Thermochemistry

8

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The candle flame gives off heat, melting the candle wax. Wax melting is a phase change from solid to liquid and an endothermic reaction.

Some say the world will end in fire,
Some say in ice.
From what I've tasted of desire
I hold with those who favor fire.

—ROBERT FROST
Fire and Ice

This chapter deals with energy and heat, two terms used widely by both the general public and scientists. Energy, in the vernacular, is equated with pep and vitality. Heat conjures images of blast furnaces and sweltering summer days. Scientifically, these terms have quite different meanings. **Energy** can be defined as the capacity to do work. **Heat** is a particular form of energy that is transferred from a body at a high temperature to one at a lower temperature when they are brought into contact with each other. Two centuries ago, heat was believed to be a material fluid (caloric); we still use the phrase "heat flow" to refer to heat transfer or to heat effects in general.

Thermochemistry refers to the study of the heat flow that accompanies chemical reactions. Our discussion of this subject will focus on

- the basic principles of heat flow (Section 8-1).
- the experimental measurement of the magnitude and direction of heat flow, known as *calorimetry* (Section 8-2).
- the concept of enthalpy, H (heat content) and *enthalpy change*, ΔH (Section 8-3).
- the calculation of ΔH for reactions, using *thermochemical equations* (Section 8-4) and *enthalpies of formation* (Section 8-5).
- heat effects in the breaking and formation of covalent bonds (Section 8-6).
- the relation between heat and other forms of energy, as expressed by the first law of thermodynamics (Section 8-7).

Chapter Outline

8-1 Principles of Heat Flow

8-2 Measurement of Heat Flow; Calorimetry

8-3 Enthalpy

8-4 Thermochemical Equations

8-5 Enthalpies of Formation

8-6 Bond Enthalpy

8-7 The First Law of Thermodynamics

8-1 Principles of Heat Flow

In any discussion of heat flow, it is important to distinguish between system and surroundings. The **system** is that part of the universe on which attention is focused. In a very simple case (Figure 8.1), it might be a sample of water in contact with a hot plate. The **surroundings,** which exchange energy with the system, make up in principle the rest of the universe. For all practical purposes, however, they include only those materials in close contact with the system. In Figure 8.1, the surroundings would consist of the hot plate, the beaker holding the water sample, and the air around it.

The universe is a big place.

When a chemical reaction takes place, we consider the substances involved, reactants and products, to be the system. The surroundings include the vessel in which the reaction takes place (test tube, beaker, and so on) and the air or other material in thermal contact with the reaction system.

State Properties

The **state** of a system is described by giving its composition, temperature, and pressure. The system at the left of Figure 8.1 consists of

$$50.0 \text{ g of } H_2O(l) \text{ at } 50.0^\circ C \text{ and } 1 \text{ atm}$$

When this system is heated, its state changes, perhaps to one described as

$$50.0 \text{ g of } H_2O(l) \text{ at } 80.0^\circ C \text{ and } 1 \text{ atm}$$

Certain quantities, called **state properties**, depend only on the state of the system, not on the way the system reached that state. Putting it another way, if X is a state property, then

The distance between two cities depends on path, so it isn't a state property.

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

That is, the change in X is the difference between its values in final and initial states. Most of the quantities that you are familiar with are state properties; volume is a common example. You may be surprised to learn, however, that heat flow is *not* a state property; its magnitude depends on how a process is carried out (Section 8-7).

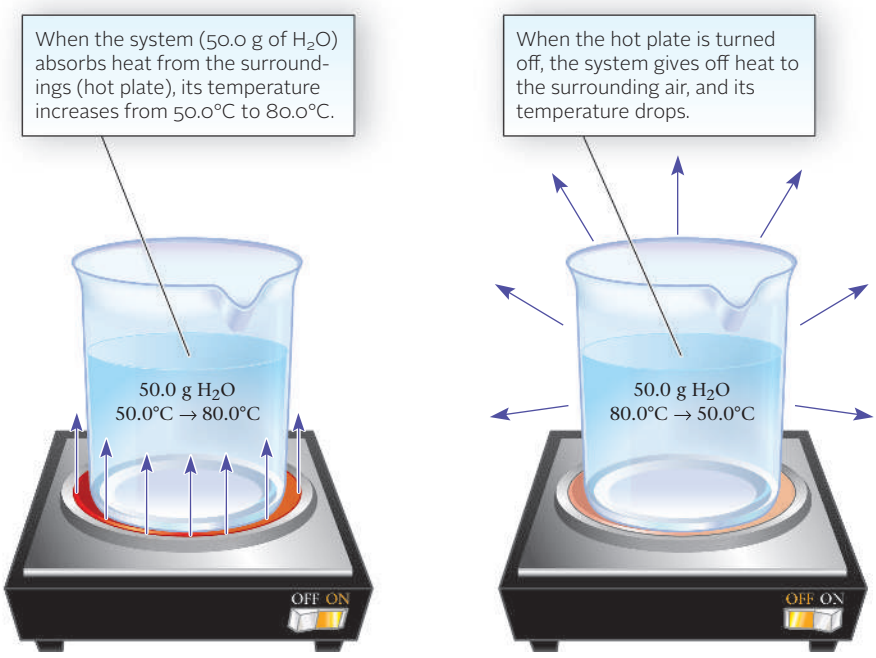

Figure 8.1 A system and its surroundings.

Direction and Sign of Heat Flow

Consider again the setup in Figure 8.1. If the hot plate is turned on, there is a flow of heat from the surroundings into the system, 50.0 g of water. This situation is described by stating that the **heat flow**, q, for the system is a positive quantity.

When money flows into your checking account, it is a positive quantity. When money flows out, it is a negative quantity.

q is positive when heat flows into the system from the surroundings.

Usually, when heat flows into a system, its temperature rises. In this case, the temperature of the 50.0-g water sample might increase from 50.0°C to 80.0°C. When the hot plate in Figure 8.1 is shut off, the hot water gives off heat to the surrounding air. In this case, q for the system is a negative quantity.

q is negative when heat flows out of the system into the surroundings.

As is usually the case, the temperature of the system drops when heat flows out of it into the surroundings. The 50.0-g water sample might cool from 80.0°C back to 50.0°C.

This same reasoning can be applied to a reaction in which the system consists of the reaction mixture (products and reactants). We can distinguish between

- ***an* endothermic *process ($q > 0$), in which heat flows from the surroundings into the reaction system.*** An example is the melting of ice:

$$H_2O(s) \longrightarrow H_2O(l) \qquad q > 0$$

  The melting of ice *absorbs* heat from the surroundings (Figure 8.2a), which might be the water in a glass of iced tea. The temperature of the surroundings drops, perhaps from 25°C to 3°C, as they give up heat to the system.
- ***an* exothermic *process ($q < 0$), in which heat flows from the reaction system into the surroundings.*** A familiar example is the combustion of methane, the major component of natural gas.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad q < 0$$

This reaction *evolves* heat to the surroundings, which might be the air around a Bunsen burner in the laboratory (Figure 8.2b) or a potato being baked in a gas oven. In either case, the effect of the heat transfer is to raise the temperature of the surroundings.

endo = into system; exo = out of system.

Magnitude of Heat Flow

In any process, we are interested not only in the direction of heat flow but also in its magnitude. We will express q in the units introduced in Chapter 6, the **joule** and the *kilojoule*. The joule is named for James Joule (1818–1889), who carried out very precise thermometric measurements that established the first law of thermodynamics (Section 8-7).

1 J = 1 kg · m^2/s^2 in SI units

In the past, chemists used the calorie* as an energy unit. This is the amount of heat required to raise the temperature of one gram of water one degree Celsius. The calorie is a larger energy unit than the joule:

$$1 \text{ cal} = 4.184 \text{ J} \qquad 1 \text{ kcal} = 4.184 \text{ kJ}$$

Most of the remainder of this chapter is devoted to a discussion of the magnitude of the heat flow in chemical reactions or phase changes. However, we will focus on a simpler process in which the only effect of the heat flow is to change the temperature of a system. In general, the relationship between the magnitude of the heat flow, q, and the temperature change, Δt, is given by the equation

$$q = C \times \Delta t \qquad (\Delta t = t_{\text{final}} - t_{\text{initial}})$$

*The "calorie" referred to by nutritionists is actually a kilocalorie (1 kcal = 10^3 cal). On a 2000-calorie per day diet, you eat food capable of producing 2000 kcal = 2×10^3 kcal = 2×10^6 cal of energy.

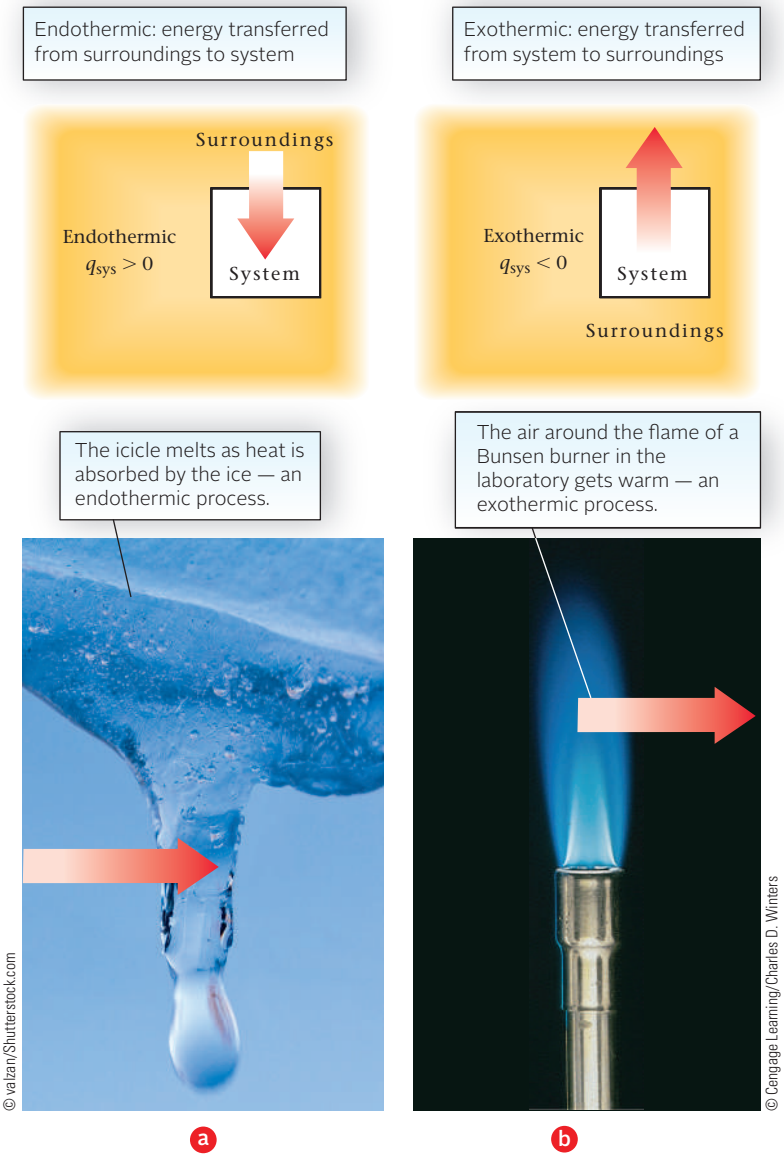

Figure 8.2 **(a) Endothermic and (b) exothermic processes.**

Figure 8.3 **Substances with varying specific heats.** The metals shown (Cu, Al, and Fe) have specific heats ranging from 0.38 J/g · °C (Cu) to 0.90 J/g · °C (Al). This explains why water warms up and cools down more slowly than a container made of aluminum, copper, or iron.

The quantity C appearing in this equation is known as the **heat capacity** of the system. It represents the amount of heat required to raise the temperature of the system 1°C and has the units J/°C.

For a pure substance of a certain mass, the expression for q can be written

$$q = \text{mass} \times c \times \Delta t \qquad (8.1)$$

The quantity c is called the **specific heat** or *specific heat capacity*. (In this text, we will use the term *specific heat*.) Specific heat is defined as the amount of heat required to raise the temperature of one gram of a substance one degree Celsius. When the mass of that substance is equal to its molar mass, then c is called the *molar heat capacity*.

Specific heat, like density or melting point, is an intensive property that can be used to identify a substance or determine its purity. Water has an unusually large specific heat, 4.18 J/g·°C. This explains why swimming is not a popular pastime in northern Minnesota in May. Even if the air temperature rises to 90°F, the water temperature will remain below 60°F. Metals have a relatively low specific heat (Table 8.1). When you heat water in a stainless steel saucepan, for example, nearly all of the heat is absorbed by the water, very little by the steel (Figure 8.3).

Table 8.1 Specific Heats of a Few Common Substances

	c (J/g · °C)		c (J/g · °C)
$Br_2(l)$	0.474	$Cu(s)$	0.382
$Cl_2(g)$	0.478	$Fe(s)$	0.446
$C_2H_5OH(l)$	2.43	$H_2O(g)$	1.87
$C_6H_6(l)$	1.72	$H_2O(l)$	4.18
$CO_2(g)$	0.843	$NaCl(s)$	0.866

EXAMPLE 8.1

Compare the amount of heat given off by 1.40 mol of liquid water when it cools from 100.0°C to 30.0°C to that given off when 1.40 mol of steam cools from 200.0°C to 110.0°C.

ANALYSIS

Information given:	$H_2O(l)$: mols (1.40), t_{final} (30.0°C), $t_{initial}$ (100.0°C) $H_2O(g)$: mols (1.40), t_{final} (110.0°C), $t_{initial}$ (200.0°C)
Information implied:	molar mass of water and steam specific heats of water and steam
Asked for:	q for both water and steam

STRATEGY

1. Recall that $\Delta t = t_{final} - t_{initial}$.
2. Convert mols to mass (in grams).
3. Use Table 8.1 to obtain the specific heats of water and steam.
4. Substitute into Equation 8.1

SOLUTION

For $H_2O(l)$:

1. Δt: $\Delta t = t_{final} - t_{initial} = 30.0°C - 100.0°C = -70.0°C$
2. mass: $1.40 \text{ mol} \times \dfrac{18.02 \text{ g}}{1 \text{ mol}} = 25.2 \text{ g}$
3. c: From Table 8.1, $c = 4.18$ J/g · °C.
4. q: $q = \text{mass} \times \Delta t \times c = (25.2 \text{ g})(4.18 \text{ J/g} \cdot °C)(-70.0°C) = -7.37 \times 10^3$ J

For $H_2O(g)$:

1. Δt: $\Delta t = t_{final} - t_{initial} = 110.0°C - 200.0°C = -90.0°C$
2. mass: $1.40 \text{ mol} \times \dfrac{18.02 \text{ g}}{1 \text{ mol}} = 25.2 \text{ g}$
3. c: From Table 8.1, $c = 1.87$ J/g · °C.
4. q: $q = \text{mass} \times \Delta t \times c = (25.2 \text{ g})(1.87 \text{ J/g} \cdot °C)(-90.0°C) = -4.24 \times 10^3$ J

END POINTS

1. The negative sign indicates that heat flows from the system (water and steam) to the surroundings.
2. Be careful when deciding on initial and final temperatures. The higher temperature is not necessarily the final temperature.

8-2 Measurement of Heat Flow; Calorimetry

To measure the heat flow in a reaction, a device known as a **calorimeter** is used. The apparatus contains water and/or other materials of known heat capacity. The walls of the calorimeter are insulated so that there is no exchange of heat with the surrounding air. It follows that the only heat flow is between the reaction system and the calorimeter. The heat flow for the reaction system is equal in magnitude but opposite in sign to that of the calorimeter:

$$q_{\text{reaction}} = -q_{\text{calorimeter}}$$

Notice that if the reaction is exothermic ($q_{\text{reaction}} < 0$), $q_{\text{calorimeter}}$ must be positive; that is, heat flows from the reaction mixture into the calorimeter. Conversely, if the reaction is endothermic, the calorimeter gives up heat to the reaction mixture.

The equation just written is basic to calorimetric measurements. It allows you to calculate the amount of heat absorbed or evolved in a reaction if you know the heat capacity, C_{cal}, and the temperature change, Δt, of the calorimeter.

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta t$$

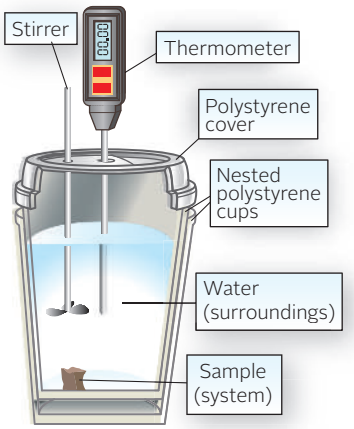

Figure 8.4 Coffee-cup calorimeter. The heat given off by the sample is absorbed by the water. If you know the mass of the water, its specific heat (4.18 J/g · °C), and the temperature change as read on the thermometer, you can calculate the heat flow, q, for the sample.

Coffee-Cup Calorimeter

Figure 8.4 shows a simple **coffee-cup calorimeter** used in the general chemistry laboratory. It consists of two nested polystyrene foam cups partially filled with water. The cups have a tightly fitting cover through which an accurate thermometer is inserted. Because polystyrene foam is a good insulator, there is very little heat flow through the walls of the cups. Essentially all the heat evolved by a reaction taking place within the calorimeter is absorbed by the water. This means that, to a good degree of approximation, the heat capacity of the coffee-cup calorimeter is that of the water:

$$C_{\text{cal}} = \text{mass}_{H_2O} \times c_{\text{water}} = \text{mass}_{\text{water}} \times 4.18 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}}$$

and hence

$$q_{\text{reaction}} = -\text{mass}_{H_2O} \times 4.18 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}} \times \Delta t \qquad (8.2)$$

EXAMPLE 8.2 GRADED

Calcium chloride, $CaCl_2$, is added to canned vegetables to maintain the vegetables' firmness. When added to water, it dissolves:

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

A calorimeter contains 50.0 g of water at 25.00°C. When 1.00 g of calcium chloride is added to the calorimeter, the temperature rises to 28.51°C. Assume that all the heat given off by the reaction is transferred to the water.

a Calculate q for the reaction system.

ANALYSIS

Information given:	mass of water (50.0 g); mass of $CaCl_2$ (1.00 g) initial temperature (25.00°C); final temperature (28.51°C)
Information implied:	specific heat of water
Asked for:	q_{reaction}

continued

STRATEGY

1. Find Δt.
2. Substitute into Equation 8.1 to find q_{H_2O}
3. Recall that q reaction $= -q_{H_2O}$.

SOLUTION

1. Δt	$\Delta t = t_{final} - t_{initial} = 28.51°C - 25.00°C = 3.51°C$
2. q_{H_2O}	$q_{H_2O} = \text{mass} \times \Delta t \times c = (50.0\ g)(4.18\ J/g \cdot °C)(3.51°C) = 734\ J$
3. $q_{reaction}$	$q_{reaction} = -q_{H_2O} = -734\ J$

b How much $CaCl_2$ must be added to raise the temperature of the solution 9.00°C?

ANALYSIS

Information given:	mass of water (50.0 g) From part (a), $q_{reaction}$ for 1.00 g of $CaCl_2$ used (−734 J). Δt (9.00°C)
Information implied:	specific heat of water
Asked for:	mass $CaCl_2$ to be added

STRATEGY

1. Find q_{H_2O} by substituting into Equation 8.1.
2. Recall $q_{reaction} = -q_{H_2O}$
3. Use −734 J/g $CaCl_2$ obtained in part (a) as a conversion factor.

SOLUTION

1. q_{H_2O}	$q_{H_2O} = \text{mass} \times \Delta t \times c = (50.0\ g)(4.18\ J/g \cdot °C)(9.00°C) = 1.88 \times 10^3\ J$
2. $q_{reaction}$	$q_{reaction} = -q_{H_2O} = -1.88 \times 10^3\ J$
3. Mass $CaCl_2$ needed	$-1.88 \times 10^3\ J \times \dfrac{1.00\ g\ CaCl_2}{-734\ J} = 2.56\ g$
Mass $CaCl_2$ to be added	$2.56 - 1.00 = 1.56\ g$

END POINT

Since the final temperature is larger than the initial temperature after the addition of $CaCl_2$, the reaction must be exothermic. Thus $q_{reaction}$ must be negative. It is!

Bomb Calorimeter

A coffee-cup calorimeter is suitable for measuring heat flow for reactions in solution. However, it cannot be used for reactions involving gases, which would escape from the cup. Neither would it be appropriate for reactions in which the products reach high temperatures. The **bomb calorimeter,** shown in Figure 8.5, is more versatile. To use it, a weighed sample of the reactant(s) is added to the heavy-walled metal vessel called a "bomb." This is then sealed and lowered into the insulated outer container. An amount of water sufficient to cover the bomb is added, and the entire apparatus is closed. The initial temperature is measured precisely. The reaction is then started, perhaps by electrical ignition. In an exothermic reaction, the hot products give off heat to the walls of the bomb and to the water. The final temperature is taken to be the highest value read on the thermometer.

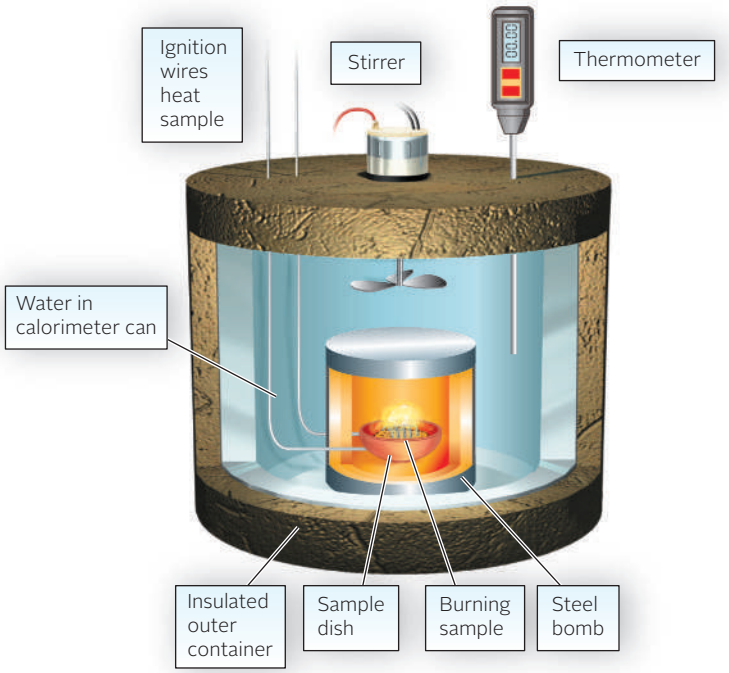

Figure 8.5 Bomb calorimeter. The heat flow, q, for the reaction is calculated from the temperature change multiplied by the heat capacity of the calorimeter, which is determined in a preliminary experiment.

All of the heat given off by the reaction is absorbed by the calorimeter, which consists of the metal bomb and the water that surrounds it. In other words,

$$q_{\text{reaction}} = -(q_{\text{calorimeter}} + q_{H_2O})$$

As discussed earlier, the heat absorbed by the water can be determined by substituting into Equation 8.1:

$$q_{H_2O} = c \times \text{mass}_{H_2O} \times \Delta t$$

The heat absorbed by the calorimeter is equal to the product of its heat capacity (unique to each calorimeter), C_{cal}, and the temperature change, Δt:

$$q_{\text{calorimeter}} = C_{\text{cal}} \times \Delta t \qquad (8.3)$$

To find the heat capacity, C_{cal}, the experiment is repeated using the same bomb and the same amount of water. This time, though, we carry out a reaction for which the amount of heat evolved is known, 93.3 kJ. The temperature increase is again measured carefully. Suppose that the water in the calorimeter can has a mass of 1.00 kg (1000 g) and the temperature rises from 20.00°C to 30.00°C, then q for the water would be 41.8 kJ and q for the calorimeter would then be

$$93.3 \text{ kJ} - 41.8 \text{ kJ} = 51.5 \text{ kJ}$$

Substituting into Equation 8.3 we obtain the heat capacity of the calorimeter.

$$C_{\text{cal}} = \frac{51.5 \text{ kJ}}{10.00°\text{C}} = 5.15 \text{ kJ/°C}$$

Knowing the heat capacity of the calorimeter, the heat flow for any reaction taking place in that calorimeter can be calculated (Example 8.3).

EXAMPLE 8.3

Hydrogen chloride is used in etching semiconductors. It can be prepared by reacting hydrogen and chlorine gases.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

It is found that when 1.00 g of H_2 is made to react completely with Cl_2 in a bomb calorimeter with a heat capacity of 5.15 kJ/°C, the temperature in the bomb rises from 20.00°C to 29.82°C. The calorimeter can hold 1.000 kg of water. How much heat is evolved by the reaction?

ANALYSIS

Information given:	mass of H_2 (1.00 g); mass of water (1.000 kg = 1.000×10^3 g) C_{cal} (5.15 kJ/°C) t_{final} (29.82°C), $t_{initial}$ (20.00°C)
Information implied:	specific heat (c) of water
Asked for:	q for the reaction

STRATEGY

1. Find q_{H_2O} by substituting into Equation 8.2.
2. Find q_{cal} by substituting into Equation 8.3.
3. Recall: $q_{reaction} = -(q_{H_2O} + q_{cal})$.

SOLUTION

1. q_{H_2O}

$$q_{H_2O} = c_{H_2O} \times \text{mass}_{H_2O} \times \Delta t$$

$$= 4.18 \frac{\text{J}}{\text{g} \cdot \text{°C}} \times 1.000 \times 10^3 \text{ g} \times (29.82 - 20.00)\text{°C}$$

$$= 4.10 \times 10^4 \text{ J} = 41.0 \text{ kJ}$$

2. q_{cal}

$$q_{cal} = C_{cal} \times \Delta t = (5.15 \text{ kJ/°C})(29.82 - 20.00)\text{°C} = 50.6 \text{ kJ}$$

3. $q_{reaction}$

$$q_{reaction} = -(q_{cal} + q_{H_2O}) = -(41.0 + 50.6)\text{kJ} = -91.6 \text{ kJ}$$

END POINT

The amount of hydrogen gas (1.00 g) that reacted is not relevant to the solution of this problem.

8-3 Enthalpy

We have referred several times to the "heat flow for the reaction system," symbolized as $q_{reaction}$. At this point, you may well find this concept a bit nebulous and wonder if it could be made more concrete by relating $q_{reaction}$ to some property of reactants and products. This can indeed be done; the situation is particularly simple for reactions taking place at constant pressure. Under that condition, the heat flow for the reaction system is equal to the difference in **enthalpy** (H) between products and reactants. The **enthalpy change** is designated as ΔH. That is,

$$q_{reaction} \text{ at constant pressure} = \Delta H = H_{products} - H_{reactants}$$

Enthalpy is a type of chemical energy, sometimes referred to as "heat content." Reactions that occur in the laboratory in an open container or in the world around us take place at a constant pressure, that of the atmosphere. For such reactions, the equation just written is valid, making enthalpy a very useful quantity.

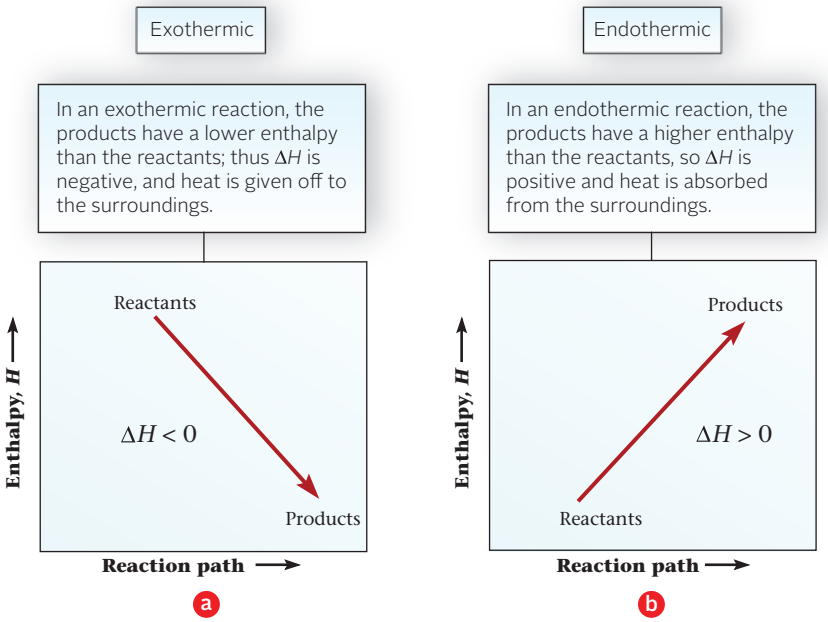

Figure 8.6 Energy diagram showing ΔH for a reaction.

Figure 8.6a shows the enthalpy relationship between reactants and products for an exothermic reaction such as

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H < 0$$

Here, the products, 1 mol of $CO_2(g)$ and 2 mol of $H_2O(l)$, have a lower enthalpy than the reactants, 1 mol of $CH_4(g)$ and 2 mol of $O_2(g)$. The decrease in enthalpy is the source of the heat evolved to the surroundings. Figure 8.6b shows the situation for an endothermic process such as

When CH_4 burns, ΔH is negative; when ice melts, ΔH is positive.

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H > 0$$

Liquid water has a higher enthalpy than ice, so heat must be transferred from the surroundings to melt the ice.

In general, the following relations apply for reactions taking place at constant pressure.

exothermic reaction: $q = \Delta H < 0$ $\quad H_{products} < H_{reactants}$

endothermic reaction: $q = \Delta H > 0$ $\quad H_{products} > H_{reactants}$

The enthalpy of a substance, like its volume, is a state property. A sample of one gram of liquid water at 25.00°C and 1 atm has a fixed enthalpy, H. In practice, no attempt is made to determine absolute values of enthalpy. Instead, scientists deal with changes in enthalpy, which are readily determined. For the process

$$1.00 \text{ g } H_2O \text{ } (l, 25.00°C, 1 \text{ atm}) \longrightarrow 1.00 \text{ g } H_2O \text{ } (l, 26.00°C, 1 \text{ atm})$$

ΔH is 4.18 J because the specific heat of water is 4.18 J/g · °C.

8-4 Thermochemical Equations

A chemical equation that shows the enthalpy relation between products and reactants is called a **thermochemical equation.** This type of equation contains, at the right of the balanced chemical equation, the appropriate value and sign for ΔH.

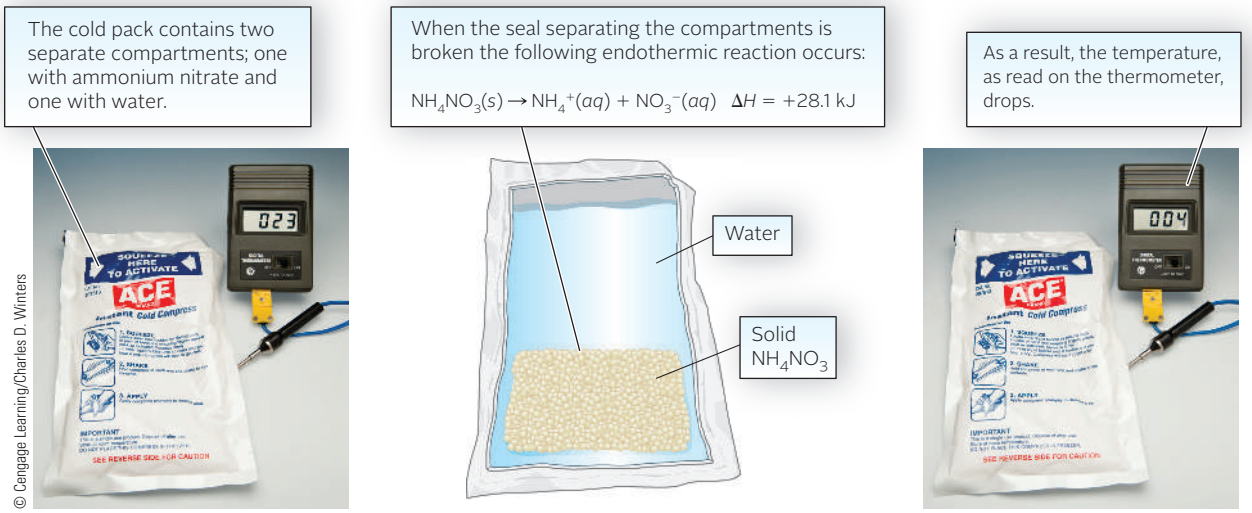

Figure 8.7 **Endothermic reaction in a cold pack.**

To see where a thermochemical equation comes from, consider the process by which ammonium nitrate dissolves in water:

$$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$$

A simple experiment with a coffee-cup calorimeter shows that when one gram of NH_4NO_3 dissolves, $q_{reaction} = 351$ J. The calorimeter is open to the atmosphere, the pressure is constant, and

$$\Delta H \text{ for dissolving 1.00 g of } NH_4NO_3 = 351 \text{ J} = 0.351 \text{ kJ}$$

When one mole (80.05 g) of NH_4NO_3 dissolves, ΔH should be 80 times as great:

$$\Delta H \text{ for dissolving 1.00 mol of } NH_4NO_3 = 0.351 \frac{\text{kJ}}{\text{g}} \times 80.05 \text{ g} = 28.1 \text{ kJ}$$

The thermochemical equation for this reaction (Figure 8.5) must then be

$$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H = +28.1 \text{ kJ}$$

By an entirely analogous procedure, the thermochemical equation for the formation of HCl from the elements (Example 8.3) is found to be

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -185 \text{ kJ}$$

In other words, 185 kJ of heat is evolved when two moles of HCl are formed from H_2 and Cl_2 (Figure 8.8).

These thermochemical equations are typical of those used throughout this text. It is important to realize that

- the sign of ΔH indicates whether the reaction, when carried out at constant pressure, is endothermic (positive ΔH) or exothermic (negative ΔH).
- in interpreting a thermochemical equation, the coefficients represent numbers of moles (ΔH is -185 kJ when ***1 mol*** H_2 + ***1 mol*** $Cl_2 \rightarrow$ ***2 mol*** HCl).
- the phases (physical states) of all species must be specified, using the symbols (s), (l), (g), or (aq). The enthalpy of one mole of $H_2O(g)$ at 25°C is 44 kJ larger than that of one mole of $H_2O(l)$; the difference, which represents the heat of vaporization of water, is clearly significant. ℹ
- the value quoted for ΔH applies when products and reactants are at the same temperature, ordinarily taken to be 25°C unless specified otherwise.

Figure 8.8 **An exothermic reaction.** Hydrogen, a colorless gas, reacts with chlorine, a pale yellow gas, to form colorless hydrogen chloride gas.

ℹ This explains why burns from steam are more painful than those from boiling water.

Rules of Thermochemistry

To make effective use of thermochemical equations, three basic rules of thermochemistry are applied.

1. ***The magnitude of ΔH is directly proportional to the amount of reactant or product.*** This is a common-sense rule, consistent with experience. The amount of heat that must be absorbed to boil a sample of water is directly proportional to its mass. In another case, the more gasoline you burn in your car's engine, the more energy you produce.

The magnitude of ΔH is dependent not only on the amount of the reactants and products but also on their physical states.

This rule allows you to find ΔH corresponding to any desired amount of reactant or product. To do this, you follow the conversion-factor approach used in Chapter 3 with ordinary chemical equations. Consider, for example,

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -185 \text{ kJ}$$

The thermochemical equation allows us to relate the enthalpy change to amounts of reactants and products, leading to conversion factors such as

$$\frac{-185 \text{ kJ}}{1 \text{ mol } Cl_2} \qquad \frac{1 \text{ mol } H_2}{-185 \text{ kJ}} \qquad \frac{-185 \text{ kJ}}{2 \text{ mol HCl}}$$

EXAMPLE 8.4 GRADED

The Bunsen burners in your labs are fueled by natural gas, which is mostly methane, CH_4. The thermochemical equation for the combustion (burning in oxygen) of methane is

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

a Calculate ΔH when 5.00 g of CH_4 react with an excess of oxygen.

ANALYSIS

Information given:	mass of CH_4 (5.00 g), excess O_2
Information implied:	molar mass of CH_4 ΔH for the reaction
Asked for:	ΔH

STRATEGY

1. Use the relationship obtained from the thermochemical equation: −890.3 kJ/mol CH_4 as a conversion factor.
2. Follow the following schematic plan.

$$\text{mass}_{CH_4} \xrightarrow{\text{MM}} \text{mol}_{CH_4} \xrightarrow{-890.3 \text{ kJ/mol } CH_4} \Delta H$$

SOLUTION

ΔH

$$5.00 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.04 \text{ g } CH_4} \times \frac{-890.3 \text{ kJ}}{1 \text{ mol } CH_4} = -278 \text{ kJ}$$

b Calculate ΔH when 2.00 L of CH_4 at 49.0°C and 782 mm Hg react with an excess of oxygen.

ANALYSIS

Information given:	CH_4 data: V (2.00 L), T (49.0°C), P (782 mm Hg). Excess O_2
Information implied:	ΔH for the reaction gas constant, R
Asked for:	ΔH

continued

STRATEGY

Follow the following schematic plan.

$$V_{CH_4} \xrightarrow{PV/RT} \text{mol}_{CH_4} \xrightarrow{-890.3\ \text{kJ}/1\ \text{mol } CH_4} \Delta H$$

SOLUTION

mol CH_4	$n = \dfrac{PV}{RT} = \dfrac{(782/760)\text{atm} \times 2.00\ \text{L}}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K}) \times 322\ \text{K}} = 0.0778\ \text{mol}$
ΔH	$0.0778\ \text{mol } CH_4 \times \dfrac{-890.3\ \text{kJ}}{1\ \text{mol } CH_4} = -69.3\ \text{kJ}$

C Calculate ΔH when 2.00 L of CH_4 react with 5.00 L of O_2 in a reaction vessel kept at 49°C and 782 mm Hg.

ANALYSIS

Information given:	V_{CH_4} (2.00 L), V_{O_2} (5.00 L), T and P are constant.
Information implied:	stoichiometric ratios ΔH for the reaction gas constant, R
Asked for:	ΔH

STRATEGY

1. Note that data about both reactants is given (limiting reactant problem) and that the reaction is at constant temperature and pressure.
2. Find V_{CO_2} obtained if CH_4 is limiting and again if O_2 is limiting. Choose the smaller value, then use the following schematic plan:

$$V_{CO_2} \xrightarrow{PV/RT} \text{mol}_{CO_2} \xrightarrow{-890.3\ \text{kJ}/1\ \text{mol } CO_2} \Delta H$$

SOLUTION

V_{CO_2} produced	If CH_4 is limiting: $2.00\ \text{L } CH_4 \times \dfrac{1\ \text{L } CO_2}{1\ \text{L } CH_4} = 2.00\ \text{L}$
	If O_2 is limiting: $5.00\ \text{L } O_2 \times \dfrac{1\ \text{L } CO_2}{2\ \text{L } O_2} = 2.50\ \text{L}$
	CH_4 is limiting and 2.00 L of CO_2 are produced.
mol CO_2	$n = \dfrac{PV}{RT} = \dfrac{782/760\ \text{atm} \times 2.00\ \text{L}}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K}) \times 322\ \text{K}} = 0.0778\ \text{mol}$
ΔH	$0.0778\ \text{mol } CO_2 \times \dfrac{-890.3\ \text{kJ}}{1\ \text{mol } CO_2} = -69.3\ \text{kJ}$

The heat absorbed when a solid melts ($s \rightarrow l$) is referred to as the **heat of fusion;** that absorbed when a liquid vaporizes ($l \rightarrow g$) is called the **heat of vaporization.** Heats of fusion (ΔH_{fus}) and vaporization (ΔH_{vap}) are most often expressed in kilojoules per mole (kJ/mol). Values for several different substances are given in Table 8.2.

2. ***ΔH for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction*** (Figure 8.9). Another way to state this rule is to say that the amount of heat evolved in a reaction is exactly equal to the amount of heat

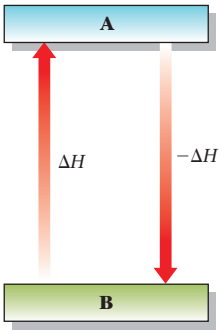

Figure 8.9 Thermochemistry rule 2.

Table 8.2 ΔH(kJ/mol) for Phase Changes

Substance		mp(°C)	ΔH_{fus}*	bp(°C)	ΔH_{vap}*
Benzene	C_6H_6	5	9.84	80	30.8
Bromine	Br_2	−7	10.8	59	29.6
Mercury	Hg	−39	2.33	357	59.4
Naphthalene	$C_{10}H_8$	80	19.3	218	43.3
Water	H_2O	0	6.00	100	40.7

*Values of ΔH_{fus} are given at the melting point, values of ΔH_{vap} at the boiling point. The heat of vaporization of water decreases from 44.9 kJ/mol at 0°C to 44.0 kJ/mol at 25°C to 40.7 kJ/mol at 100°C.

absorbed in the reverse reaction. This again is a common-sense rule. If 6.00 kJ of heat is absorbed when a mole of ice melts,

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = +6.00 \text{ kJ}$$

then 6.00 kJ of heat should be evolved when a mole of liquid water freezes.

$$H_2O(l) \longrightarrow H_2O(s) \qquad \Delta H = -6.00 \text{ kJ}$$

EXAMPLE 8.5

Given

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -571.6 \text{ kJ}$$

calculate ΔH for the equation

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

STRATEGY

1. Note that the second equation is the reverse of the first. Apply Rule 2.
2. The coefficients of the second equation are half those of the given equation. Apply Rule 1.

SOLUTION

Apply Rule 2.	$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$	$\Delta H = -(-571.6 \text{ kJ}) = 571.6 \text{ kJ}$
Apply Rule 1.	$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g)$	$\Delta H = \tfrac{1}{2}(+571.6 \text{ kJ}) = 285.8 \text{ kJ}$

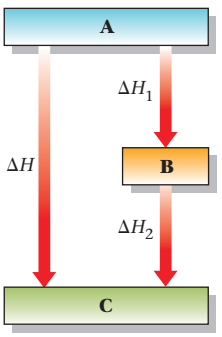

Figure 8.10 Thermochemistry rule 3, Hess's law, $\Delta H = \Delta H_1 + \Delta H_2$ because H is a state property.

3. ***The value of ΔH for a reaction is the same whether it occurs in one step or in a series of steps*** (Figure 8.10). If a thermochemical equation can be expressed as the sum of two or more equations,

$$\text{equation} = \text{equation (1)} + \text{equation (2)} + \cdots$$

then ΔH for the overall equation is the sum of the ΔH's for the individual equations:

$$\Delta H = \Delta H_1 + \Delta H_2 + \cdots$$

This relationship is referred to as **Hess's law,** after Germain Hess (1802–1850), professor of chemistry at the University of St. Petersburg, who deduced it in 1840. Hess's law is a direct consequence of the fact that enthalpy is a state property, dependent only on initial and final states.◂ This means that, in Figure 8.10, ΔH *must* equal the sum of ΔH_1 and ΔH_2, because the final and initial states are the same for the two processes.

Hess's law is very convenient for obtaining values of ΔH for reactions that are difficult to carry out in a calorimeter. Consider, for example, the formation of the

ΔH must be independent of path, since H is a state property.

toxic gas carbon monoxide from the elements

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$$

It is difficult, essentially impossible, to measure ΔH for this reaction because when carbon burns, the major product is always carbon dioxide, CO_2. It is possible, however, to calculate ΔH using thermochemical data for two other reactions that are readily carried out in the laboratory (Example 8.6).

EXAMPLE 8.6

Carbon monoxide, CO, is a poisonous gas. It can be obtained by burning carbon in a limited amount of oxygen. Given

(1) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H = -393.5$ kJ

(2) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ $\quad \Delta H = -566.0$ kJ

calculate ΔH for the reaction

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = ?$$

STRATEGY

1. Work with the given equations until you arrive at two equations that will add to give the equation
   $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$
2. Focus on species that appear in only one of the thermochemical equations. In this case C appears only in Equation (1) and CO appears only in Equation (2).
3. For CO
   Compare position and number of moles of CO in Equation 2 and in the desired equation.
   Position: Equation (2)—on the left Desired equation—on the right
   Moles: Equation (2)—2 moles Desired equation—1 mole
   Apply Rule 2 to reverse Equation (2) (to put CO on the right).
   Apply Rule 1 and divide Equation (2) by 2 (to get a coefficient of 1 for CO).
4. For C
   Compare position and number of moles of C in Equation (1) and in the desired equation.
   Position: Equation (1)—on the left Desired equation—on the left
   Moles: Equation (2)—1 mole Desired equation—1 mole
   Both the position and coefficient for C are okay, so use Equation (1) "as is."
5. Add the "revised" Equation (2c) to Equation (1).

SOLUTION

For Equation (2)		
Apply Rule 2	(2a) $2CO_2(g) \longrightarrow 2CO(g) + O_2(g)$	$\Delta H = -(-566.0\text{ kJ}) = 566.0$ kJ
Apply Rule 1	(2b) $CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g)$	$\Delta H = \frac{1}{2}(566.0\text{ kJ}) = 283.0$ kJ
"Revised" Equation 2	(2c) $CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g)$	$\Delta H_2 = \frac{1}{2}(566.0\text{ kJ}) = 283.0$ kJ
Equation (1) "as is"	(1) $C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H_1 = -393.5$ kJ
Apply Hess's law	Add "revised" Equation (2c) to Equation (1)	
	(2c) ~~$CO_2(g)$~~ $\longrightarrow CO(g) + \frac{1}{2}$~~$O_2(g)$~~	$\Delta H_2 = 283.0$ kJ
	(1) $C(s) + $~~$O_2(g)$~~ $\longrightarrow$ ~~$CO_2(g)$~~	$\Delta H_1 = -393.5$ kJ
	$\downarrow$ $\frac{1}{2}O_2(g)$	
$\Delta H = \Delta H_1 + \Delta H_2$	$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	$\Delta H = 283.0\text{ kJ} + (-393.5)\text{ kJ} = -110.5$ kJ

Summarizing the rules of thermochemistry:

1. ΔH is directly proportional to the amount of reactant or product.
2. ΔH changes sign when a reaction is reversed.
3. ΔH for a reaction has the same value regardless of the number of steps.

8-5 Enthalpies of Formation

We have now written several thermochemical equations. In each case, we have cited the corresponding value of ΔH. Literally thousands of such equations would be needed to list the ΔH values for all the reactions that have been studied. Clearly, there has to be some more concise way of recording data of this sort. These data should be in a form that can easily be used to calculate ΔH for any reaction. It turns out that there is a simple way to do this, using quantities known as enthalpies of formation.

Meaning of ΔH_f°

Often called "heat of formation."

The standard molar **enthalpy of formation** of a compound, ΔH_f°, is equal to the enthalpy change when one mole of the compound is formed at a constant pressure of 1 atm and a fixed temperature, ordinarily 25°C, from the elements in their stable states at that pressure and temperature (Figure 8.11). From the equations

$$\text{Ag}(s, 25^\circ\text{C}) + \tfrac{1}{2}\text{Cl}_2(g, 25^\circ\text{C}, 1\text{ atm}) \longrightarrow \text{AgCl}(s, 25^\circ\text{C}) \qquad \Delta H = -127.1\text{ kJ}$$

$$\tfrac{1}{2}\text{N}_2(g, 1\text{ atm}, 25^\circ\text{C}) + \text{O}_2(g, 1\text{ atm}, 25^\circ\text{C}) \longrightarrow \text{NO}_2(g, 1\text{ atm}, 25^\circ\text{C}) \qquad \Delta H = +33.2\text{ kJ}$$

it follows that

$$\Delta H_f^\circ\ \text{AgCl}(s) = -127.1\text{ kJ/mol} \qquad \Delta H_f^\circ\ \text{NO}_2(g) = +33.2\text{ kJ/mol}$$

Enthalpies of formation for a variety of compounds are listed in Table 8.3. Notice that, with a few exceptions, enthalpies of formation are negative quantities. This means that the formation of a compound from the elements is ordinarily exothermic. Conversely, when a compound decomposes to the elements, heat usually must be absorbed.

However, ΔH_f° $\text{Br}_2(g)$ is +29.6 kJ/mol. Explain.

You will note from Table 8.3 that there are no entries for elemental species such as $\text{Br}_2(l)$ and $\text{O}_2(g)$. This is a consequence of the way in which enthalpies of formation are defined. In effect, the enthalpy of formation of an element in its stable state at 25°C and 1 atm is taken to be zero. That is,

$$\Delta H_f^\circ\ \text{Br}_2(l) = \Delta H_f^\circ\ \text{O}_2(g) = 0$$

The standard enthalpies of formation of ions in aqueous solution listed at the bottom of Table 8.3 are relative values, established by taking

$$\Delta H_f^\circ\ \text{H}^+(aq) = 0$$

From the values listed we see that the Cu^{2+} ion has a heat of formation *greater* than that of H^+ by about 65 kJ/mol, and Cd^{2+} has a heat of formation about 76 kJ/mol *less* than that of H^+.

Figure 8.11 Enthalpy of formation. Magnesium ribbon reacts with oxygen to give MgO, a white solid, and 601.7 kJ of heat per mole of MgO formed. Hence $\Delta H_f^\circ \text{MgO}(s) = -601.7$ kJ/mol.

Calculation of ΔH°

Enthalpies of formation can be used to calculate ΔH° for a reaction. To do this, apply this general rule:

> ***The* standard enthalpy change, ΔH°, *for a given thermochemical equation is equal to the sum of the standard enthalpies of formation of the product compounds minus the sum of the standard enthalpies of formation of the reactant compounds.***

Table 8.3 Standard Enthalpies of Formation at 25°C (kJ/mol) of Compounds at 1 atm, Aqueous Ions at 1 *M*

Compounds							
$AgBr(s)$	−100.4	$CaCl_2(s)$	−795.8	$H_2O(g)$	−241.8	$NH_4NO_3(s)$	−365.6
$AgCl(s)$	−127.1	$CaCO_3(s)$	−1206.9	$H_2O(l)$	−285.8	$NO(g)$	+90.2
$AgI(s)$	−61.8	$CaO(s)$	−635.1	$H_2O_2(l)$	−187.8	$NO_2(g)$	+33.2
$AgNO_3(s)$	−124.4	$Ca(OH)_2(s)$	−986.1	$H_2S(g)$	−20.6	$N_2O_4(g)$	+9.2
$Ag_2O(s)$	−31.0	$CaSO_4(s)$	−1434.1	$H_2SO_4(l)$	−814.0	$NaCl(s)$	−411.2
$Al_2O_3(s)$	−1675.7	$CdCl_2(s)$	−391.5	$HgO(s)$	−90.8	$NaF(s)$	−573.6
$BaCl_2(s)$	−858.6	$CdO(s)$	−258.2	$KBr(s)$	−393.8	$NaOH(s)$	−425.6
$BaCO_3(s)$	−1216.3	$Cr_2O_3(s)$	−1139.7	$KCl(s)$	−436.7	$NiO(s)$	−239.7
$BaO(s)$	−553.5	$CuO(s)$	−157.3	$KClO_3(s)$	−397.7	$PbBr_2(s)$	−278.7
$BaSO_4(s)$	−1473.2	$Cu_2O(s)$	−168.6	$KClO_4(s)$	−432.8	$PbCl_2(s)$	−359.4
$CCl_4(l)$	−135.4	$CuS(s)$	−53.1	$KNO_3(s)$	−494.6	$PbO(s)$	−219.0
$CHCl_3(l)$	−134.5	$Cu_2S(s)$	−79.5	$MgCl_2(s)$	−641.3	$PbO_2(s)$	−277.4
$CH_4(g)$	−74.8	$CuSO_4(s)$	−771.4	$MgCO_3(s)$	−1095.8	$PCl_3(g)$	−287.0
$C_2H_2(g)$	+226.7	$Fe(OH)_3(s)$	−823.0	$MgO(s)$	−601.7	$PCl_5(g)$	−374.9
$C_2H_4(g)$	+52.3	$Fe_2O_3(s)$	−824.2	$Mg(OH)_2(s)$	−924.5	$SiO_2(s)$	−910.9
$C_2H_6(g)$	−84.7	$Fe_3O_4(s)$	−1118.4	$MgSO_4(s)$	−1284.9	$SnO_2(s)$	−580.7
$C_3H_8(g)$	−103.8	$HBr(g)$	−36.4	$MnO(s)$	−385.2	$SO_2(g)$	−296.8
$CH_3OH(l)$	−238.7	$HCl(g)$	−92.3	$MnO_2(s)$	−520.0	$SO_3(g)$	−395.7
$C_2H_5OH(l)$	−277.7	$HF(g)$	−271.1	$NH_3(g)$	−46.1	$ZnI_2(s)$	−208.0
$CO(g)$	−110.5	$HI(g)$	+26.5	$N_2H_4(l)$	+50.6	$ZnO(s)$	−348.3
$CO_2(g)$	−393.5	$HNO_3(l)$	−174.1	$NH_4Cl(s)$	−314.4	$ZnS(s)$	−206.0
Cations				**Anions**			
$Ag^+(aq)$	+105.6	$Hg^{2+}(aq)$	+171.1	$Br^-(aq)$	−121.6	$HPO_4^{2-}(aq)$	−1292.1
$Al^{3+}(aq)$	−531.0	$K^+(aq)$	−252.4	$CO_3^{2-}(aq)$	−677.1	$HSO_4^-(aq)$	−887.3
$Ba^{2+}(aq)$	−537.6	$Mg^{2+}(aq)$	−466.8	$Cl^-(aq)$	−167.2	$I^-(aq)$	−55.2
$Ca^{2+}(aq)$	−542.8	$Mn^{2+}(aq)$	−220.8	$ClO_3^-(aq)$	−104.0	$MnO_4^-(aq)$	−541.4
$Cd^{2+}(aq)$	−75.9	$Na^+(aq)$	−240.1	$ClO_4^-(aq)$	−129.3	$NO_2^-(aq)$	−104.6
$Cu^+(aq)$	+71.7	$NH_4^+(aq)$	−132.5	$CrO_4^{2-}(aq)$	−881.2	$NO_3^-(aq)$	−205.0
$Cu^{2+}(aq)$	+64.8	$Ni^{2+}(aq)$	−54.0	$Cr_2O_7^{2-}(aq)$	−1490.3	$OH^-(aq)$	−230.0
$Fe^{2+}(aq)$	−89.1	$Pb^{2+}(aq)$	−1.7	$F^-(aq)$	−332.6	$PO_4^{3-}(aq)$	−1277.4
$Fe^{3+}(aq)$	−48.5	$Sn^{2+}(aq)$	−8.8	$HCO_3^-(aq)$	−692.0	$S^{2-}(aq)$	+33.1
$H^+(aq)$	0.0	$Zn^{2+}(aq)$	−153.9	$H_2PO_4^-(aq)$	−1296.3	$SO_4^{2-}(aq)$	−909.3

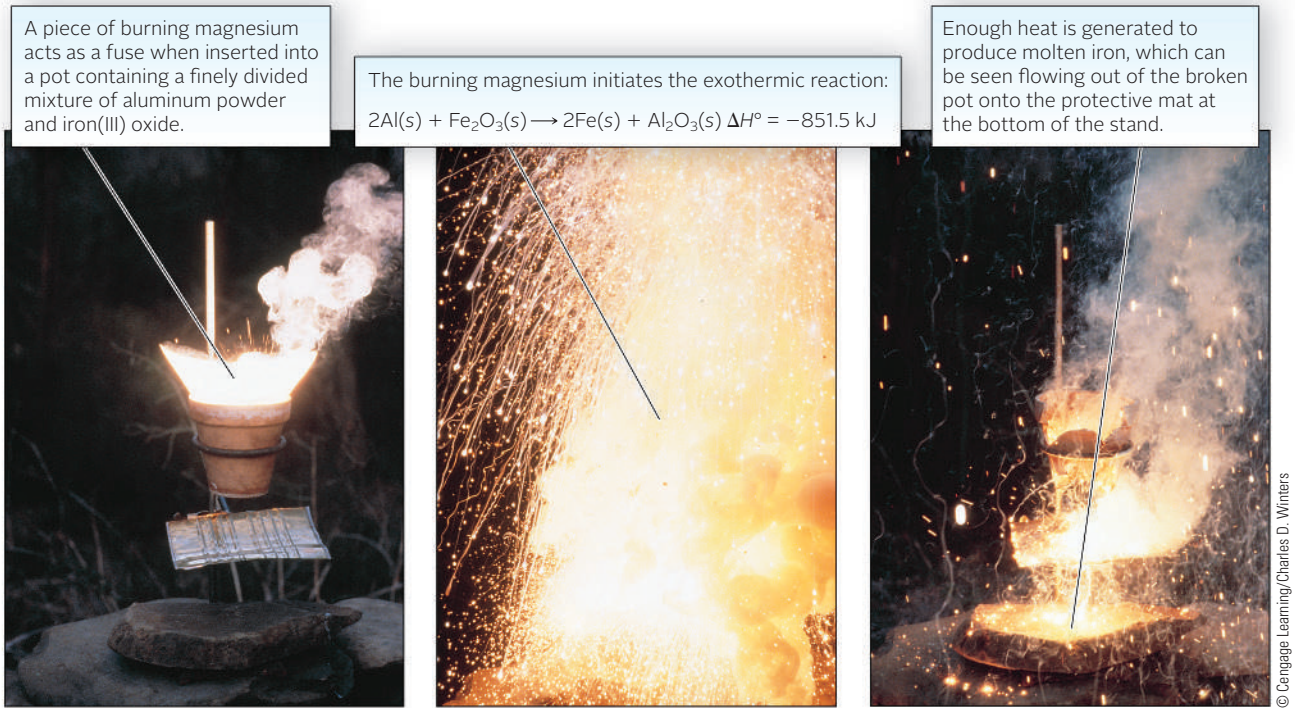

Figure 8.12 **A thermite reaction.**

Using the symbol Σ to represent "the sum of,"

$$\Delta H^\circ = \Sigma\ \Delta H_f^\circ \text{ products} - \Sigma\ \Delta H_f^\circ \text{ reactants} \qquad (8.4)$$

This is a very useful equation, one we will use again and again.

In applying this equation

- ***elements in their standard states can be omitted,*** because their heats of formation are zero. To illustrate, consider the thermite reaction once used to weld rails (Figure 8.12).

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

We can write, quite simply,

$$\Delta H^\circ = \Sigma\ \Delta H_f^\circ \text{ products} - \Sigma\ \Delta H_f^\circ \text{ reactants} = \Delta H_f^\circ\ Al_2O_3(s) - \Delta H_f^\circ\ Fe_2O_3(s)$$

- ***the coefficients of products and reactants in the thermochemical equation must be taken into account.*** For example, consider the reaction:

$$2Al(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

for which:

$$\Delta H^\circ = 2\Delta H_f^\circ\ Al^{3+}(aq) - 3\Delta H_f^\circ\ Cu^{2+}(aq)$$

Strictly speaking, ΔH° calculated from enthalpies of formation listed in Table 8.3 represents the enthalpy change at 25°C and 1 atm. Actually, ΔH is independent of pressure and varies relatively little with temperature, changing by perhaps 1 to 10 kJ per 100°C.

EXAMPLE 8.7 GRADED

Benzene, C_6H_6, used in the manufacture of plastics, is a carcinogen affecting the bone marrow. Long-term exposure has been shown to cause leukemia and other blood disorders. The combustion of benzene is given by the following equation:

$$C_6H_6(l) + \tfrac{15}{2}\ O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l) \qquad \Delta H^\circ = -3267.4 \text{ kJ}$$

continued

a Calculate the heat of formation of benzene.

ANALYSIS

Information given:	thermochemical equation for the combustion of benzene
Information implied:	ΔH_f° for all species except benzene (Table 8.3)
Asked for:	ΔH_f° for benzene

STRATEGY

1. Find ΔH° for all the species (besides benzene) in Table 8.3 and substitute into Equation 8.4.
2. Recall that ΔH° for $O_2(g)$ is zero.

SOLUTION

Equation 8.4

$$-3267.4 \text{ kJ} = 6(\Delta H_f^\circ \text{ CO}_2) + 3(\Delta H_f^\circ \text{ H}_2\text{O}) - (\Delta H_f^\circ \text{ C}_6\text{H}_6)$$

ΔH_f° for $C_6H_6(l)$

$$\Delta H_f^\circ = 3267.4 \text{ kJ} + 6 \text{ mol}\left(-393.5 \frac{\text{kJ}}{\text{mol}}\right) + 3 \text{ mol}\left(-285.8 \frac{\text{kJ}}{\text{mol}}\right)$$

$$= +49.0 \text{ kJ/mol}$$

b Calculate ΔH° for the reaction

$$12CO_2(g) + 6H_2O(l) \longrightarrow 2C_6H_6(l) + 15O_2(g)$$

ANALYSIS

Information given:	thermochemical equation for the combustion of benzene
Asked for:	ΔH° for the reaction: $12CO_2(g) + 6H_2O(l) \longrightarrow 2C_6H_6(l) + 15O_2(g)$

STRATEGY

Note that the given equation is the reverse of the combustion equation and that the coefficients have been doubled. Apply Rules 1 and 2.

SOLUTION

Rule 2

$$\Delta H^\circ = -(-3267.4) \text{ kJ} = 3267.4 \text{ kJ}$$

Rule 1

$$\Delta H^\circ = 2(3267.4 \text{ kJ}) = 6534.8 \text{ kJ}$$

c Calculate ΔH° for the reaction

$$C_6H_6(g) + \tfrac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$$

ANALYSIS

Information given:	thermochemical equation for the combustion of benzene
Information implied:	ΔH_{vap} for water and benzene (Table 8.2)
Asked for:	$C_6H_6(g) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$

STRATEGY

1. Notice that the given equation is identical to the combustion equation except for the physical states of benzene and water.
2. a. Write the thermochemical equation for the vaporization of water.
   b. Multiply the equation by 3 since there are three moles of H_2O in the combustion reaction.
3. a. Write the thermochemical equation for the vaporization of benzene.
   b. Note that $C_6H_6(g)$ is a reactant in the equation where ΔH° is needed.
   c. Reverse the vaporization equation for benzene and change the sign of its ΔH°.
4. Apply Hess's law by adding all the equations so you come up with ΔH° for the overall given equation.

continued

SOLUTION		
$\Delta H_1°$: ($3 \times \Delta H_{vap}$ H_2O)	$3(H_2O(l) \longrightarrow H_2O(g)) = 3(40.7 \text{ kJ/mol})$	$\Delta H_1° = 122.1 \text{ kJ}$
$\Delta H_2°$: (reverse ΔH_{vap} C_6H_6)	$C_6H_6(g) \longrightarrow C_6H_6(l) = -(30.8) \text{ kJ/mol}$	$\Delta H_2° = -30.8 \text{ kJ}$
Apply Hess's law	Equation (1) + Equation (2) + combustion equation	
	(1) $3H_2O(l) \longrightarrow 3H_2O(g)$	$\Delta H_1° = 122.1 \text{ kJ}$
	(2) $C_6H_6(g) \longrightarrow C_6H_6(l)$	$\Delta H_2° = -30.8 \text{ kJ}$
	$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$	$\Delta H° = -3267.4 \text{ kJ}$
Overall equation	$C_6H_6(g) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$	
$\Delta H°$	$122.1 \text{ kJ} + (-30.8 \text{ kJ}) + (-3267.4 \text{ kJ}) = -3176.1 \text{ kJ}$	

The relation between $\Delta H°$ and enthalpies of formation is perhaps used more often than any other in thermochemistry. Its validity depends on the fact that enthalpy is a state property. For any reaction, $\Delta H°$ can be obtained by imagining that the reaction takes place in two steps. First, the reactants (compounds or ions) are converted to the elements:

$$\text{reactants} \longrightarrow \text{elements} \qquad \Delta H_1° = -\Sigma \Delta H_f° \text{ reactants}$$

Then the elements are converted to products:

$$\text{elements} \longrightarrow \text{products} \qquad \Delta H_2° = \Sigma \Delta H_f° \text{ products}$$

Applying a basic rule of thermochemistry, Hess's law,

$$\Delta H° = \Delta H_1° + \Delta H_2° = \Sigma\, \Delta H_f° \text{ products} + (-\Sigma\, \Delta H_f° \text{ reactants})$$

Enthalpy changes for reactions in solution can be determined using standard enthalpies of formation of aqueous ions, applying the general relation

$$\Delta H° = \Sigma\, \Delta H_f° \text{ products} - \Sigma\, \Delta H_f° \text{ reactants}$$

and taking account of the fact that $\Delta H_f° \, H^+(aq) = 0$ (Example 8.8).

EXAMPLE 8.8 GRADED

Copper carbonate is used to control algae in farm ponds. When hydrochloric acid is added to a solution of copper carbonate, carbon dioxide gas is formed (Figure 8.13). The equation for the reaction is

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O(l)$$

a Calculate $\Delta H°$ for the thermochemical equation.

ANALYSIS	
Information given:	Equation for the reaction: $[2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O(l)]$
Information implied:	$\Delta H_f°$ for all the species in the reaction (Table 8.3)
Asked for:	$\Delta H°$ for the reaction

STRATEGY

Use Table 8.3 and recall that $\Delta H_f°$ for H^+ is zero.

SOLUTION	
$\Delta H°$	$\Delta H° = \Delta H_f° \, CO_2 + \Delta H_f° \, H_2O - [2\, \Delta H_f° \, H^+ + \Delta H_f° \, CO_3^{2-}]$
	$= 1 \text{ mol}\left(-393.5 \frac{\text{kJ}}{\text{mol}}\right) + 1 \text{ mol}\left(-285.8 \frac{\text{kJ}}{\text{mol}}\right) - \left[0 + 1 \text{ mol}\left(-677.1 \frac{\text{kJ}}{\text{mol}}\right)\right]$
	$= -2.2 \text{ kJ}$

continued

b Calculate $\Delta H°$ when 25.00 mL of 0.186 M HCl is added to copper carbonate.

ANALYSIS

Information given:	V_{HCl} (25.00 mL); M_{HCl} (0.186) From part (a): $\Delta H°$ for the reaction (−2.2 kJ)
Asked for:	ΔH when given amounts of HCl are used.

STRATEGY

1. Find moles of H^+ actually used and convert to kJ by using the following plan:

$$(V \times M) \longrightarrow \text{mol HCl} \xrightarrow{1 \text{ mol HCl}/1 \text{ mol } H^+} \text{mol } H^+ \xrightarrow{\Delta H°/2 \text{ mol } H^+} \text{kJ}$$

2. Find $\Delta H°$ for the amount of H^+ used. $\Delta H°$ given is for 2 mol H^+.

SOLUTION

mol H^+	$V \times M = (0.02500 \text{ L})(0.186 \text{ mol/L}) = 0.00465 \text{ mol HCl} = \text{mol } H^+$
$\Delta H°$	$0.00465 \text{ mol } H^+ \times \dfrac{-2.2 \text{ kJ}}{2 \text{ mol } H^+} = -5.1 \times 10^{-3} \text{ kJ}$

END POINT

When you use Table 8.3 to figure out $\Delta H°$ for a reaction, make sure you consider the physical state of the species. Water, for example, has two different $\Delta H_f°$ values given: one for liquid and the other for gas. By the same token, do not forget to write the physical state of each species when you write an equation to represent a reaction.

8-6 Bond Enthalpy

For many reactions, ΔH is a large negative number; the reaction gives off a lot of heat. In other cases, ΔH is positive; heat must be absorbed for the reaction to occur. You may well wonder why the enthalpy change should vary so widely from one reaction to another. Is there some basic property of the molecules involved in the reaction that determines the sign and magnitude of ΔH?

These questions can be answered on a molecular level in terms of a quantity known as bond enthalpy. (More commonly but less properly it is called bond energy.) The **bond enthalpy** is defined as ΔH when one mole of bonds is broken in the gaseous state. From the equations (see also Figure 8.14, page 208).

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = +436 \text{ kJ}$$

$$Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H = +243 \text{ kJ}$$

it follows that the H—H bond enthalpy is +436 kJ/mol and that for Cl—Cl is 243 kJ/mol. In both reactions, one mole of bonds (H—H and Cl—Cl) is broken.

Bond enthalpies for a variety of single and multiple bonds are listed in Table 8.4. Note that bond enthalpy is always a positive quantity; heat is always

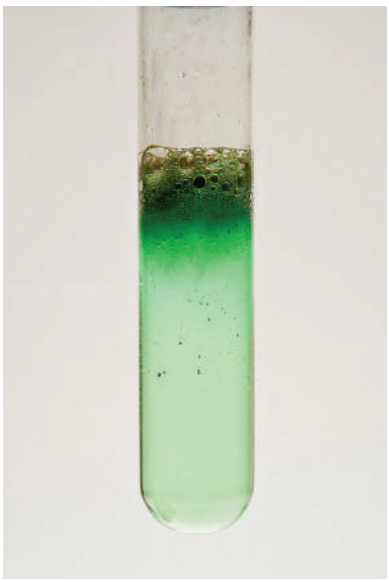

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Figure 8.13 Reaction of an acid with a carbonate. Hydrochloric acid added to copper carbonate solution produces CO_2 gas.

What is $\Delta H_f°$ for H(*g*)? Cl(*g*)? Answer: 218 and 122 kJ/mol, respectively.

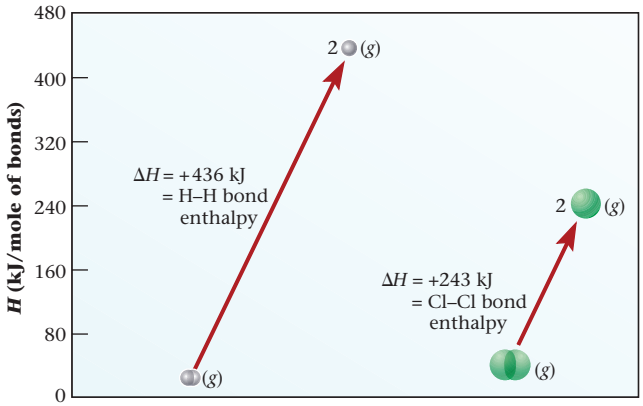

Figure 8.14 Bond enthalpies for H_2 and Cl_2. The H—H bond enthalpy is greater than the Cl—Cl bond enthalpy (+436 kJ/mol versus +243 kJ/mol). This means that the bond in H_2 is stronger than that in Cl_2.

The higher the bond enthalpy, the stronger the bond.

absorbed when chemical bonds are broken. Conversely, heat is given off when bonds are formed from gaseous atoms. Thus

$$H(g) + Cl(g) \longrightarrow HCl(g) \quad \Delta H = -431 \text{ kJ}$$

$$H(g) + F(g) \longrightarrow HF(g) \quad \Delta H = -565 \text{ kJ}$$

Using bond enthalpies, it is possible to explain why certain gas phase reactions are endothermic and others are exothermic. In general, a reaction is expected to be endothermic (i.e., heat must be absorbed) if

Table 8.4 Bond Enthalpies

Single Bond Enthalpy (kJ/mol)									
	H	C	N	O	S	F	Cl	Br	I
H	436	414	389	464	339	565	431	368	297
C		347	293	351	259	485	331	276	218
N			159	222	—	272	201	243	—
O				138	—	184	205	201	201
S					226	285	255	213	—
F						153	255	255	277
Cl							243	218	209
Br								193	180
I									151

Multiple Bond Enthalpy (kJ/mol)					
C=C	612	N=N	418	C≡C	820
C=N	615	N=O	607	C≡N	890
C=O	715	O=O	498	C≡O	1075
C=S	477	S=O	498	N≡N	941

- *the bonds in the reactants are stronger than those in the products.* Consider, for example, the decomposition of hydrogen fluoride to the elements, which can be shown to be endothermic from the data in Table 8.3.

$$2HF(g) \longrightarrow H_2(g) + F_2(g) \qquad \Delta H = -2\Delta H_f^\circ \text{ HF} = +542.2 \text{ kJ}$$

  The bonds in HF (565 kJ/mol) are stronger than the average of those in H_2 and F_2: (436 kJ/mol + 153 kJ/mol)/2 = 295 kJ/mol.

- *there are more bonds in the reactants than in the products.* For the reaction

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = -2\Delta H_f^\circ \, H_2O(g) = +483.6 \text{ kJ}$$

  there are four moles of O—H bonds in two moles of H_2O as compared with only three moles of bonds in the products (two moles of H—H bonds, one mole of O═O bonds).

You will note from Table 8.4 that the bond enthalpy is larger for a multiple bond than for a single bond between the same two atoms. Thus

bond enthalpy C—C = 347 kJ/mol
bond enthalpy C═C = 612 kJ/mol
bond enthalpy C≡C = 820 kJ/mol

But, the double bond enthalpy is less than twice that for a single bond.

This effect is a reasonable one; the greater the number of bonding electrons, the more difficult it should be to break the bond between two atoms.

We should point out a serious limitation of the bond enthalpies listed in Table 8.4. *Whenever the bond involves two different atoms* (e.g., O—H) *the value listed is approximate rather than exact,* because it represents an average taken over two or more different species. Consider, for example, the O—H bond where we find

$$H—O—H(g) \longrightarrow H(g) + OH(g) \qquad \Delta H = +499 \text{ kJ}$$
$$H—O(g) \longrightarrow H(g) + O(g) \qquad \Delta H = +428 \text{ kJ}$$

Both of these reactions involve breaking a mole of O—H bonds, yet the experimental values of ΔH are quite different. The bond enthalpy listed in Table 8.4, 464 kJ/mol, is an average of these two values.

This limitation explains why, whenever possible, we use enthalpies of formation (ΔH_f°) rather than bond enthalpies to calculate the value of ΔH for a reaction. Calculations involving enthalpies of formation are expected to be accurate within ±0.1 kJ; the use of bond enthalpies can result in an error of 10 kJ or more.

8-7 The First Law of Thermodynamics

So far in this chapter our discussion has focused on thermochemistry, the study of the heat effects in chemical reactions. Thermochemistry is a branch of *thermodynamics,* which deals with all kinds of energy effects in all kinds of processes. Thermodynamics distinguishes between two types of energy. One of these is heat (q); the other is **work,** represented by the symbol w. The thermodynamic definition of work is quite different from its colloquial meaning. Quite simply, ***work includes all forms of energy except heat.***

The **law of conservation of energy** states that energy (E) can be neither created nor destroyed; it can only be transferred between system and surroundings. That is,

$$\Delta E_{system} = -\Delta E_{surroundings}$$

Table 8.5 Heat, Work, and Energy

	q	w	$\Delta E = q + w$	Remarks
I	+ heat absorbed by the system	+ work done on the system	+ energy absorbed by the system	
II	+ heat absorbed by the system	− work done by the system	+ or −	depends on the magnitude of q and w
III	− heat given off by the system	− work done by the system	− energy given off by the system	
IV	− heat given off by the system	+ work done on the system	+ or −	depends on the magnitude of q and w

The **first law of thermodynamics** goes a step further. Taking account of the fact that there are two kinds of energy, heat and work, the first law states:

> ***In any process, the total change in energy of a system, ΔE, is equal to the sum of the heat, q, and the work, w, transferred between the system and the surroundings.***

$$\Delta E = q + w \tag{8.5}$$

In applying the first law, note (Table 8.5) that q and w are positive when heat or work enters the system from the surroundings. If the transfer is in the opposite direction, from system to surroundings, q and w are negative.

If work is done on the system or if heat is added to it, its energy increases.

EXAMPLE 8.9

Calculate ΔE of a gas for a process in which the gas

(a) absorbs 20 J of heat and does 12 J of work by expanding.

(b) evolves 30 J of heat and has 52 J of work done on it as it contracts.

ANALYSIS

Information given:	(a) heat absorbed (20 kJ), work done by the system (12 kJ) (b) heat evolved (30 kJ), work done on the system (52 kJ)
Asked for:	ΔE for both (a) and (b)

STRATEGY

1. Decide on the signs for work (w) and heat (q).

   Recall that quantites are positive when they enter the system (absorbed, work done on the system) and negative when they leave the system (evolved, work done by the system).

2. Substitute into Equation 8.5.

   $\Delta E = w + q$

SOLUTION

(a) Signs for w and q	w is negative (work is done by the system) q is positive (heat is absorbed)
ΔE	$\Delta E = q + w = 20\ \text{J} + (-12\ \text{J}) = 8\ \text{J}$
(b) Signs for w and q	w is positive (work is done on the system; enters the system) q is negative (heat is evolved)
ΔE	$\Delta E = q + w = -30\ \text{J} + 52\ \text{J} = 22\ \text{J}$

Ordinarily, when a chemical reaction is carried out in the laboratory, any energy evolved is in the form of heat. Consider, for example, the reaction of oxygen with methane, the principal constituent of natural gas.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta E = -885 \text{ kJ}$$

When you ignite methane in a Bunsen burner, the amount of heat evolved is very close to 885 kJ/mol. There is a small work effect, due to the decrease in volume that occurs when the reaction takes place (Figure 8.15), but this amounts to less than 1% of the energy change.

The situation changes if methane is used as a substitute for gasoline in an internal combustion engine. Here a significant fraction of the energy evolved in combustion is converted to useful work, propelling your car uphill, overcoming friction, charging the battery, or whatever. Depending on the efficiency of the engine, as much as 25% of the available energy might be converted to work; the amount of heat evolved through the tail pipe or radiator drops accordingly.

Finally, the energy available from the above reaction might be used to operate a fuel cell such as those involved in the space program. In that case, as much as 818 kJ/mol of useful electrical work could be obtained; relatively little heat is evolved. Summarizing this discussion in terms of an energy balance (per mole of methane reacting):

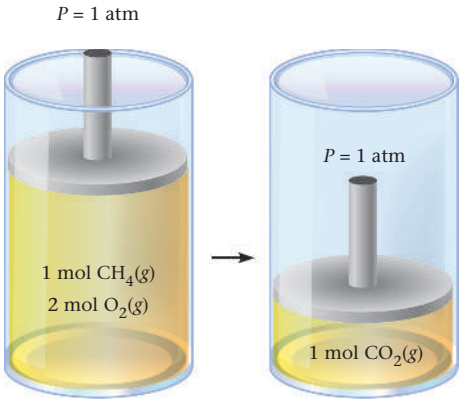

Figure 8.15 Pressure-volume work. When the reaction

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

is carried out in a cylinder fitted with a piston that exerts a pressure of 1 atm, a contraction occurs (3 mol gas → 1 mol gas). The piston falls, and a small amount of work is done on the reaction system.

	ΔE	q	w
Bunsen burner	−885 kJ	−890 kJ	+5 kJ
Automobile engine	−885 kJ	−665 kJ	−220 kJ
Fuel cell	−885 kJ	−67 kJ	−818 kJ

Notice that ΔE, like ΔH, is a *state property;* it has the same value regardless of how or where or why the reaction is carried out. In contrast, q and w are path-dependent; their values vary depending on whether the reaction is carried out in the atmosphere, an engine, or an electrical cell.

ΔH Versus ΔE

As noted earlier, for a reaction at constant pressure, such as that taking place in an open coffee-cup calorimeter, the heat flow is equal to the change in enthalpy. If a reaction is carried out at constant volume (as is the case in a sealed bomb calorimeter) and there is no mechanical or electrical work involved, no work is done. Under these conditions, with $w = 0$, the heat flow is equal to the change in energy, ΔE. Hence we have

$$\Delta H = q_p \qquad \Delta E = q_v$$

(q_p = heat flow at constant pressure, q_v = heat flow at constant volume).

Almost always, when you carry out a reaction in the laboratory, you do so at constant pressure, that of the atmosphere. That is why we devoted 90% of the space in this chapter to ΔH rather than ΔE.

We can obtain a relation between ΔH and ΔE for a chemical reaction at constant temperature by starting with the defining equation relating enthalpy, H, to energy, E:

$$H = E + PV$$

where V is the volume at pressure P. It follows that

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

To evaluate $\Delta(PV)$ for a reaction note that

- the PV product for a liquid or solid can be ignored, since their molar volume is typically only about 0.1% of that for a gas.
- gases taking part in the reaction can be assumed to obey the ideal gas law, $PV = nRT$.

It follows that

$$\Delta(PV) = \Delta n_g RT$$

where Δn_g is the change in the number of moles of gas when the reaction takes place. Finally, we obtain the relation

$$\Delta H = \Delta E + \Delta n_g RT \qquad (8.6)$$

For the reaction at 25°C

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

$$\Delta n_g = n \text{ gaseous products} - n \text{ gaseous reactants}$$
$$= 1 \text{ mol} - 3 \text{ mol} = -2 \text{ mol}$$
$$R = 8.31 \text{ J/mol} \cdot \text{K} \qquad \text{(recall Table 5.1)}$$
$$T = (273 + 25) \text{ K} = 298 \text{ K}$$

Hence:

$$\Delta H = \Delta E - 2 \text{ mol } (8.31 \text{ J/mol} \cdot \text{K})(298 \text{ K})$$
$$= \Delta E - 5.0 \times 10^3 \text{ J} = \Delta E - 5.0 \text{ kJ}$$

Energy can also be expressed in liter-atmospheres: 1 L · atm = 0.1013 kJ.

Recall that ΔE for this reaction is −885 kJ; it follows that ΔH is −890 kJ. The difference between ΔE and ΔH is less than 1%, which is typical for most reactions. Figure 8.15 illustrates the volume change that represents work being done on a system.

EXAMPLE 8.10

Calculate ΔH and ΔE at 25°C for the reaction that takes place when an oxyacetylene torch is used.

$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$$

ANALYSIS

Information given:	chemical equation; T (25°C)
Information implied:	ΔH_f° from Table 8.3 moles of products and reactants R with energy units
Asked for:	ΔH and ΔE

STRATEGY

1. Use Table 8.3 to calculate ΔH for the reaction. Remember ΔH_f° for $O_2(g)$ is zero.
2. Find Δn: $\Delta n = n_{\text{products}} - n_{\text{reactants}}$
3. Recall that R is 8.31 J/mol · K when energy units are involved (Table 5.1).
4. Substitute into Equation 8.6 to find ΔE.

$$\Delta H = \Delta E + \Delta n_g RT$$

continued

SOLUTION

1. ΔH

$$\Delta H = 2\Delta H_f^\circ\ CO_2(g) + \Delta H_f^\circ\ H_2O(g) - \Delta H_f^\circ\ C_2H_2(g)$$
$$= 2\ (-393.5\ \text{kJ}) + (-241.8\ \text{kJ}) - (226.7\ \text{kJ}) = -1255.5\ \text{kJ}$$

2. Δn_g

$$(2\ \text{mol}\ CO_2 + 1\ \text{mol}\ H_2O) - (1\ \text{mol}\ C_2H_2 + \tfrac{5}{2}\ \text{mol}\ O_2) = -\tfrac{1}{2}\ \text{mol}$$

3. ΔE

$$\Delta H = \Delta E + \Delta n_g RT$$
$$-1255.5\ \text{kJ} = \Delta E + (-0.5\ \text{mol})\left(8.31 \times 10^{-3}\ \frac{\text{kJ}}{\text{mol} \cdot \text{K}}\right)(298\ \text{K})$$
$$\Delta E = -1255.5\ \text{kJ} + 1.24\ \text{kJ} = -1254.3\ \text{kJ}$$

END POINT

Note that in this case ΔH and ΔE differ from one another only by 1.2 kJ (about 0.1%), a very small difference indeed.

CHEMISTRY **BEYOND** THE CLASSROOM

Energy Balance in the Human Body

All of us require energy to maintain life processes and do the muscular work associated with such activities as studying, writing, walking, or jogging. The fuel used to produce that energy is the food we eat. In this discussion, we focus on energy input or energy output and the balance between them.

Energy Input

Energy values of food can be estimated on the basis of the content of carbohydrate, protein, and fat:

carbohydrate:	17 kJ (4.0 kcal) of energy per gram*
protein:	17 kJ (4.0 kcal) of energy per gram
fat:	38 kJ (9.0 kcal) of energy per gram

Alcohol, which doesn't fit into any of these categories, furnishes about 29 kJ (7.0 kcal) per gram.

Using these guidelines, it is possible to come up with the data given in Table A, which lists approximate energy values for standard portions of different types of foods. With a little practice, you can use the table to estimate your energy input within ±10%.

Energy Output

Energy output can be divided, more or less arbitrarily, into two categories.

1. Metabolic energy. This is the largest item in most people's energy budget; it comprises the energy necessary to

*In most nutrition texts, energy is expressed in kilocalories rather than kilojoules, although that situation is changing. Remember that 1 kcal = 4.18 kJ; 1 kg = 2.20 lb.

Table A Energy Values of Food Portions*

		kJ	kcal
Skim milk	8-oz glass (250 g)	347	83
Whole milk	8-oz glass (250 g)	610	146
Beer	12-oz glass (375 g)	493	118
Mixed vegetables	1/2 cup (125 g)	247	59
Broccoli	1/2 cup (125 g)	63	15
Yellow corn	1 ear	447	107
Fruit cocktail	1/2 cup (125 g)	230	55
Whole wheat bread	1 slice	272	65
Baked potato	1 item	920	220
Black beans	1/2 cup (125 g)	477	114
Lean ground beef	3 oz (84 g)	966	231
Ground turkey	3 oz (84 g)	836	200
Butter	1 tablespoon (15 g)	451	108
Olive oil	1 tablespoon (15 g)	497	119
Canola oil	1 tablespoon (15 g)	502	120
Sugar	1 teaspoon (5 g)	63	15

*Adapted from Michelle McGuire and Kathy A. Beerman: *Table of Food Composition for Nutritional Sciences: From Fundamentals to Food*, Thomson Wadsworth, Belmont, CA, 2007.

maintain life. Metabolic rates are ordinarily estimated based on a person's sex, weight, and age. For a young adult female, the metabolic rate is about 100 kJ per day per kilogram of body weight. For a 20-year-old woman weighing 120 lb

$$\text{metabolic rate} = 120 \text{ lb} \times \frac{1 \text{ kg}}{2.20 \text{ lb}} \times 100 \frac{\text{kJ}}{\text{d} \cdot \text{kg}}$$

$$= 5500 \text{ kJ/d } (1300 \text{ kcal/day})$$

For a young adult male of the same weight, the figure is about 15% higher.

2. Muscular activity. Energy is consumed whenever your muscles contract, whether in writing, walking, playing tennis, or even sitting in class. Generally speaking, energy expenditure for muscular activity ranges from 50% to 100% of metabolic energy, depending on lifestyle. If the 20-year-old woman referred to earlier is a student who does nothing more strenuous than lift textbooks, the energy spent on muscular activity might be

$$0.50 \times 5500 \text{ kJ} = 2800 \frac{\text{kJ}}{\text{d}}$$

Her total energy output per day would be 5500 kJ + 2800 kJ = 8300 kJ (2000 kcal).

Energy Balance

To maintain constant weight, your daily energy input, as calculated from the foods you eat, should be about 700 kJ (170 kcal) greater than output. The difference allows for the fact that about 40 g of protein is required to maintain body tissues and fluids. If the excess of input over output is greater than 700 kJ/day, the unused food (carbohydrate, protein, or fat) is converted to fatty tissue and stored as such in the body.

Fatty tissue consists of about 85% fat and 15% water; its energy value is

$$0.85 \times 9.0 \frac{\text{kcal}}{\text{g}} \times \frac{454 \text{ g}}{1 \text{ lb}} = 3500 \text{ kcal/lb}$$

This means that to lose one pound of fat, energy input from foods must be decreased by about 3500 kcal. To lose weight at a sensible rate of one pound per week, it is necessary to cut down by 500 kcal (2100 kJ) per day.

It's also possible, of course, to lose weight by increasing muscular activity. Table B shows the amount of energy consumed per hour with various types of exercise. In principle, a person weighing 150 lbs can lose approximately a pound a week by playing a Wii game of tennis for 2.5 hours.

The values listed in Table B reflect both the energy spent in physical activity and the amount used for basal metabolic rate (BMR). To calculate kcalories spent per minute of activity for your own body weight, multiply kcal/lb/hr by your exact weight and then multiply that number by the number of hours spent in the activity.

Table B Energy Spent on Various Activities*

Activity	kcal/lb/hr
Aerobic dance (vigorous)	3.7
Basketball (vigorous, full court)	5.8
Bicycling	
13 mph	2.7
15 mph	2.9
Cross-country skiing	
8 mph	6.2
Running	
5 mph	3.7
6 mph	4.4
Studying	0.66
Swimming	
20 yd/min	1.9
45 yd/min	3.5
50 yd/min	4.2
Walking (brisk pace)	
3.5 mph	2.1
4.5 mph	2.9
Wii games	
Bowling	1.3
Tennis	1.3

*Adapted from Linda Kelly DeBruyne and Kathryn Pinna, *Nutrition for Health and Healthcare, 5th Edition*, Table 6.2, pp. 148–149, Cengage, 2014.

Key Concepts

1. Relate heat flow to specific heat, mass, and Δt. **(Example 8.1; Problems 1–6)**
2. Calculate q for a reaction from calorimetric data. **(Examples 8.2, 8.3; Problems 7–20)**
3. Apply the rules of thermochemistry **(Examples 8.4, 8.5; Problems 21–30)**
4. Apply Hess's law to calculate ΔH. **(Example 8.6; Problems 31–36)**
5. Relate $\Delta H°$ to enthalpies of formation. **(Examples 8.7, 8.8; Problems 37–52)**
6. Relate ΔE, q, and w. **(Example 8.9; Problems 53–58)**
7. Relate ΔH and ΔE. **(Example 8.10; Problems 59–62)**

Key Equations

Heat flow	$q = mass \times c \times \Delta t$
Coffee-cup calorimeter	$q_{reaction} = -mass_{water} \times 4.18\ J/g \cdot °C \times \Delta t$
Bomb calorimeter	$q_{cal} = C_{cal} \times \Delta t$
	$q_{reaction} = -(q_{cal} + qH_2O)$
Standard enthalpy change	$\Delta H° = \Sigma\ \Delta H_f°$ products $- \Sigma\ \Delta H_f°$ reactants
First law of thermodynamics	$\Delta E = q + w$
ΔH versus ΔE	$\Delta H = \Delta E + \Delta n_g RT$

Key Terms

bond enthalpy
calorimeter
—bomb calorimeter
—coffee-cup calorimeter
endothermic
exothermic
enthalpy
—enthalpy of formation
heat
—heat capacity
—heat of fusion
—heat of vaporization
Hess's law
joule
specific heat
state properties
surroundings
system
thermochemical equation
work

Summary Problem

Ethane, C_2H_6, is a by-product of petroleum refining. The thermochemical equation for the combustion of ethane is:

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

$$\Delta H = -1559.7\ kJ$$

(a) Find ΔH for the thermochemical equations

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

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

(b) The heat of vaporization for $H_2O(l)$ is +44.0 kJ/mol. Calculate ΔH for the equation

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

(c) The heats of formation of $CO_2(g)$ and $H_2O(l)$ are −393.5 and −285.8 kJ/mol, respectively. What is $\Delta H_f°$ for $C_2H_6(g)$?

(d) How much heat is evolved when 1.00 g of $C_2H_6(g)$ is burned in an open container to give $CO_2(g)$ and $H_2O(l)$?

(e) When 1.00 g of C_2H_6 is burned in a bomb calorimeter, the temperature rises from 22.00°C to 33.13°C. In a separate experiment, it is found that absorption of 10.0 kJ of heat by the calorimeter raises the temperature of the calorimeter by 2.15°C. Find $C_{calorimeter}$ and $q_{reaction}$.

(f) Find $\Delta E = q_v$ at 25°C for the combustion of one mole of ethane where $\Delta H = q_p = -1559.7$ kJ.

(g) Using bond enthalpies estimate ΔH for the formation of one mole of ethane gas from its elements.

Answers

(a) **−3119.4 kJ; +1559.7 kJ**
(b) **−1427.7 kJ**
(c) **−84.7 kJ**
(d) **51.9 kJ**
(e) **4.65 kJ/°C; −51.8 kJ**
(f) **−1553.5 kJ**
(g) **−1523 kJ**

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

8-1 Principles of Heat Flow

1. Titanium is a metal used in jet engines. Its specific heat is 0.523 J/g · °C. If 5.88 g of titanium absorb 4.78 J, what is the change in temperature?

2. Gold has a specific heat of 0.129 J/g · °C. When a 5.00-g piece of gold absorbs 1.33 J of heat, what is the change in temperature?

3. Copper is used in building the integrated circuits, chips, and printed circuit boards for computers. When 228 J of heat are absorbed by 125 g of copper at 22.38°C, the temperature rises to 27.12°C. What is the specific heat of copper?

4. Mercury was once used in thermometers and barometers. When 46.9 J of heat are absorbed by 100.0 g of mercury at 25.00°C, the temperature increases to 28.35°C. What is the specific heat of mercury?

5. The specific heat of aluminum is 0.902 J/g · °C. How much heat is absorbed by an aluminum pie tin with a mass of 473 g to raise its temperature from room temperature (23.00°C) to oven temperature (375°F)?

6. Chromium has a specific heat of 0.450 J/g · °C. How much heat is absorbed by 35.0 g of chromium if the temperature increases from 45°F to 88°F?

8-2 Measurement of Heat Flow; Calorimetry

7. Magnesium sulfate is often used in first-aid hot packs, giving off heat when dissolved in water. A coffee-cup calorimeter at 25°C contains 15.0 mL of water at 25°C. A 2.00-g sample of $MgSO_4$ is dissolved in the water and 1.51 kJ of heat are evolved. (You can make the following assumptions about the solution: volume = 15.0 mL, density = 1.00 g/mL, specific heat = 4.18 J/g · °C.)

(**a**) Write a balanced equation for the solution process.
(**b**) Is the process exothermic?
(**c**) What is q_{H_2O}?
(**d**) What is the final temperature of the solution?
(**e**) What are the initial and final temperatures in °F?

8. Sodium chloride is added in cooking to enhance the flavor of food. When 10.00 g of NaCl are dissolved in 200.0 mL of water at 25.0°C in a coffee-cup calorimeter, 669 J of heat are absorbed. (You can make the following assumptions about the solution: volume = 200.0 mL, density = 1.00 g/mL, specific heat = 4.18 J/g · °C)

(**a**) Is the solution process exothermic?
(**b**) What is q_{H_2O}?
(**c**) What is the final temperature of the solution?

9. When 375 mL of water (d = 1.00 g/mL) at 32°C are mixed with 125 mL of water at 92°C , what is the final temperature of the mixture? (Assume no heat is lost to the surroundings.)

10. How many mL of water at 10°C (2 significant figures) must be added to 75 mL of water at 35°C to obtain a final temperature of 19°C? (Make the same assumptions as in Question 9.)

11. When one mol of KOH is neutralized by sulfuric acid, $q = -56$ kJ. (This is called the heat of neutralization.) At 23.7°C, 25.0 mL of 0.475 M H_2SO_4 is neutralized by 0.613 M KOH in a coffee-cup calorimeter. Assume that the specific heat of all solutions is 4.18 J/g · °C, that the density of all solutions is 1.00 g/mL, and that volumes are additive.

(**a**) How many mL of KOH is required to neutralize H_2SO_4?
(**b**) What is the final temperature of the solution?

12. The heat of neutralization, ΔH_{neut}, can be defined as the amount of heat released (or absorbed), q, per mole of acid (or base) neutralized. ΔH_{neut} for nitric acid is −52 kJ/mol HNO_3. At 27.3°C, 50.00 mL of 0.743M HNO_3 is neutralized by 1.00 M $Sr(OH)_2$ in a coffee-cup calorimeter.

(**a**) How many mL of $Sr(OH)_2$ were used in the neutralization?
(**b**) What is the final temperature of the resulting solution? (Use the assumptions in Question 11.)

13. Fructose is a sugar commonly found in fruit. A sample of fructose, $C_6H_{12}O_6$, weighing 4.50 g is burned in a bomb calorimeter that contains 1.00 L of water (d = 1.00 g/mL). The heat capacity of the calorimeter is 16.97 kJ/°C. The temperature of the calorimeter and water rise from 23.49°C to 27.72°C.

(**a**) What is q for the calorimeter?
(**b**) What is q for water in the calorimeter?
(**c**) What is q when 4.50 g of fructose are burned in the calorimeter?
(**d**) What is q for the combustion of one mole of fructose?

14. In earlier times, ethyl ether was commonly used as an anesthetic. It is, however, highly flammable. When five milliliters of ethyl ether, $C_4H_{10}O(l)$ (d = 0.714 g/mL), are burned in a bomb calorimeter, the temperature rises from 23.5°C to 39.7°C. The calorimeter contains 1.200 kg of water and has a heat capacity of 5.32 kJ/°C.

(**a**) What is q_{H_2O}?
(**b**) What is q_{cal}?
(**c**) What is q for the combustion of 5.00 mL of ethyl ether?
(**d**) What is q for the combustion of one mole of ethyl ether?

15. Isooctane is a primary component of gasoline and gives gasoline its octane rating. Burning 1.00 mL of isooctane (d = 0.688 g/mL) releases 33.0 kJ of heat. When 10.00 mL of isooctane are burned in a bomb calorimeter, the temperature in the bomb and water rises from 23.2°C to 66.5°C. The bomb contains 1.00 kg of water. What is the heat capacity of the calorimeter?

16. Ethyl alcohol, C_2H_5OH, is the intoxicating agent in liquor. Burning 1.00 g of ethyl alcohol in an excess of oxygen at 23.28°C and constant volume releases 29.52 kJ of heat. When 7.40 g of ethyl alcohol is burned in oxygen under the same conditions in a bomb calorimeter, the temperature of the bomb and water rises from 23.28°C to 48.04°C. The bomb holds 0.750 kg of water.

(**a**) What is q for the combustion of the ethyl alcohol in the bomb calorimeter?
(**b**) What is q_{H_2O}?
(**c**) What is q_{cal}?
(**d**) What is the heat capacity of the calorimeter?

17. Acetic acid, $HC_2H_3O_2$, is responsible for the sour taste of vinegar. Combustion of acetic acid gives off 14.52 kJ/g of heat. When 15.00 g of acetic acid is burned in a bomb calorimeter (heat capacity = 2.166 kJ/°C) containing 0.800 kg of water, the final temperature in the calorimeter is 64.14°C. What was the initial temperature of the calorimeter?

18. Acetylene, C_2H_2, is used in welding torches. It releases a lot of energy when burned in oxygen. The combustion of one gram of acetylene releases 48.2 kJ. A 0.750-g sample of acetylene is burned in a bomb calorimeter (heat capacity = 1.117 kJ/°C) that contains 800.0 g of water. The final temperature of the bomb and water after combustion is 35.2°C. What is the initial temperature of the bomb and water?

19. Salicylic acid, $C_7H_6O_3$, is one of the starting materials in the manufacture of aspirin. When 1.00 g of salicylic acid burns in a bomb calorimeter, the temperature of the bomb and water goes from 23.11°C to 28.91°C. The calorimeter and water absorb 21.9 kJ of heat. How much heat is given off when one mole of salicylic acid burns?

20. Methanol (CH_3OH) is also known as wood alcohol and can be used as a fuel. When one mole of methanol is burned, 1453 kJ of heat are evolved. When methanol is burned in a bomb calorimeter, 71.8 kJ of heat are evolved by the methanol. How many mL of methanol (d = 0.791 g/mL) were burned?

8-4 Thermochemical Equations

21. Nitrogen oxide (NO) has been found to be a key component in many biological processes. It also can react with oxygen to give the brown gas NO_2. When one mole of NO reacts with oxygen, 57.0 kJ of heat are evolved.

(**a**) Write the thermochemical equation for the reaction between one mole of nitrogen oxide and oxygen.

(**b**) Is the reaction exothermic or endothermic?

(**c**) Draw an energy diagram showing the path of this reaction. (Figure 8.6 is an example of such an energy diagram.)

(**d**) What is ΔH when 5.00 g of nitrogen oxide react?

(**e**) How many grams of nitrogen oxide must react with an excess of oxygen to liberate ten kilojoules of heat?

22. Small amounts of oxygen gas can be prepared in the laboratory by decomposing potassium chlorate with heat. A by-product of the decomposition is potassium chloride. When one mole of potassium chlorate decomposes, 44.7 kJ are evolved.

(**a**) Write a balanced thermochemical equation for the decomposition of one mole of potassium chlorate.

(**b**) Is the reaction exothermic?

(**c**) Draw an energy diagram showing the path of this reaction. (Figure 8.6 is an example of such an energy diagram.)

(**d**) What is ΔH when 3.00 g of potassium chlorate decompose?

(**e**) How many grams of potassium chlorate need to be decomposed to liberate fifteen kilojoules of heat?

23. In the late eighteenth century Priestley prepared ammonia by reacting $HNO_3(g)$ with hydrogen gas. The thermodynamic equation for the reaction is

$$HNO_3(g) + 4H_2(g) \longrightarrow NH_3(g) + 3H_2O(g) \quad \Delta H = -637 \text{ kJ}$$

(**a**) Calculate ΔH when one mole of hydrogen gas reacts.

(**b**) What is ΔH when 10.00 g of $NH_3(g)$ are made to react with an excess of steam to form HNO_3 and H_2 gases?

24. Barium chloride is sometimes used in fireworks to give a bright green color. It gives off heat when dissolved in water.

$$BaCl_2(s) \longrightarrow Ba^{2+}(aq) + 2Cl^-(aq)$$

(**a**) What is ΔH when one mol of $BaCl_2$ precipitates from solution?

(**b**) What is ΔH when 15.00 g of $BaCl_2$ precipitate?

25. Strontium metal is responsible for the red color in fireworks. Fireworks manufacturers use strontium carbonate, which can be produced by combining strontium metal, graphite (C), and oxygen gas. The formation of one mole of $SrCO_3$ releases 1.220×10^3 kJ of energy.

(**a**) Write a balanced thermochemical equation for the reaction.

(**b**) What is ΔH when 10.00 L of oxygen at 25°C and 1.00 atm are used by the reaction?

26. Nitroglycerin, $C_3H_5(NO_3)_3(l)$, is an explosive most often used in mine or quarry blasting. It is a powerful explosive because four gases (N_2, O_2, CO_2, and steam) are formed when nitroglycerin is detonated. In addition, 6.26 kJ of heat are given off per gram of nitroglycerin detonated.

(**a**) Write a balanced thermochemical equation for the reaction.

(**b**) What is ΔH when 4.65 mol of products are formed?

27. A typical fat in the body is glyceryl trioleate, $C_{57}H_{104}O_6$. When it is metabolized in the body, it combines with oxygen to produce carbon dioxide, water, and 3.022×10^4 kJ of heat per mole of fat.

(**a**) Write a balanced thermochemical equation for the metabolism of fat.

(**b**) How many kilojoules of energy must be evolved in the form of heat if you want to get rid of five pounds of this fat by combustion?

(**c**) How many nutritional calories is this? (1 nutritional calorie = 1×10^3 calories)

28. Use the same fat described in Question 27.

(**a**) Write a thermochemical equation for the metabolism of fat.

(**b**) A dieter reduces his food intake by 425 nutritional calories a day (1 nutritional calorie = 1000 calories). How many kJ can he lose in one day?

(**c**) How many pounds of fat are "lost" in one week with this diet?

29. Which requires the absorption of a greater amount of heat—vaporizing 100.0 g of benzene or boiling 20.0 g of water? (Use Table 8.2.)

30. Which evolves more heat—freezing 100.0 g of benzene or 100.0 g of bromine?

31. A student is asked to calculate the amount of heat involved in changing 10.0 g of liquid bromine at room temperature (22.5°C) to vapor at 59.0°C. To do this, one must use Tables 8.1 and 8.2 for information on the specific heat, boiling point, and heat of vaporization of bromine. In addition, the following step-wise process must be followed.

(**a**) Calculate ΔH for: $Br_2(l, 22.5°C) \longrightarrow Br_2(l, 59.0°C)$

(**b**) Calculate ΔH for: $Br_2(l, 59.0°C) \longrightarrow Br_2(g, 59.0°C)$

(**c**) Using Hess's law, calculate ΔH for: $Br_2(l, 22.5°C) \longrightarrow Br_2(g, 59.0°C)$

32. Follow the step-wise process outlined in Problem 31 to calculate the amount of heat involved in condensing 100.00 g of benzene gas (C_6H_6) at 80.00°C to liquid benzene at 25.00°C. Use Tables 8.1 and 8.2 for the specific heat, boiling point, and heat of vaporization of benzene.

33. A lead ore, galena, consisting mainly of lead(II) sulfide, is the principal source of lead. To obtain the lead, the ore is first heated in the air to form lead oxide.

$$PbS(s) + \tfrac{3}{2}O_2(g) \longrightarrow PbO(s) + SO_2(g) \quad \Delta H = -415.4 \text{ kJ}$$

The oxide is then reduced to metal with carbon.

$$PbO(s) + C(s) \longrightarrow Pb(s) + CO(g) \quad \Delta H = +108.5 \text{ kJ}$$

Calculate ΔH for the reaction of one mole of lead(II) sulfide with oxygen and carbon, forming lead, sulfur dioxide, and carbon monoxide.

34. A reaction used to produce the silicon for semiconductors from sand (SiO_2), can be broken up into three steps:

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g) \quad \Delta H = 689.9 \text{ kJ}$$
$$Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(g) \quad \Delta H = -657.0 \text{ kJ}$$
$$SiCl_4(g) + 2Mg(s) \longrightarrow 2MgCl_2(s) + Si(s) \quad \Delta H = -625.6 \text{ kJ}$$

(a) Write a thermochemical equation for the overall reaction where silicon is obtained from silicon dioxide and CO and $MgCl_2$ are by-products.
(b) What is ΔH for the formation of one mole of silicon?
(c) Is the overall reaction exothermic?

35. Given the following thermochemical equations,

$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l) \quad \Delta H = -1299.5 \text{ kJ}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -285.8 \text{ kJ}$$

calculate ΔH for the decomposition of one mole of acetylene, $C_2H_2(g)$, to its elements in their stable state at 25°C and 1 atm.

36. Given the following thermochemical equations:

$$4B(s) + 3O_2(g) \longrightarrow 2B_2O_3(s) \quad \Delta H° = -2543.8 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta H° = -241.8 \text{ kJ}$$
$$B_2H_6(s) + 3O_2 \longrightarrow B_2O_3(s) + 3H_2O(g) \quad \Delta H° = -2032.9 \text{ kJ}$$

Calculate $\Delta H°$ for the decomposition of B_2H_6 into its elements.

8-5 Enthalpies of Formation

37. Write thermochemical equations for the decomposition of one mole of the following compounds into the elements in their stable states at 25°C and 1 atm.
(a) ethyl alcohol, C_2H_5OH (l)
(b) sodium fluoride (s)
(c) magnesium sulfate (s)
(d) ammonium nitrate (s)

38. Write thermochemical equations for the formation of one mole of the following compounds from the elements in their native states at 25°C and 1 atm.
(a) solid potassium chlorate
(b) liquid carbon tetrachloride
(c) gaseous hydrogen iodide
(d) solid silver(I) oxide

39. Given

$$2Al_2O_3(s) \longrightarrow 4Al(s) + 3O_2(g) \quad \Delta H° = 3351.4 \text{ kJ}$$

(a) What is the heat of formation of aluminum oxide?
(b) What is $\Delta H°$ for the formation of 12.50 g of aluminum oxide?

40. Given

$$2Cr_2O_3(s) \longrightarrow 4Cr(s) + 3O_2(g) \quad \Delta H° = +2269.4 \text{ kJ}$$

(a) What is the heat of formation of chromium(III) oxide?
(b) What is $\Delta H°$ for the formation of 13.65 g of chromium (III) oxide?

41. Limestone, $CaCO_3$, when subjected to a temperature of 900°C in a kiln, decomposes to calcium oxide and carbon dioxide. How much heat is evolved or absorbed when one gram of limestone decomposes? (Use Table 8.3.)

42. When hydrazine reacts with oxygen, nitrogen gas and steam are formed.
(a) Write a thermochemical equation for the reaction.
(b) How much heat is evolved or absorbed if 1.683 L of steam at 125°C and 772 mm Hg are obtained?

43. Use Table 8.3 to obtain $\Delta H°$ for the following thermochemical equations:
(a) $Mg(OH)_2(s) + 2NH_4^+(aq) \longrightarrow Mg^{2+}(aq) + 2NH_3(g) + 2H_2O(l)$
(b) $PbO(s) + C(s) \longrightarrow CO(g) + Pb(s)$
(c) $Mn(s) + 4H^+(aq) + SO_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + SO_2(g) + 2H_2O(l)$

44. Use Table 8.3 to obtain $\Delta H°$ for the following thermochemical equations:
(a) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$
(b) $2H_2S(g) + 3O_2(g) \longrightarrow 2SO_2(g) + 2H_2O(g)$
(c) $3Ni(s) + 2NO_3^-(aq) + 8H^+(aq) \longrightarrow 3Ni^{2+}(aq) + 2NO(g) + 4H_2O(l)$

45. Use the appropriate tables to calculate $\Delta H°$ for
(a) the reaction between copper(II) oxide and carbon monoxide to give copper metal and carbon dioxide.
(b) the decomposition of one mole of methyl alcohol (CH_3OH) to methane and oxygen gases.

46. Use the appropriate tables to calculate $\Delta H°$ for
(a) the reaction between $MgCO_3(s)$ and a strong acid to give $Mg^{2+}(aq)$, $CO_2(g)$, and water.
(b) the precipitation of iron(III) hydroxide from the reaction between iron(III) and hydroxide ions.

47. When one mole of nitroglycerine, $C_3H_5(NO_3)_3(l)$ decomposes, nitrogen, oxygen, carbon dioxide, and liquid water are formed. The decomposition liberates 5725 kJ of heat.
(a) Write a balanced thermochemical equation for the reaction.
(b) Using Table 8.3, calculate $\Delta H_f°$ for nitroglycerine.

48. When one mole of calcium carbonate reacts with ammonia, solid calcium cyanamide, $CaCN_2$, and liquid water are formed. The reaction absorbs 90.1 kJ of heat.
(a) Write a balanced thermochemical equation for the reaction.
(b) Using Table 8.3, calculate $\Delta H_f°$ for calcium cyanamide.

49. Chlorine trifluoride is a toxic, intensely reactive gas. It was used in World War II to make incendiary bombs. It reacts with ammonia and forms nitrogen, chlorine, and

hydrogen fluoride gases. When two moles of chlorine trifluoride react, 1196 kJ of heat are evolved.

(a) Write a thermochemical equation for the reaction.

(b) What is ΔH_f° for ClF_3?

50. When one mole of ethylene gas, C_2H_4, reacts with fluorine gas, hydrogen fluoride and carbon tetrafluoride gases are formed and 2496.7 kJ of heat are given off. What is ΔH_f° for $CF_4(g)$?

51. Glucose, $C_6H_{12}O_6(s)$, ($\Delta H_f^\circ = -1275.2$ kJ/mol) is converted to ethyl alcohol, $C_2H_5OH(l)$, and carbon dioxide in the fermentation of grape juice. What quantity of heat is liberated when 750.0 mL of wine containing 12.0% ethyl alcohol by volume ($d = 0.789$ g/cm^3) are produced by the fermentation of grape juice?

52. When ammonia reacts with dinitrogen oxide gas ($\Delta H_f^\circ =$ 82.05 kJ/mol), liquid water and nitrogen gas are formed. How much heat is liberated or absorbed by the reaction that produces 345 mL of nitrogen gas at 25°C and 717 mm Hg?

8-7 First Law of Thermodynamics

53. How many kJ are equal to 3.27 L · atm of work?

54. How many L · atm are equal to 12.2 kJ of work?

55. Find

(a) ΔE when a gas absorbs 18 J of heat and has 13 J of work done on it.

(b) q when 72 J of work are done on a system and its energy is increased by 61 J.

56. Calculate

(a) q when a system does 54 J of work and its energy decreases by 72 J.

(b) ΔE for a gas that releases 38 J of heat and has 102 J of work done on it.

57. Consider the following reaction in a vessel with a movable piston.

$$R(g) + T(g) \longrightarrow X(g)$$

As the reaction takes place, the piston loses 1072 J of heat. The piston moves down and the surroundings do 549 J of work on the system. What is ΔE?

58. Consider the following reaction in the vessel described in Question 57.

$$A(g) + B(g) \longrightarrow C(s)$$

For this reaction, $\Delta E = 286$ J, the piston moves up and the system absorbs 388 J of heat from its surroundings.

(a) Is work done by the system?

(b) How much work?

59. Determine the difference between ΔH and ΔE at 25°C for

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

60. For the vaporization of one mole of bromine at 59°C, determine

(a) ΔH (Table 8.2)

(b) ΔPV

(c) ΔE

61. Consider the combustion of propane, C_3H_8, the fuel that is commonly used in portable gas barbeque grills. The products of combustion are carbon dioxide and liquid water.

(a) Write a thermochemical equation for the combustion of one mole of propane.

(b) Calculate ΔE for the combustion of propane at 25°C.

62. Consider the combustion of one mole of methyl alcohol, $CH_3OH(l)$, which yields carbon dioxide gas and steam.

(a) Write a thermochemical equation for the reaction. (Use Table 8.2.)

(b) Calculate ΔE at 25°C.

Unclassified

63. Butane gas, C_4H_{10}, is sold to campers as bottled fuel. Its density at 25°C and 1.00 atm is 2.38 g/L. What volume of butane gas at 25°C and 1.00 atm is required to heat one gallon of water ($d = 1.00$ g/mL) from 25°C to 98°C ? The reaction for the combustion of butane ($\Delta H_f^\circ = -125.6$ kJ/mol) is

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g)$$

64. The BTU (British thermal unit) is the unit of energy most commonly used in the United States. One joule = 9.48×10^{-4} BTU. What is the specific heat of water in BTU/lb · °F? (Specific heat of water is 4.18 J/g · °C.)

65. Natural gas companies in the United States use the "therm" as a unit of energy. One therm is 1×10^5 BTU.

(a) How many joules are in one therm? (1 J = 9.48×10^{-4} BTU)

(b) When propane gas, C_3H_8, is burned in oxygen, CO_2 and steam are produced. How many therms of energy are given off by 1.00 mol of propane gas?

66. A 12-oz can of most colas has about 120 nutritional calories (1 nutritional calorie = 1 kcal). Approximately how many minutes of walking are required to burn up as energy the calories taken in after drinking a can of cola? (Walking uses up about 250 kcal/h.)

67. Given the following reactions,

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(g) \quad \Delta H^\circ = -534.2 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta H^\circ = -241.8 \text{ kJ}$$

Calculate the heat of formation of hydrazine.

68. In World War II, the Germans made use of otherwise unusable airplane parts by grinding them up into powdered aluminum. This was made to react with ammonium nitrate to produce powerful bombs. The products of this reaction were nitrogen gas, steam, and aluminum oxide. If 10.00 kg of ammonium nitrate are mixed with 10.00 kg of powdered aluminum, how much heat is generated?

69. One way to lose weight is to exercise. Playing tennis for half an hour consumes about 225 kcal of energy. How long would you have to play tennis to lose one pound of body fat? (One gram of body fat is equivalent to 32 kJ of energy.)

70. Consider the reaction between methane and oxygen producing carbon dioxide and water. Suppose that the reaction is carried out in a furnace used to heat a house. If $q = -890$ kJ and $w = +5$ kJ, what is ΔE? ΔH at 25°C?

71. Consider burning ethane gas, C_2H_6 in oxygen (combustion) forming CO_2 and water.

(a) How much energy (in J) is produced in the combustion of one molecule of ethane?

(b) What is the energy of a photon of ultraviolet light with a wavelength of 12.6 nm?

(c) Compare your answers for (a) and (b).

72. On complete combustion at constant pressure, a 1.00-L sample of a gaseous mixture at 0°C and 1.00 atm (STP)

evolves 75.65 kJ of heat. If the gas is a mixture of ethane (C_2H_6) and propane (C_3H_8), what is the mole fraction of ethane in the mixture?

73. Microwave ovens convert radiation to energy. A microwave oven uses radiation with a wavelength of 12.5 cm. Assuming that all the energy from the radiation is converted to heat without loss, how many moles of photons are required to raise the temperature of a cup of water (350.0 g, specific heat = 4.18 J/g · °C) from 23.0°C to 99.0°C?

74. In 2010, 3.30×10^9 gallons of gasoline were consumed in the United States. The following assumptions can be made:

- Gasoline is mainly n-octane, C_8H_{18} (d = 0.7028 g/mL).
- Burning one mole of n-octane in oxygen releases 5564.2 kJ of heat.
- The heat capacity C of the surface region of the earth is 2.6×10^{23} J/K.

What is the increase in temperature of the surface region of the earth due to gasoline consumption in the United States?

75. Some solar-heated homes use large beds of rocks to store heat.

(a) How much heat is absorbed by 100.0 kg of rocks if their temperature increases by 12°C? (Assume that c = 0.82 J/g · °C.)

(b) Assume that the rock pile has total surface area 2 m^2. At maximum intensity near the earth's surface, solar power is about 170 watts/m^2. (1 watt = 1 J/s.) How many minutes will it take for solar power to produce the 12°C increase in part (a)?

Conceptual Questions

76. Consider a solution prepared by dissolving 10.00 g of NaOH in 1.00 L of water.

(a) When the solid dissolves, will the temperature of the solution increase?

(b) What is the sign of H for the process?

(c) Will dissolving 5.00 g of NaOH increase Δt?

(d) Will dissolving one mole of NaOH in 1.00 L of water increase t_f ?

77. Draw a cylinder with a movable piston containing six molecules of a liquid. A pressure of 1 atm is exerted on the piston. Next draw the same cylinder after the liquid has been vaporized. A pressure of one atmosphere is still exerted on the piston. Is work done *on* the system or *by* the system?

78. Redraw the cylinder in Question 77 after work has been done on the system.

79. Which statement(s) is/are true about bond enthalpy?

(a) The bond energy for a triple bond between A and B is three times that of a single bond between A and B.

(b) ΔH for the breaking of a bond is always a negative number.

(c) Energy is required to make a bond.

(d) Bond enthalpy is defined only for bonds broken or formed in the gaseous state.

(e) The presence of π bonds does not influence the geometry of a molecule. However, the presence of π bonds affects the value of the bond enthalpy between two atoms.

80. Equal masses of liquid A, initially at 100°C, and liquid B, initially at 50°C, are combined in an insulated container. The final temperature of the mixture is 80°C. All the heat flow occurs between the two liquids. The two liquids do not react with each other. Is the specific heat of liquid A larger than, equal to, or smaller than the specific heat of liquid B?

81. Determine whether the statements given below are true or false. Consider an endothermic process taking place in a beaker at room temperature.

(a) Heat flows from the surroundings to the system.

(b) The beaker is cold to the touch.

(c) The pressure of the system decreases.

(d) The value of q for the system is positive.

82. An exothermic reaction is carried out in a coffee-cup calorimeter. Which of the following statements is/are NOT true for the process?

(a) The temperature of the water increases.

(b) Heat is absorbed by the water.

(c) The enthalpy of the products is higher than the enthalpy of the reactants.

(d) $q_{H_2O} = q_{rxn}$

(e) $q_{rxn} > 0$

(f) $q_{rxn} + q_{H_2O} = 0$

83. Determine whether the statements given below are true or false. Consider enthalpy (H).

(a) It is a state property.

(b) $q_{reaction}$ (at constant P) = $\Delta H = H_{products} - H_{reactants}$

(c) The magnitude of ΔH is independent of the amount of reactant.

(d) In an exothermic process, the enthalpy of the system remains unchanged.

Challenge Problems

84. Microwave ovens emit microwave radiation that is absorbed by water. The absorbed radiation is converted to heat that is transferred to other components of the food. Suppose the microwave radiation has wavelength 12.5 cm. How many photons are required to increase the temperature of 1.00×10^2 mL of water (d = 1.0 g/mL) from 20°C to 100°C if all the energy of the photons is converted to heat?

85. On a hot day, you take a six-pack of soda on a picnic, cooling it with ice. Each empty (aluminum) can weighs 12.5 g. A can contains 12.0 oz of soda. The specific heat of aluminum is 0.902 J/g · °C; take that of soda to be 4.10 J/g · °C.

(a) How much heat must be absorbed from the six-pack to lower the temperature from 25.0° to 5.0°C?

(b) How much ice must be melted to absorb this amount of heat? (ΔH_{fus} of ice is given in Table 8.2.)

86. A cafeteria sets out glasses of tea at room temperature. The customer adds ice. Assuming that the customer wants to have some ice left when the tea cools to 0°C, what fraction of the total volume of the glass should be left empty for adding ice? Make any reasonable assumptions needed to work this problem.

87. The thermite reaction was once used to weld rails:

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

(a) Using heat of formation data, calculate ΔH for this reaction.

(**b**) Take the specific heats of Al_2O_3 and Fe to be 0.77 and 0.45 J/g · °C, respectively. Calculate the temperature to which the products of this reaction will be raised, starting at room temperature, by the heat given off in the reaction.

(**c**) Will the reaction produce molten iron (mp Fe = 1535°C, ΔH_{fus} = 270 J/g)?

88. A sample of sucrose, $C_{12}H_{22}O_{11}$, is contaminated by sodium chloride. When the contaminated sample is burned in a bomb calorimeter, sodium chloride does not burn. What is the percentage of sucrose in the sample if a temperature increase of 1.67°C is observed when 3.000 g of the sample are burned in the calorimeter? Sucrose gives off 5.64×10^3 kJ/mol when burned. The heat capacity of the calorimeter and water is 22.51 kJ/°C.

89. A wad of steel wool (specific heat = 0.45 J/g · °C) at 25°C is misplaced in a microwave oven, which later is accidentally turned on high. The oven generates microwaves of 13.5 cm wavelength at the rate of 925 moles of those photons per second. All of the photons are converted to high-heat energy, raising the temperature of the steel wool. Steel wool reacts explosively with the oxygen in the oven when the steel wool reaches 400.0°C. If the steel wool explodes after 1.55 seconds, how many grams of steel wool were accidentally put into the oven?

90. Consider a metal ion A^{2+} and its nitrate salt, $A(NO_3)_2$. In an experiment, 35.00 mL of a 0.217 *M* solution of $A(NO_3)_2$ is made to react with 25.00 mL of 0.195 *M* NaOH. A precipitate, $A(OH)_2$, forms. Along with the precipitation, the temperature increases from 24.8°C to 28.2°C. What is ΔH for the precipitation of $A(OH)_2$? The following assumptions can be made.

- The density of the solution is 1.00 g/mL.
- Volumes are additive.
- The specific heat of the solution is 4.18 J/g · °C.