy in walking a kilometer. The energy is supplied by the metabolic breakdown of food intake and has a 35 percent efficiency. How much energy does she save by walking the kilometer instead of driving a car that gets 8.2 km

per liter of gasoline (approximately 20 mi/gal)? The density of gasoline is 0.71 g/mL, and its enthalpy of combustion is –49 kJ/g.

10.117 The carbon dioxide exhaled by sailors in a submarine is often removed by reaction with an aqueous lithium hydroxide solution. (a) Write a balanced equation for this process. (*Hint*: The products are water and a soluble salt.) (b) If every sailor consumes 1.2×10^4 kJ of energy every day and assuming that this energy is totally supplied by the metabolism of glucose (C₆H₁₂O₆), calculate the amounts of CO₂ produced and LiOH required to purify the air.

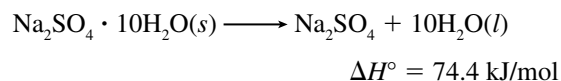
10.118 The enthalpy of combustion of benzoic acid (C₆H₅COOH) is commonly used as the standard for calibrating constant-volume bomb calorimeters; its value has been accurately determined to be –3226.7 kJ/mol. When 1.9862 g of benzoic acid are burned in a calorimeter, the temperature rises from 21.84°C to 25.67°C. What is the heat capacity of the bomb? (Assume that the quantity of water surrounding the bomb is exactly 2000 g.)

10.119 Calcium oxide (CaO) is used to remove sulfur dioxide generated by coal-burning power stations:



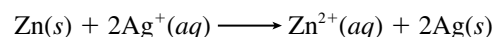
Calculate the enthalpy change if 6.6×10^5 g of SO₂ is removed by this process.

10.120 Glauber's salt, sodium sulfate decahydrate (Na₂SO₄ · 10H₂O), undergoes a phase transition (that is, melting or freezing) at a convenient temperature of about 32°C:



As a result, this compound is used to regulate the temperature in homes. It is placed in plastic bags in the ceiling of a room. During the day, the endothermic melting process absorbs heat from the surroundings, cooling the room. At night, it gives off heat as it freezes. Calculate the mass of Glauber's salt in kilograms needed to lower the temperature of air in a room by 8.2°C. The mass of air in the room is 605.4 kg; the specific heat of air is 1.2 J/g · °C.

10.121 An excess of zinc metal is added to 50.0 mL of a 0.100 M AgNO₃ solution in a constant-pressure calorimeter like the one pictured in Figure 10.8. As a result of the reaction

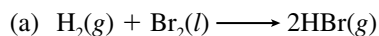


the temperature rises from 19.25°C to 22.17°C. If the heat capacity of the calorimeter is 98.6 J/°C, calculate the enthalpy change for the given reaction on a molar basis. Assume that the density and specific heat of the solution are the same as those for water, and ignore the specific heats of the metals.

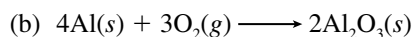
10.122 (a) A person drinks four glasses of cold water (3.0°C) every day. The volume of each glass is 2.5×10^2 mL. How much heat (in kJ) does the body have to supply to raise the temperature of the water to 37°C, the body temperature? (b) How much heat would your body lose

if you were to ingest 8.0×10^2 g of snow at 0°C to quench your thirst? (The amount of heat necessary to melt snow is 6.01 kJ/mol.)

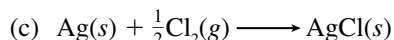
- 10.123** Which of the following $\Delta H_{\text{rxn}}^\circ$ values is a ΔH_f° value? For any that is not a ΔH_f° value, explain why it is not.



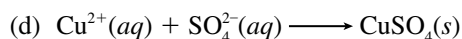
$$\Delta H_{\text{rxn}}^\circ = -72.4 \text{ kJ/mol}$$



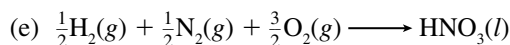
$$\Delta H_{\text{rxn}}^\circ = -3339.6 \text{ kJ/mol}$$



$$\Delta H_{\text{rxn}}^\circ = -127.0 \text{ kJ/mol}$$



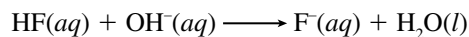
$$\Delta H_{\text{rxn}}^\circ = +73.25 \text{ kJ/mol}$$



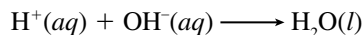
$$\Delta H_{\text{rxn}}^\circ = -173.2 \text{ kJ/mol}$$

- 10.124 At 25°C the standard enthalpy of formation of $\text{HF}(\text{aq})$ is -320.1 kJ/mol; of $\text{OH}^-(\text{aq})$, it is -229.6 kJ/mol; of $\text{F}^-(\text{aq})$, it is -329.1 kJ/mol; and of $\text{H}_2\text{O}(\text{l})$, it is -285.8 kJ/mol.

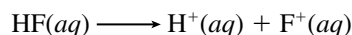
- (a) Calculate the standard enthalpy of neutralization of $\text{HF}(\text{aq})$:



- (b) Using the value of -56.2 kJ as the standard enthalpy change for the reaction



calculate the standard enthalpy change for the reaction



- 10.125** Why are cold, damp air and hot, humid air more uncomfortable than dry air at the same temperatures? [The specific heats of water vapor and air are approximately 1.9 J/(g \cdot $^\circ\text{C}$) and 1.0 J/(g \cdot $^\circ\text{C}$), respectively.]

- 10.126 Vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$) differs from ethylene (C_2H_4) in that one of the H atoms is replaced with a Cl atom. Vinyl chloride is used to prepare poly(vinyl chloride), which is an important polymer used in pipes. Calculate the enthalpy change when 1.0×10^3 kg of vinyl chloride forms poly(vinyl chloride).

- 10.127** A 46-kg person drinks 500 g of milk, which has a “caloric” value of approximately 3.0 kJ/g. If only 17 percent of the energy in milk is converted to mechanical work, how high (in meters) can the person climb based on this energy intake? [Hint: The work done in ascending is given by mgh , where m is the mass (in kg), g is the gravitational acceleration (9.8 m/s²), and h is the height (in meters).]

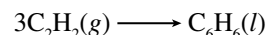
- 10.128 The height of Niagara Falls on the American side is 51 m. (a) Calculate the potential energy of 1.0 g of water at the top of the falls relative to the ground level. (b) What is the speed of the falling water if all the potential energy is converted to kinetic energy?

(c) What would be the increase in temperature of the water if all the kinetic energy were converted to heat? (See Problem 10.127 for information.)

- 10.129** In the nineteenth century, two scientists named Dulong and Petit noticed that for a solid element, the product of its molar mass and its specific heat is approximately 25 J/ $^\circ\text{C}$. This observation, now called Dulong and Petit’s law, was used to estimate the specific heat of metals. Verify the law for the metals listed in Table 10.2. The law does not apply to one of the metals. Which one is it? Why?

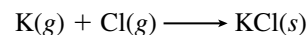
- 10.130 Determine the standard enthalpy of formation of ethanol ($\text{C}_2\text{H}_5\text{OH}$) from its standard enthalpy of combustion (-1367.4 kJ/mol).

- 10.131** Acetylene (C_2H_2) and benzene (C_6H_6) have the same empirical formula. In fact, benzene can be made from acetylene as follows:



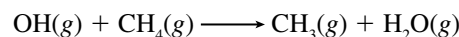
The enthalpies of combustion for C_2H_2 and C_6H_6 are -1299.4 and -3267.4 kJ/mol, respectively. Calculate the standard enthalpies of formation of C_2H_2 and C_6H_6 and hence the enthalpy change for the formation of C_6H_6 from C_2H_2 .

- 10.132 From the lattice energy of KCl in Table 5.1, and the first ionization energy of K and electron affinity of Cl in Figures 4.8 and 4.10, calculate the ΔH° for the reaction



- 10.133** The hydroxyl radical (OH) plays an important role in atmospheric chemistry. It is highly reactive and has a tendency to combine with an H atom from other compounds, causing them to break up. Thus, OH is sometimes called a “detergent” radical because it helps to clean up the atmosphere.

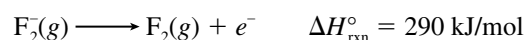
- (a) Estimate the enthalpy change for the following reaction:



- (b) The radical is generated when sunlight hits water vapor. Calculate the maximum wavelength (in nm) required to break an O–H bond in H_2O .

- 10.134 How much metabolic energy must a 5.2-g hummingbird expend to fly to a height of 12 m? (See the hint in Problem 10.127.)

- 10.135** (a) From the following data, calculate the bond enthalpy of the F_2^- ion.



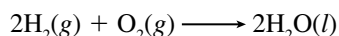
- (b) Explain the difference between the bond enthalpies of F_2 and F_2^- .

- 10.136 The average temperature in deserts is high during the day but quite cool at night, whereas that in regions along the coastline is more moderate. Explain.

- 10.137** Both glucose and fructose are simple sugars with the same molecular formula of $\text{C}_6\text{H}_{12}\text{O}_6$. Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), or table sugar, consists of a glucose molecule bonded to a fructose molecule (a water molecule is eliminated in the formation of sucrose).

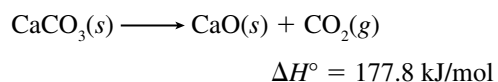
(a) Calculate the energy released when a 2.0-g glucose tablet is burned in air. (b) To what height can a 65-kg person climb after ingesting such a tablet, assuming only 30 percent of the energy released is available for work. (See the hint for Problem 10.127.) Repeat the calculations for a 2.0-g sucrose tablet.

- 10.138 About 6.0×10^{13} kg of CO_2 is fixed (converted to more complex organic molecules) by photosynthesis every year. (a) Assuming all the CO_2 ends up as glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), calculate the energy (in kJ) stored by photosynthesis per year. (b) A typical coal-burning electric power station generates about 2.0×10^6 W per year. How many such stations are needed to generate the same amount of energy as that captured by photosynthesis ($1 \text{ W} = 1 \text{ J/s}$)?
- 10.139 Experiments show that it takes 1656 kJ/mol to break all the bonds in methane (CH_4) and 4006 kJ/mol to break all the bonds in propane (C_3H_8). Based on these data, calculate the average bond enthalpy of the C–C bond.
- 10.140 From a thermochemical point of view, explain why a carbon dioxide fire extinguisher or water should not be used on a magnesium fire.
- 10.141 Consider the reaction

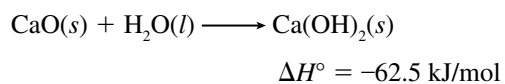


Under atmospheric conditions (1.00 atm), it was found that the formation of water resulted in a decrease in volume equal to 73.4 L. Calculate ΔU for the process $\Delta H = -571.6$ kJ/mol. (The conversion factor is $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$.)

- 10.142 *Lime* is a term that includes calcium oxide (CaO , also called quicklime) and calcium hydroxide [$\text{Ca}(\text{OH})_2$, also called slaked lime]. It is used in the steel industry to remove acidic impurities, in air-pollution control to remove acidic oxides such as SO_2 , and in water treatment. Quicklime is made industrially by heating limestone (CaCO_3) above 2000°C :



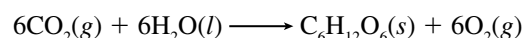
Slaked lime is produced by treating quicklime with water:



The exothermic reaction of quicklime with water and the rather small specific heats of both quicklime [$0.946 \text{ J}/(\text{g} \cdot ^\circ\text{C})$] and slaked lime [$1.20 \text{ J}/(\text{g} \cdot ^\circ\text{C})$] make it hazardous to store and transport lime in vessels made of wood. Wooden sailing ships carrying lime would occasionally catch fire when water leaked into the hold. (a) If a 500.0-g sample of water reacts with an equimolar amount of CaO (both at an initial temperature of 25°C), what is the final temperature of the product, $\text{Ca}(\text{OH})_2$? Assume that the product absorbs all the heat released in the reaction. (b) Given that the standard enthalpies of formation of CaO and H_2O are

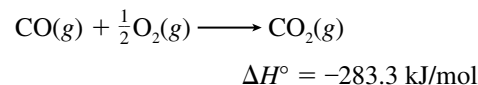
-635.6 and -285.8 kJ/mol, respectively, calculate the standard enthalpy of formation of $\text{Ca}(\text{OH})_2$.

- 10.143 A 4.117-g impure sample of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) was burned in a constant-volume calorimeter having a heat capacity of $19.65 \text{ kJ}/^\circ\text{C}$. If the rise in temperature is 3.134°C , calculate the percent by mass of the glucose in the sample. Assume that the impurities are unaffected by the combustion process and that $\Delta U = \Delta H$. See Appendix 2 for thermodynamic data.
- 10.144 The combustion of 0.4196 g of a hydrocarbon releases 17.55 kJ of heat. The masses of the products are $\text{CO}_2 = 1.419 \text{ g}$ and $\text{H}_2\text{O} = 0.290 \text{ g}$. (a) What is the empirical formula of the compound? (b) If the approximate molar mass of the compound is 76 g/mol , calculate its standard enthalpy of formation.
- 10.145 Photosynthesis produces glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and oxygen from carbon dioxide and water:

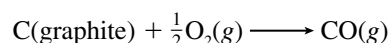


(a) How would you determine experimentally the ΔH_f° value for this reaction? (b) Solar radiation produces about 7.0×10^{14} kg of glucose a year on Earth. What is the corresponding ΔH° change?

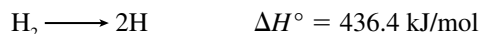
- 10.146 Ice at 0°C is placed in a Styrofoam cup containing 361 g of a soft drink at 23°C . The specific heat of the drink is about the same as that of water. Some ice remains after the ice and soft drink reach an equilibrium temperature of 0°C . Determine the mass of ice that has melted. Ignore the heat capacity of the cup. (*Hint:* It takes 334 J to melt 1 g of ice at 0°C .)
- 10.147 Acetylene (C_2H_2) can be made by combining calcium carbide (CaC_2) with water. (a) Write an equation for the reaction. (b) What is the maximum amount of heat (in joules) that can be obtained from the combustion of acetylene, starting with 74.6 g of CaC_2 ?
- 10.148 In 1998, scientists using a special type of electron microscope were able to measure the force needed to break a *single* chemical bond. If $2.0 \times 10^{-9} \text{ N}$ was needed to break a C–Si bond, estimate the bond enthalpy in kJ/mol. Assume that the bond has to be stretched by a distance of 2 \AA ($2 \times 10^{-10} \text{ m}$) before it is broken.
- 10.149 A driver's manual states that the stopping distance quadruples as the speed doubles; that is, if it takes 30 ft to stop a car moving at 25 mph, then it would take 120 ft to stop a car moving at 50 mph. Justify this statement by using mechanics and the first law of thermodynamics. [Assume that when a car is stopped, its kinetic energy ($\frac{1}{2}mv^2$) is totally converted to heat.]
- 10.150 From the enthalpy of formation for CO_2 and the following information, calculate the standard enthalpy of formation for carbon monoxide (CO).



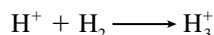
Why can't we obtain the standard enthalpy of formation directly by measuring the enthalpy of the following reaction?



- 10.151** The atoms in the H_3^+ ion are arranged in an equilateral triangle. Given the following information



calculate ΔH° for the reaction



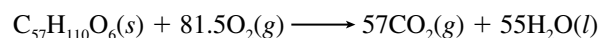
- 10.152** A man ate 0.50 lb of cheese (an energy intake of 4×10^3 kJ). Suppose that none of the energy was stored in his body. What mass (in grams) of water would he need to perspire to maintain his original temperature? (It takes 44.0 kJ to vaporize 1 mole of water.)
- 10.153** When 1.034 g of naphthalene (C_{10}H_8) is burned in a constant-volume bomb calorimeter at 298 K, 41.56 kJ of heat is evolved. Calculate ΔU and w for the reaction on a molar basis.
- 10.154** A hemoglobin molecule (molar mass = 65,000 g) can bind up to four oxygen molecules. In a certain experiment, a 0.085-L solution containing 6.0 g of deoxyhemoglobin (hemoglobin without oxygen molecules bound to it) was combined with an excess of oxygen in a constant-pressure calorimeter of negligible heat capacity. Calculate the enthalpy of reaction per mole of oxygen bound if the temperature rose by 0.044°C. Assume the solution is dilute so that the specific heat of the solution is equal to that of water.
- 10.155** A gas company in Massachusetts charges 27 cents for a mole of natural gas (CH_4). Calculate the cost of heating 200 mL of water (enough to make a cup of coffee or tea) from 20°C to 100°C. Assume that only 50 percent of the heat generated by the combustion is used to heat the water; the rest of the heat is lost to the surroundings.



- 10.156** A 12.1-g piece of aluminum at 81.7°C is added to a sample of water at 23.4°C in a constant-pressure calorimeter. If the final temperature of the water is 24.9°C, and the heat capacity of the calorimeter is 19.8 J/°C, calculate the mass of the water in the calorimeter.

- 10.157** Using Table 10.4, compare the following bond enthalpies: C–C in C_2H_6 , N–N in N_2H_4 , and O–O in H_2O_2 . What effect do lone pairs on adjacent atoms appear to have on bond enthalpy? (*Hint*: Start by drawing Lewis structures of each molecule.)

- 10.158** According to information obtained from www.krispykreme.com, a Krispy Kreme original glazed doughnut weighs 52 g and contains 200 Cal and 12 g of fat. (a) Assuming that the fat in the doughnut is metabolized according to the given equation for tristearin



$$\Delta H^\circ = -37,760 \text{ kJ/mol}$$

calculate the number of Calories in the reported 12 g of fat in each doughnut. (b) If all the energy contained in a Krispy Kreme doughnut (and just in the fat) were transferred to 6.00 kg of water originally at 25.5°C, what would be the final temperature of the water? (c) When a Krispy Kreme apple fritter weighing 101 g is burned in a bomb calorimeter with $C_{\text{cal}} = 95.3 \text{ kJ/}^\circ\text{C}$, the measured temperature increase is 16.7°C. Calculate the number of Calories in a Krispy Kreme apple fritter. (d) What would the ΔH° value be for the metabolism of 1 mole of the fat tristearin if the water produced by the reaction were gaseous instead of liquid? [*Hint*: Use data from Appendix 2 to determine the ΔH° value for the reaction $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$.]

Answers to In-Chapter Materials

PRACTICE PROBLEMS

10.1A -4.32×10^4 kJ. **10.1B** 6.95×10^5 kJ, heat is absorbed.
10.2A (a) -270 J, (b) 4.02 J, (c) -202 J. **10.2B** (a) 0.487 atm, (b) 73.4 mL, (c) 326.6 mL. **10.3A** 8.174×10^4 kJ. **10.3B** 1.71×10^3 g.
10.4A 151 kJ. **10.4B** 52.2°C. **10.5A** 28°C. **10.5B** 42 g. **10.6A** 14.5 kJ/g.
10.6B 10.5°C rise. **10.7A** -1103 kJ/mol. **10.7B** 113.2 kJ/mol.
10.8A 177.8 kJ/mol. **10.8B** -697.6 kJ/mol. **10.9A** 87.3 kJ/mol.
10.9B $\text{NH}_3(\text{g}) + \text{HCl}(\text{g})$, 176.8 kJ/mol. **10.10A** -557 kJ/mol. (See footnote to Table 10.4 regarding the C=O bond enthalpy in CO_2 .)
10.10B 328 kJ/mol. **10.11A** 629 kJ/mol. **10.11B** -841 kJ/mol. (Remember that we define electron affinity as the energy *given off* [*Section 4.4*]. A negative EA value indicates that energy is *absorbed*, as we would expect to be the case with any *second EA*.)

SECTION REVIEW

10.1.1 172.80 cal. **10.1.2** 9.00×10^5 J. **10.1.3** (a) $2\text{AX}(\text{g}) + \text{B}_2(\text{g}) \longrightarrow \text{A}_2(\text{g}) + \text{B}_2\text{X}_2(\text{g})$, (b) $\text{A}_2(\text{g}) + \text{B}_2\text{X}_2(\text{g}) \longrightarrow 2\text{AX}(\text{g}) + \text{B}_2(\text{g})$.
10.2.1 -43 J. **10.2.2** $w = -5.4 \times 10^2$ kJ, done by the system.
10.3.1 453 kJ. **10.3.2** 11.2 kg. **10.4.1** 6.95 kJ/°C. **10.4.2** 58.1°C.
10.4.3 88.3°C. **10.4.4** 31.1°C. **10.5.1** -867.7 kJ/mol.
10.5.2 -1300.0 kJ/mol. **10.6.1** -543.2 kJ/mol. **10.6.2** -58.04 kJ/mol.
10.6.3 -110.5 kJ/mol. **10.7.1** -119 kJ/mol. **10.7.2** 13.6 kJ/mol.
10.7.3 -114 kJ/mol. **10.7.4** -2.00×10^2 kJ/mol. **10.8.1** (a) $\text{KF} < \text{LiF}$, (b) $\text{KF} > \text{KCl}$, (c) $\text{KF} > \text{KI}$. **10.8.2** 808 kJ/mol.

Key Skills

Enthalpy of Reaction

Using tabulated ΔH_f° values, we can calculate the standard enthalpy of reaction ($\Delta H_{\text{rxn}}^\circ$) using Equation 10.18:

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

This method of calculating thermodynamic quantities such as enthalpy of reaction is important not only in this chapter, but also in Chapters 14 and 18. The following examples illustrate the use of Equation 10.18 and data from Appendix 2. Each example provides a specific reminder of one of the important facets of this approach.

Look up ΔH_f° values for reactants and products. Sum all ΔH_f° values for products. Sum all ΔH_f° values for reactants. Subtract reactant sum from product sum.

$\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$

	ΔH_f° (kJ/mol)
$\text{CO}_2(g)$	-393.5
$\text{CaO}(s)$	-635.6
$\text{CaCO}_3(s)$	-1206.9

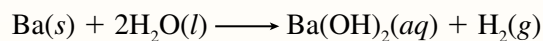
$\Delta H_f^\circ = [(-635.6) + (-393.5)] - (-1206.9) = +187.8 \text{ kJ/mol}$

Each ΔH_f° value must be multiplied by the corresponding stoichiometric coefficient in the balanced equation.

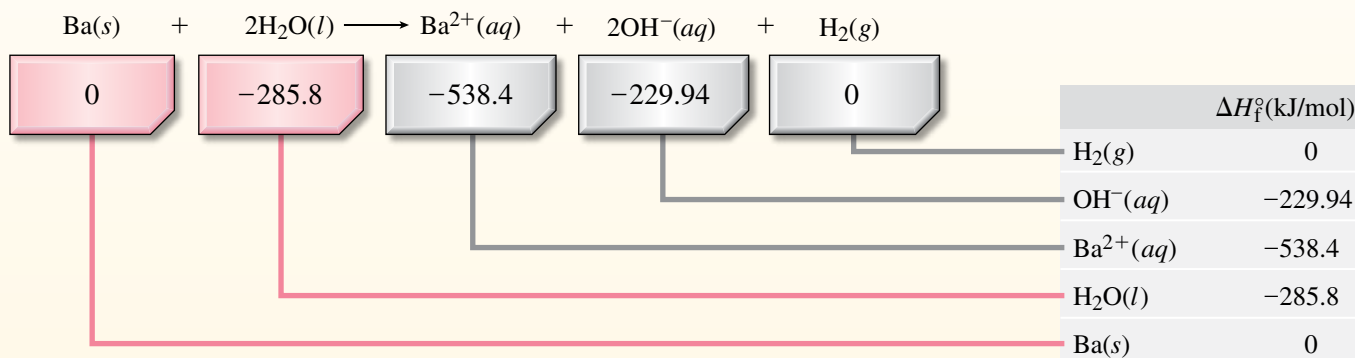
$\text{N}_2\text{H}_4(l) + 2\text{N}_2\text{O}_4(g) \longrightarrow 6\text{NO}(g) + 2\text{H}_2\text{O}(l)$

	ΔH_f° (kJ/mol)
$\text{H}_2\text{O}(l)$	-285.8
$\text{NO}(g)$	90.4
$\text{N}_2\text{O}_4(g)$	9.66
$\text{N}_2\text{H}_4(l)$	50.4

$\Delta H_f^\circ = [6(90.4) + 2(-285.8)] - [(50.4) + 2(9.66)] = -53.92 \text{ kJ/mol}$

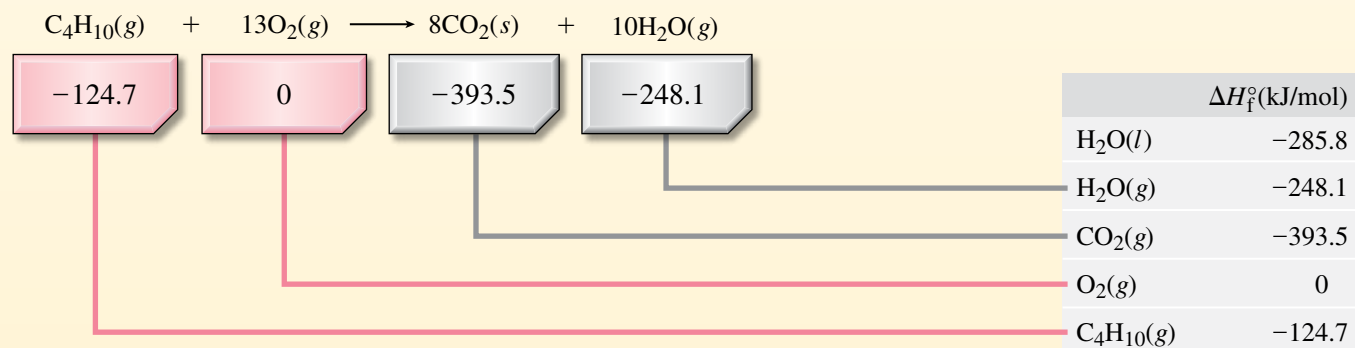


By definition, the standard enthalpy of formation for an element in its standard state is zero. In addition, many tables of thermodynamic data, including Appendix 2, do not contain values for aqueous strong electrolytes such as barium hydroxide. However, the tables do include values for the individual aqueous ions. Therefore, determination of this enthalpy of reaction is facilitated by rewriting the equation with $\text{Ba}(\text{OH})_2$ written as separate ions:



$$\Delta H_f^\circ = [(-538.4) + 2(-229.94) + (0)] - [(0) + 2(-285.8)] = -426.7 \text{ kJ/mol}$$

You will find more than one tabulated ΔH_f° value for some substances, such as water. It is important to select the value that corresponds to the phase of matter represented in the chemical equation. In previous examples, water has appeared in the balanced equations as a liquid. It can also appear as a gas.

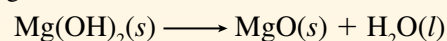


$$\Delta H_f^\circ = [8(-393.5) + 10(-248.1)] - [(-124.7) + 0] = -5504.3 \text{ kJ/mol}$$

Key Skills Problems

10.1

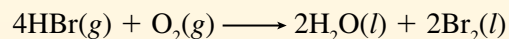
Using data from Appendix 2, calculate the standard enthalpy of the following reaction:



- (a) -608.7 kJ/mol (b) -81.1 kJ/mol (c) -37.1 kJ/mol
(d) +81.1 kJ/mol (e) +37.1 kJ/mol

10.2

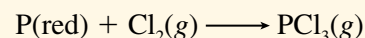
Using data from Appendix 2, calculate the standard enthalpy of the following reaction:



- (a) -426.8 kJ/mol (b) -338.8 kJ/mol (c) -249.6 kJ/mol
(d) +426.8 kJ/mol (e) +338.8 kJ/mol

10.3

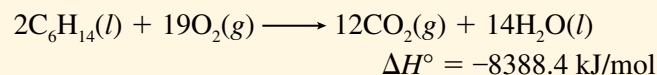
Using data from Appendix 2, calculate the standard enthalpy of the following reaction (you must first balance the equation):



- (a) -576.1 kJ/mol (b) -269.7 kJ/mol (c) -539.3 kJ/mol
(d) -602.6 kJ/mol (e) +639.4 kJ/mol

10.4

Using only whole-number coefficients, the combustion of hexane can be represented as:



Using this and data from Appendix 2, determine the standard enthalpy of formation of hexane.

- (a) -334.8 kJ/mol (b) -167.4 kJ/mol (c) -669.6 kJ/mol
(d) +334.8 kJ/mol (e) +669.6 kJ/mol