15

Chemical Thermodynamics

OUTLINE

The launch of the space shuttle requires about 2×10^{10} kilojoules of energy. About one sixth of this comes from the combustion of hydrogen, H_2, in oxygen, O_2. The rest comes from the explosive decomposition of ammonium perchlorate, NH_4ClO_4, in solid-fuel rockets.

OBJECTIVES

After you have finished studying this chapter, you should be able to

- *Understand the terminology of thermodynamics, and the meaning of the signs of changes*
- *Use the concept of state functions*
- *Carry out calculations of calorimetry to determine changes in energy and enthalpy*
- *Use Hess's Law to find the enthalpy change, ΔH, for a reaction by combining thermochemical equations with known ΔH values*
- *Use Hess's Law to find the enthalpy change, ΔH, for a reaction by using tabulated values of standard molar enthalpies of formation*
- *Use Hess's Law to find the enthalpy of formation given ΔH for a reaction and the known enthalpies of formation of the other substances in the reaction*
- *Use the First Law of Thermodynamics to relate heat, work, and energy changes*
- *Relate the work done on or by a system to changes in its volume*
- *Use bond energies to estimate heats of reaction for gas phase reactions; use ΔH values for gas phase reactions to find bond energies*
- *Understand what is meant by a product-favored process; by a reactant-favored process*
- *Understand the relationship of entropy to the order or disorder of a system*
- *Understand how the spontaneity of a process is related to entropy changes—the Second Law of Thermodynamics*
- *Use tabulated values of absolute entropies to calculate the entropy change, ΔS*
- *Calculate changes in Gibbs free energy, ΔG, (a) from values of ΔH and ΔS and (b) from tabulated values of standard molar free energies of formation; know when to use each type of calculation*
- *Use ΔG to predict whether a process is product-favored at constant T and P*
- *Understand how changes in temperature can affect the spontaneity of a process*
- *Predict the temperature range of spontaneity of a chemical or physical process*

Energy is very important in every aspect of our daily lives. The food we eat supplies the energy to sustain life with all of its activities and concerns. The availability of relatively inexpensive energy is an important factor in our technological society. This is seen in the costs of fuel, heating and cooling our homes and workplaces, and the electricity to power our lights, appliances, and computers. It is also seen in the costs of the goods and services we purchase, because a substantial part of the cost of production is for energy in one form or another. We must understand the storage and use of energy on a scientific basis to learn how to decrease our dependence on consumable oil and natural gas as our main energy sources. Such understanding has profound ramifications, ranging from our daily lifestyles to international relations.

The concept of energy is at the very heart of science. All physical and chemical processes are accompanied by the transfer of energy. Because energy cannot be created or destroyed, we must understand how to do the "accounting" of energy transfers from one body or one substance to another or from one form of energy to another.

In **thermodynamics** we study the energy changes that accompany physical and chemical processes. Usually these energy changes involve *heat*—hence the "thermo-" part of the term. In this chapter we study the two main aspects of thermodynamics. The first is **thermochemistry.** This practical subject is concerned with how we *observe*, *measure*, and *predict* energy changes for both physical changes and chemical reactions. The second part of the chapter addresses a more fundamental aspect of thermodynamics. There we will learn to use energy changes to tell whether or not a given process can occur under specified conditions to give predominantly products (or reactants) and how to make a process more (or less) favorable.

Some forms of energy are potential, kinetic, electrical, nuclear, heat, and light.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 6.4, Energy, and Screen 6.5, Forms of Energy.

As matter falls from a higher to a lower level, its gravitational potential energy is converted into kinetic energy. A hydroelectric power plant converts the kinetic energy of falling water into electrical (potential) energy.

HEAT CHANGES AND THERMOCHEMISTRY

15-1 THE FIRST LAW OF THERMODYNAMICS

We can define energy as follows.

> Energy is the capacity to do work or to transfer heat.

We classify energy into two general types: kinetic and potential. **Kinetic energy** is the energy of motion. The kinetic energy of an object is equal to one half its mass, m, times the square of its velocity, v.
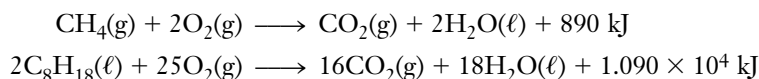
$$E_{\text{kinetic}} = \tfrac{1}{2}mv^2$$

The heavier a hammer is and the more rapidly it moves, the greater its kinetic energy and the more work it can accomplish.

Potential energy is the energy that a system possesses by virtue of its position or composition. The work that we do to lift an object is stored in the object as energy; we describe this as potential energy. If we drop a hammer, its potential energy is converted into kinetic energy as it falls, and it could do work on something it hits—for example, drive a nail or break a piece of glass. Similarly, an electron in an atom has potential energy because of the electrostatic force on it that is due to the positively charged nucleus and the other electrons in that atom and surrounding atoms. Energy can take many other forms: electrical energy, radiant energy (light), nuclear energy, and chemical energy. At

the atomic or molecular level, we can think of each of these as either kinetic or potential energy.

The chemical energy in a fuel or food comes from potential energy stored in atoms due to their arrangements in the molecules. This stored chemical energy can be released when compounds undergo chemical changes, such as those that occur in combustion and metabolism. Reactions that release energy in the form of heat are called **exothermic** reactions.

Combustion reactions of fossil fuels are familiar examples of exothermic reactions. Hydrocarbons—including methane, the main component of natural gas, and octane, a minor component of gasoline—undergo combustion with an excess of O_2 to yield CO_2 and H_2O. These reactions release heat energy. The amounts of heat energy released at constant pressure are shown for the reactions of one mole of methane and of two moles of octane.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell) + 890 \text{ kJ}$$
$$2C_8H_{18}(\ell) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(\ell) + 1.090 \times 10^4 \text{ kJ}$$

In such reactions, the total energy of the products is lower than that of the reactants by the amount of energy released, most of which is heat. Some initial activation (e.g., by heat) is needed to get these reactions started. This is shown for CH_4 in Figure 15-1. This activation energy *plus* 890 kJ is released as one mole of $CO_2(g)$ and two moles of $H_2O(\ell)$ are formed. A process that absorbs energy from its surroundings is called **endothermic.** One such process is shown in Figure 15-2.

Energy changes accompany physical changes, too (Chapter 13). For example, the melting of one mole of ice at 0°C at constant pressure must be accompanied by the absorption of 6.02 kJ of energy.

$$H_2O(s) + 6.02 \text{ kJ} \longrightarrow H_2O(\ell)$$
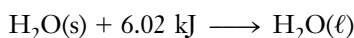
This tells us that the total energy of the water is raised by 6.02 kJ in the form of heat during the phase change.
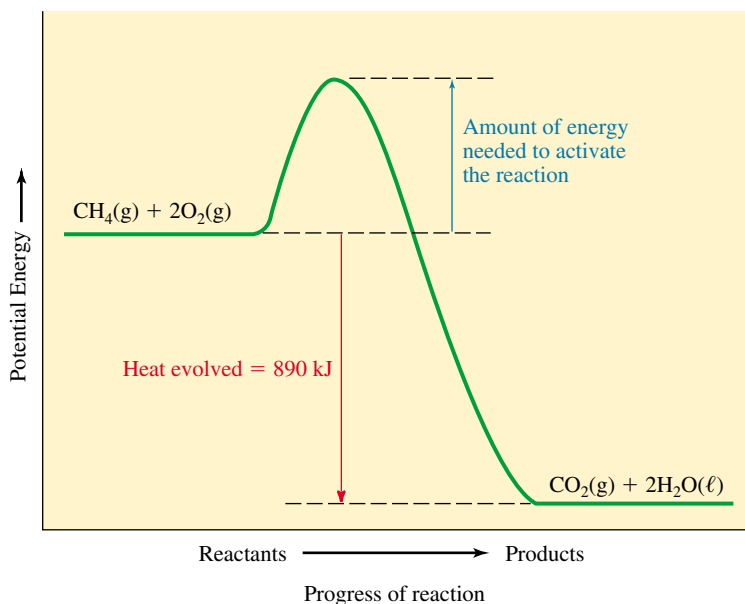
See the *Saunders Interactive General Chemistry CD-ROM,* Screen 6.12, Energy Changes in Chemical Processes.

A hydrocarbon is a binary compound of only hydrogen and carbon. Hydrocarbons may be gaseous, liquid, or solid. All burn.

The amount of heat shown in such an equation always refers to the reaction for the number of moles of reactants and products specified by the coefficients. We call this *one mole of reaction*. It is important to specify the physical states of all substances, because different physical states have different energy contents.

Figure 15-1 The difference between the potential energy of the reactants—one mole of $CH_4(g)$ and two moles of $O_2(g)$—and that of the products—one mole of $CO_2(g)$ and two moles of $H_2O(\ell)$—is the amount of heat evolved in this *exothermic* reaction at constant pressure. For this reaction, it is 890 kJ/mol of reaction. In this chapter, we see how to measure the heat absorbed or released and how to calculate it from other known heat changes. Some initial activation, for example by heat, is needed to get the reaction started. In the absence of such activation energy, a mixture of CH_4 and O_2 can be kept at room temperature for a long time without reacting. For an *endothermic* reaction, the final level is higher than the initial level.
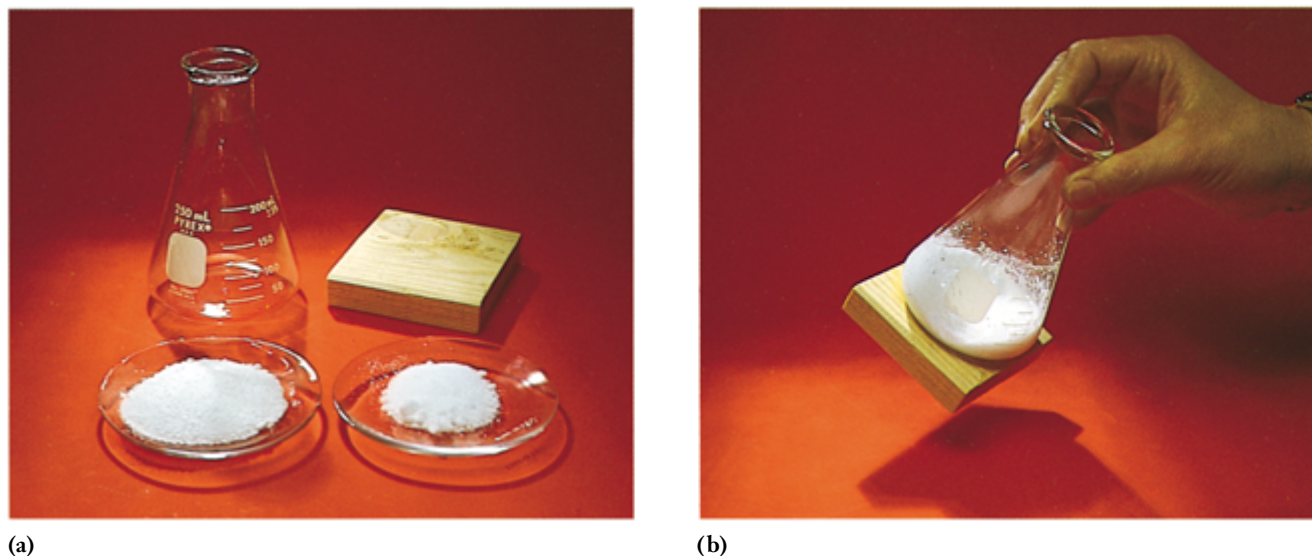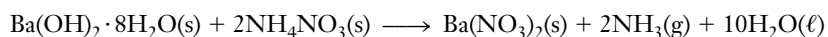
(a)

(b)

Figure 15-2   An endothermic process. (a) When solid hydrated barium hydroxide, $Ba(OH)_2 \cdot 8H_2O$, and *excess* solid ammonium nitrate, NH_4NO_3, are mixed, a reaction occurs.

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4NO_3(s) \longrightarrow Ba(NO_3)_2(s) + 2NH_3(g) + 10H_2O(\ell)$$

The excess ammonium nitrate dissolves in the water produced in the reaction. (b) The dissolution process is very endothermic. If the flask is placed on a wet wooden block, the water freezes and attaches the block to the flask.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 6.13, The First Law of Thermodynamics.

Some important ideas about energy are summarized in the **First Law of Thermodynamics.**

In Chapter 1 we pointed out the equivalence of matter and energy. The word "energy" is understood to include the energy equivalent of all matter in the universe. Stated differently, the total amount of mass and energy in the universe is constant.

The total amount of energy in the universe is constant.

The **Law of Conservation of Energy** is just another statement of the First Law of Thermodynamics.

Energy is neither created nor destroyed in ordinary chemical reactions and physical changes.

15-2 SOME THERMODYNAMIC TERMS

The substances involved in the chemical and physical changes that we are studying are called the **system.** Everything in the system's environment constitutes its **surroundings.** The **universe** is the system plus its surroundings. The system may be thought of as the part of the universe under investigation. The First Law of Thermodynamics tells us that energy is neither created nor destroyed; it is only transferred between the system and its surroundings.

The **thermodynamic state of a system** is defined by a set of conditions that completely specifies all the properties of the system. This set commonly includes the temperature, pressure, composition (identity and number of moles of each component), and physical state (gas, liquid, or solid) of each part of the system. Once the state has been specified, all other properties—both physical and chemical—are fixed.

The properties of a system—such as P, V, T—are called **state functions.** The *value* of a state function depends *only* on the state of the system and not on the way in which the system came to be in that state. A *change* in a state function describes a *difference* between the two states. It is independent of the process or pathway by which the change occurs.

For instance, consider a sample of one mole of pure liquid water at 30°C and 1 atm pressure. If at some later time the temperature of the sample is 22°C at the same pressure, then it is in a different thermodynamic state. We can tell that the *net* temperature change is −8°C. It does not matter whether (1) the cooling took place directly (either slowly or rapidly) from 30°C to 22°C, or (2) the sample was first heated to 36°C, then cooled to 10°C, and finally warmed to 22°C, or (3) any other conceivable path was followed from the initial state to the final state. The change in other properties (e.g., the pressure) of the sample is likewise independent of path.

The most important use of state functions in thermodynamics is to describe *changes*. We describe the difference in any quantity, X, as

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

When X increases, the final value is greater than the initial value, so ΔX is *positive*; a decrease in X makes ΔX a *negative* value.

You can consider a state function as analogous to a bank account. With a bank account, at any time you can measure the amount of money in your account (your balance) in convenient terms—dollars and cents. Changes in this balance can occur for several reasons, such as deposit of your paycheck, writing of checks, or service charges assessed by the bank. In our analogy these transactions are *not* state functions, but they do cause *changes in* the state function (the balance in the account). You can think of the bank balance on a vertical scale; a deposit of $150 changes the balance by +$150, no matter what it was at the start, just as a withdrawal of $150 would change the balance by −$150. Similarly, we shall see that the energy of a system is a state function that can be changed—for instance, by an energy "deposit" of heat absorbed or work done on the system, or by an energy "withdrawal" of heat given off or work done by the system.

We can describe *differences* between levels of a state function, regardless of where the zero level is located. In the case of a bank balance, the "natural" zero level is obviously the point at which we open the account, before any deposits or withdrawals. In contrast, the zero levels on most temperature scales are set arbitrarily. When we say that the temperature of an ice–water mixture is "zero degrees Celsius," we are not saying that the mixture contains no temperature! We have simply chosen to describe this point on the temperature scale by the number *zero;* conditions of higher temperature are described by positive temperature values, and those of lower temperature have negative values, "below zero." The phrase "15 degrees cooler" has the same meaning anywhere on the scale. Many of the scales that we use in thermodynamics are arbitrarily defined in this way. Arbitrary scales are useful when we are interested only in *changes* in the quantity being described.

Any property of a system that depends only on the values of its state functions is also a state function. For instance, the volume of a given sample of water depends only on temperature, pressure, and physical state; volume is a state function. We shall encounter other thermodynamic state functions.

State functions are represented by capital letters. Here P refers to pressure, V to volume, and T to absolute temperature.
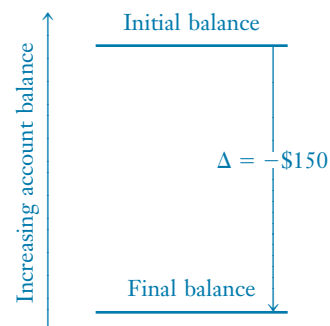
Here is a graphical representation of a $150 decrease in your bank balance. We express the change in your bank balance as $\Delta\$ = \$_{\text{final}} - \$_{\text{initial}}$. Your final balance is *less* than your initial balance, so the result is *negative*, indicating a *decrease*. There are many ways to get this same net change—one large withdrawal or some combination of deposits, withdrawals, interest earned, and service charges. All of the Δ values we will see in this chapter can be thought of in this way.

15-3 ENTHALPY CHANGES

Most chemical reactions and physical changes occur at constant (usually atmospheric) pressure.

> The quantity of heat transferred into or out of a system as it undergoes a chemical or physical change at constant pressure, q_p, is defined as the **enthalpy change, ΔH,** of the process.

An enthalpy change is sometimes loosely referred to as a *heat change* or a *heat of reaction*. The enthalpy change is equal to the enthalpy or "heat content," H, of the substances produced minus the enthalpy of the substances consumed.

$$\Delta H = H_{\text{final}} - H_{\text{initial}} \quad \text{or} \quad \Delta H = H_{\text{substances produced}} - H_{\text{substances consumed}}$$

It is impossible to know the absolute enthalpy (heat content) of a system. *Enthalpy is a state function*, however, and it is the *change in enthalpy* in which we are interested; this can be measured for many processes. In the next several sections we focus on chemical reactions and the enthalpy changes that occur in these processes. We first discuss the experimental determination of enthalpy changes.

15-4 CALORIMETRY

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 6.10, Heat Transfer Between Substances, and Screen 6.18, Measuring Heats of Reaction: Calorimetry.

We can determine the energy change associated with a chemical or physical process by using an experimental technique called **calorimetry.** This technique is based on observing the temperature change when a system absorbs or releases energy in the form of heat. The experiment is carried out in a device called a **calorimeter,** in which the temperature change of a known amount of substance (often water) of known specific heat is measured. The temperature change is caused by the absorption or release of heat by the chemical or physical process under study. A review of calculations involved with heat transfer (Sections 1-13, 13-9, and 13-11) may be helpful for understanding this section.

A "coffee-cup" calorimeter (Figure 15-3) is often used in laboratory classes to measure "heats of reaction" at constant pressure, q_p, in aqueous solutions. Reactions are chosen so that there are no gaseous reactants or products. Thus, all reactants and products remain in the vessel throughout the experiment. Such a calorimeter could be used to measure the amount of heat absorbed or released when a reaction takes place in aqueous solution. We can consider the reactants and products as the system and the calorimeter plus the solution (mostly water) as the surroundings. For an exothermic reaction, the amount of heat evolved by the reaction can be calculated from the amount by which it causes the temperature of the calorimeter and the solution to rise. The heat can be visualized as divided into two parts.

The polystyrene insulation of the coffee-cup calorimeter ensures that little or no heat escapes from or enters the container.

$$\begin{pmatrix} \text{amount of heat} \\ \text{released by reaction} \end{pmatrix} = \begin{pmatrix} \text{amount of heat gained} \\ \text{by calorimeter} \end{pmatrix} + \begin{pmatrix} \text{amount of heat} \\ \text{gained by solution} \end{pmatrix}$$

The amount of heat absorbed by a calorimeter is sometimes expressed as the *heat capacity* of the calorimeter, in joules per degree.

The heat capacity of a calorimeter is determined by adding a known amount of heat and measuring the rise in temperature of the calorimeter and of the solution it contains. This heat capacity of a calorimeter is sometimes called its *calorimeter constant.*
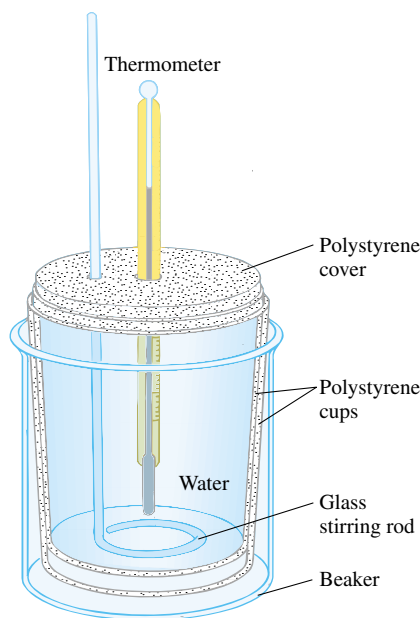
Figure 15-3 A coffee-cup calorimeter. The stirring rod is moved up and down to ensure thorough mixing and uniform heating of the solution during reaction. The polystyrene walls and top provide insulation so that very little heat escapes. This kind of calorimeter measures q_p, the heat transfer due to a reaction occurring at constant *pressure*.

EXAMPLE 15-1   *Heat Capacity of a Calorimeter*

We add 3.358 kJ of heat to a calorimeter that contains 50.00 g of water. The temperature of the water and the calorimeter, originally at 22.34°C, increases to 36.74°C. Calculate the heat capacity of the calorimeter in J/°C. The specific heat of water is 4.184 J/g·°C.

One way to add heat is to use an electric heater.

Plan

We first calculate the amount of heat gained by the water in the calorimeter. The rest of the heat must have been gained by the calorimeter, so we can determine the heat capacity of the calorimeter.

Solution

$$50.00 \text{ g H}_2\text{O}(\ell) \text{ at } 22.34°C \longrightarrow 50.00 \text{ g H}_2\text{O}(\ell) \text{ at } 36.74°C$$
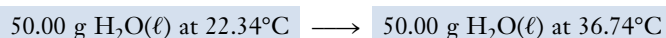
The temperature change is $(36.74 - 22.34)°C = 14.40°C$.

$$\underline{?} \text{ J} = 50.00 \text{ g} \times \frac{4.184 \text{ J}}{\text{g} \cdot °C} \times 14.40°C = 3.012 \times 10^3 \text{ J}$$

The total amount of heat added was 3.358 kJ or 3.358×10^3 J. The difference between these heat values is the amount of heat absorbed by the calorimeter.

$$\underline{?} \text{ J} = 3.358 \times 10^3 \text{ J} - 3.012 \times 10^3 \text{ J} = 0.346 \times 10^3 \text{ J, or 346 J absorbed by calorimeter}$$

To obtain the heat capacity of the calorimeter, we divide the amount of heat absorbed by the calorimeter, 346 J, by its temperature change.

$$\underline{?} \frac{\text{J}}{°C} = \frac{346 \text{ J}}{14.40°C} = \boxed{24.0 \text{ J/°C}}$$

The calorimeter absorbs 24.0 J of heat for each degree Celsius increase in its temperature.

You should now work Exercise 58.

EXAMPLE 15-2   *Heat Measurements Using a Calorimeter*

A 50.0-mL sample of 0.400 M copper(II) sulfate solution at 23.35°C is mixed with 50.0 mL of 0.600 M sodium hydroxide solution, also at 23.35°C, in the coffee-cup calorimeter of Example 15-1. After the reaction occurs, the temperature of the resulting mixture is measured to be 25.23°C. The density of the final solution is 1.02 g/mL. Calculate the amount of heat evolved. Assume that the specific heat of the solution is the same as that of pure water, 4.184 J/g·°C.

$$CuSO_4(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + Na_2SO_4(aq)$$
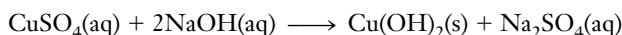
Plan

The amount of heat released by the reaction is absorbed by the calorimeter *and* by the solution. To find the amount of heat absorbed by the solution, we must know the mass of solution; to find that, we assume that the volume of the reaction mixture is the sum of volumes of the original solutions.

Solution

The mass of solution is

$$\underline{?}\text{ g soln} = (50.0 + 50.0)\text{ mL} \times \frac{1.02\text{ g soln}}{\text{mL}} = 102\text{ g soln}$$

The amount of heat absorbed by the calorimeter *plus* the amount absorbed by the solution is

$$\underline{?}\text{ J} = \overbrace{\frac{24.0\text{ J}}{°C} \times (25.23 - 23.35)°C}^{\substack{\text{amount of heat} \\ \text{absorbed by calorimeter}}} + \overbrace{102\text{ g} \times \frac{4.18\text{ J}}{\text{g}·°C} \times (25.23 - 23.35)°C}^{\substack{\text{amount of heat} \\ \text{absorbed by solution}}}$$

$$= 45\text{ J} + 801\text{ J} = 846\text{ J absorbed by solution plus calorimeter}$$

Thus, the reaction must have liberated 846 J, or 0.846 kJ, of heat.

You should now work Exercise 62(a).

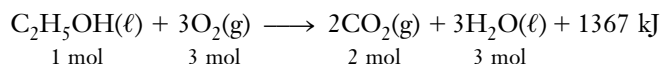The heat released by the reaction of HCl(aq) with NaOH(aq) causes the temperature of the solution to rise.

15-5 THERMOCHEMICAL EQUATIONS

A balanced chemical equation, together with its value of ΔH, is called a **thermochemical equation.** For example,

$$\underset{\text{1 mol}}{C_2H_5OH(\ell)} + \underset{\text{3 mol}}{3O_2(g)} \longrightarrow \underset{\text{2 mol}}{2CO_2(g)} + \underset{\text{3 mol}}{3H_2O(\ell)} + 1367\text{ kJ}$$

is a thermochemical equation that describes the combustion (burning) of one mole of liquid ethanol at a particular temperature and pressure. The coefficients in such a description *must* be interpreted as *numbers of moles.* Thus, 1367 kJ of heat is released when *one* mole of $C_2H_5OH(\ell)$ reacts with *three* moles of $O_2(g)$ to give *two* moles of $CO_2(g)$ and *three* moles of $H_2O(\ell)$. We can refer to this amount of reaction as one **mole of reaction,** which we abbreviate "mol rxn." This interpretation allows us to write various unit factors as desired.

$$\frac{1\text{ mol }C_2H_5OH(\ell)}{1\text{ mol rxn}}, \quad \frac{2\text{ mol }CO_2(g)}{1\text{ mol rxn}}, \quad \text{and so on}$$

We can also write the thermochemical equation as

$$C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell) \qquad \Delta H = -1367 \text{ kJ/mol rxn}$$
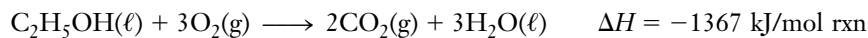
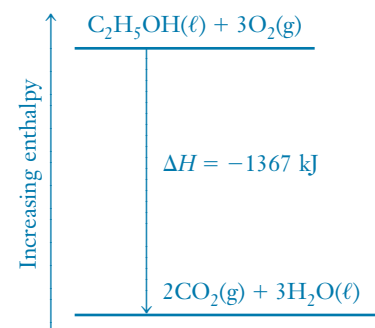The negative sign indicates that this is an *exothermic* reaction (i.e., it gives *off* heat).

> We always interpret ΔH as the enthalpy change for the reaction as written; that is, as (enthalpy change)/(mole of reaction), where the denominator means "for the number of moles of each substance shown in the balanced equation."
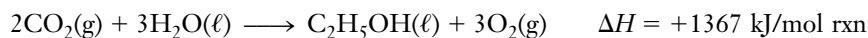
We can then use several unit factors to interpret this thermochemical equation.

$$\frac{1367 \text{ kJ given off}}{\text{mol of reaction}} = \frac{1367 \text{ kJ given off}}{\text{mol } C_2H_5OH(\ell) \text{ consumed}} = \frac{1367 \text{ kJ given off}}{3 \text{ mol } O_2(g) \text{ consumed}}$$

$$= \frac{1367 \text{ kJ given off}}{2 \text{ mol } CO_2(g) \text{ formed}} = \frac{1367 \text{ kJ given off}}{3 \text{ mol } H_2O(\ell) \text{ formed}}$$

The reverse reaction would require the absorption of 1367 kJ under the same conditions;

$$1367 \text{ kJ} + 2CO_2(g) + 3H_2O(\ell) \longrightarrow C_2H_5OH(\ell) + 3O_2(g)$$
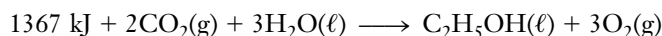
That is, it is *endothermic*, with $\Delta H = +1367$ kJ.

$$2CO_2(g) + 3H_2O(\ell) \longrightarrow C_2H_5OH(\ell) + 3O_2(g) \qquad \Delta H = +1367 \text{ kJ/mol rxn}$$

It is important to remember the following conventions regarding thermochemical equations:

1. The coefficients in a balanced thermochemical equation refer to the numbers of *moles* of reactants and products involved. In the thermodynamic interpretation of equations we *never* interpret the coefficients as *numbers of molecules*. Thus, it is acceptable to write coefficients as fractions rather than as integers, when necessary.

2. The numerical value of ΔH (or any other thermodynamic change) refers to the *number of moles* of substances specified by the equation. This amount of change of substances is called *one mole of reaction*, so we can express ΔH in units of energy/mol rxn. For brevity, the units of ΔH are sometimes written kJ/mol or even just kJ. No matter what units are used, be sure that you interpret the thermodynamic change *per mole of reaction for the balanced chemical equation to which it refers*. If a different amount of material is involved in the reaction, then the ΔH (or other change) must be scaled accordingly.

3. The physical states of all species are important and must be specified. Heat is given off or absorbed when phase changes occur, so different amounts of heat could be involved in a reaction depending on the phases of reactants and products.

4. The value of ΔH usually does not change significantly with moderate changes in temperature.

$C_2H_5OH(\ell) + 3O_2(g)$

Increasing enthalpy

$\Delta H = -1367$ kJ

$2CO_2(g) + 3H_2O(\ell)$

Before we know what a value of ΔH means, we must know the balanced chemical equation to which it refers.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 6.15, Enthalpy Changes for Chemical Reactions.

EXAMPLE 15-3   *Thermochemical Equations*

When 2.61 grams of dimethyl ether, CH_3OCH_3, is burned at constant pressure, 82.5 kJ of heat is given off. Find ΔH for the reaction

$$CH_3OCH_3(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$$
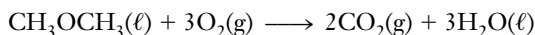
Plan

We scale the amount of heat given off in the experiment to correspond to the amount of CH_3OCH_3 shown in the balanced equation.

Solution

$$\frac{?\ kJ\ given\ off}{mol\ rxn} = \frac{82.5\ kJ\ given\ off}{2.61\ g\ CH_3OCH_3} \times \frac{46.0\ g\ CH_3OCH_3}{mol\ CH_3OCH_3} \times \frac{1\ mol\ CH_3OCH_3}{mol\ rxn}$$

$$= 1450\ kJ/mol\ rxn$$

Because heat is given off, we know that the reaction is exothermic and the value of ΔH is negative, so

$$\Delta H = -1450\ kJ/mol\ rxn$$

You should now work Exercise 19.

EXAMPLE 15-4   *Thermochemical Equations*

Write the thermochemical equation for the reaction in Example 15-2.

Plan

We must determine *how much* reaction occurred—that is, how many moles of reactants were consumed. We first multiply the volume, in liters, of each solution by its concentration in mol/L (molarity) to determine the number of moles of each reactant mixed. Then we identify the limiting reactant. We scale the amount of heat released in the experiment to correspond to the number of moles of that reactant shown in the balanced equation.

Solution

Using the data from Example 15-2,

$$\underline{?}\ mol\ CuSO_4 = 0.0500\ L \times \frac{0.400\ mol\ CuSO_4}{1.00\ L} = 0.0200\ mol\ CuSO_4$$

$$\underline{?}\ mol\ NaOH = 0.0500\ L \times \frac{0.600\ mol\ NaOH}{1.00\ L} = 0.0300\ mol\ NaOH$$

We determine which is the limiting reactant (see Section 3-3).

Required Ratio	Available Ratio
$\dfrac{1\ mol\ CuSO_4}{2\ mol\ NaOH} = \dfrac{0.50\ mol\ CuSO_4}{1.00\ mol\ NaOH}$	$\dfrac{0.0200\ mol\ CuSO_4}{0.0300\ mol\ NaOH} = \dfrac{0.667\ mol\ CuSO_4}{1.00\ mol\ NaOH}$

NaOH is the limiting reactant.

More $CuSO_4$ is available than is required to react with the NaOH. Thus, 0.846 kJ of heat was given off during the consumption of 0.0300 mol of NaOH. The amount of heat given off per "mole of reaction" is

$$\frac{?\ kJ\ released}{mol\ rxn} = \frac{0.846\ kJ\ given\ off}{0.0300\ mol\ NaOH} \times \frac{2\ mol\ NaOH}{mol\ rxn} = \frac{56.4\ kJ\ given\ off}{mol\ rxn}$$

Thus, when the reaction occurs *to the extent indicated by the balanced chemical equation*, 56.4 kJ is released. Remembering that exothermic reactions have negative values of ΔH_{rxn}, we write

$$CuSO_4(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + Na_2SO_4(aq) \qquad \Delta H_{rxn} = -56.4 \text{ kJ/mol rxn}$$
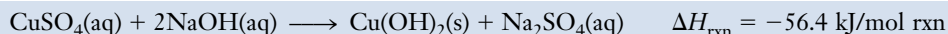
You should now work Exercise 62(b).

Heat is released, so this is an exothermic reaction.

EXAMPLE 15-5 *Amount of Heat Versus Extent of Reaction*

When aluminum metal is exposed to atmospheric oxygen (as in aluminum doors and windows), it is oxidized to form aluminum oxide. How much heat is released by the complete oxidation of 24.2 grams of aluminum at 25°C and 1 atm? The thermochemical equation is
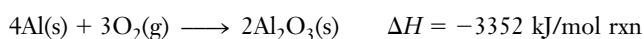
$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s) \qquad \Delta H = -3352 \text{ kJ/mol rxn}$$

Plan

The thermochemical equation tells us that 3352 kJ of heat is released for every mole of reaction, that is, for every 4 moles of Al that reacts. We convert 24.2 g of Al to moles, and then calculate the number of kilojoules corresponding to that number of moles of Al, using the unit factors

$$\frac{-3352 \text{ kJ}}{\text{mol rxn}} \quad \text{and} \quad \frac{1 \text{ mol rxn}}{4 \text{ mol Al}}$$

Solution

For 24.2 g Al,

$$\underline{?}\ kJ = 24.2 \text{ g Al} \times \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \times \frac{1 \text{ mol rxn}}{4 \text{ mol Al}} \times \frac{-3352 \text{ kJ}}{\text{mol rxn}} = -751 \text{ kJ}$$

This tells us that 751 kJ of heat is released to the surroundings during the oxidation of 24.2 grams of aluminum.

You should now work Exercises 14 and 15.

The *sign* tells us that heat was released, but it would be grammatical nonsense to say in words that "-751 kJ of heat was released." As an analogy, suppose you give your friend \$5. Your Δ\$ is $-\$5$, but in describing the transaction you would not say "I gave her minus five dollars," but rather "I gave her five dollars."

✓ Problem-Solving Tip: *Mole of Reaction*

Remember that a thermochemical equation can imply *different* numbers of moles of *different* reactants or products. In Example 15-5 one mole of reaction also corresponds to 3 moles of $O_2(g)$ and to 2 moles of $Al_2O_3(s)$.

15-6 STANDARD STATES AND STANDARD ENTHALPY CHANGES

The **thermodynamic standard state** of a substance is its most stable pure form under standard pressure (one atmosphere)* and at some specific temperature (25°C or 298 K unless otherwise specified). Examples of elements in their standard states at 25°C are hydrogen, gaseous diatomic molecules, $H_2(g)$; mercury, a silver-colored liquid metal,

*IUPAC has changed the standard pressure from 1 atm to 1 bar. Because 1 bar is equal to 0.987 atm, the differences in thermodynamic calculations are negligible except in work of very high precision. Many tables of thermodynamic data are still based on a standard pressure of 1 atm, so we will use it in this book.

A temperature of 25°C is 77°F. This is slightly above typical room temperature. Notice that these thermodynamic "standard conditions" are not the same as the "standard temperature and pressure (STP)" that we used in gas calculations involving standard molar volume (Chapter 12).
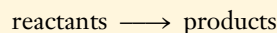
Hg(ℓ); sodium, a silvery white solid metal, Na(s); and carbon, a grayish black solid called graphite, C(graphite). We use C(graphite) instead of C(s) to distinguish it from other solid forms of carbon, such as C(diamond). The reaction C(diamond) $\rightarrow$ C(graphite) would be *exothermic* by 1.897 kJ/mol rxn; C(graphite) is thus more stable than C(diamond). Examples of standard states of compounds include ethanol (ethyl alcohol or grain alcohol), a liquid, $C_2H_5OH(\ell)$; water, a liquid, $H_2O(\ell)$; calcium carbonate, a solid, $CaCO_3$(s); and carbon dioxide, a gas, CO_2(g). Keep in mind the following conventions for thermochemical standard states.

> 1. For a *pure* substance in the liquid or solid phase, the standard state is the pure liquid or solid.
>
> 2. For a gas, the standard state is the gas at a pressure of *one atmosphere;* in a mixture of gases, its partial pressure must be one atmosphere.
>
> 3. For a substance in solution, the standard state refers to *one-molar* concentration.

For ease of comparison and tabulation, we often refer to thermochemical or thermodynamic changes "at standard states" or, more simply, to a *standard change.* To indicate a change at standard pressure, we add a superscript zero. If some temperature other than standard temperature of 25°C (298 K) is specified, we indicate it with a subscript; if no subscript appears, a temperature of 25°C (298 K) is implied.

> The **standard enthalpy change, ΔH^0_{rxn},** for reaction
>
> $$\text{reactants} \longrightarrow \text{products}$$
>
> refers to the ΔH when the specified number of moles of reactants, all at standard states, are converted *completely* to the specified number of moles of products, all at standard states.

We allow a reaction to take place, with changes in temperature or pressure if necessary; when the reaction is complete, we return the products to the same conditions of temperature and pressure that we started with, *keeping track of energy or enthalpy changes* as we do so. When we describe a process as taking place "at constant T and P," we mean that the initial and final conditions are the same. Because we are dealing with changes in state functions, the net change is the same as the change we would have obtained hypothetically with T and P actually held constant.

15-7 STANDARD MOLAR ENTHALPIES OF FORMATION, ΔH^0_f

It is not possible to determine the total enthalpy content of a substance on an absolute scale. We need to describe only *changes* in this state function, however, so we can define an *arbitrary scale* as follows.

> The **standard molar enthalpy of formation, ΔH^0_f,** of a substance is the enthalpy change for the reaction in which *one mole* of the substance in a specified state is formed from its elements in their standard states. By convention, the ΔH^0_f value for any *element in its standard state* is zero.

If the substance exists in several different forms, we take the form that is most stable at 25°C and 1 atm as the standard state.

This is sometimes referred to as the standard heat of reaction.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 6.17, Standard Enthalpy of Formation.

We can think of ΔH^0_f as the enthalpy content of each substance, in its standard state, relative to the enthalpy content of the elements, in their standard states. This is why ΔH^0_f for an element in its standard state is zero.

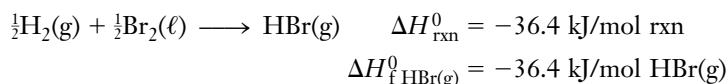| TABLE 15-1	*Selected Standard Molar Enthalpies of Formation at 298 K*		
Substance	**ΔH_f^0 (kJ/mol)**	**Substance**	**ΔH_f^0 (kJ/mol)**
$Br_2(\ell)$	0	HgS(s) red	−58.2
$Br_2(g)$	30.91	$H_2(g)$	0
C(diamond)	1.897	HBr(g)	−36.4
C(graphite)	0	$H_2O(\ell)$	−285.8
$CH_4(g)$	−74.81	$H_2O(g)$	−241.8
$C_2H_4(g)$	52.26	NO(g)	90.25
$C_6H_6(\ell)$	49.03	Na(s)	0
$C_2H_5OH(\ell)$	−277.7	NaCl(s)	−411.0
CO(g)	−110.5	$O_2(g)$	0
$CO_2(g)$	−393.5	$SO_2(g)$	−296.8
CaO(s)	−635.5	$SiH_4(g)$	34.0
$CaCO_3(s)$	−1207.0	$SiCl_4(g)$	−657.0
$Cl_2(g)$	0	$SiO_2(s)$	−910.9

The ΔH_f^0 values of $Br_2(g)$ and C(diamond) are *not equal to 0* at 298 K. The standard states of these elements are $Br_2(\ell)$ and C(graphite), respectively.

Standard molar enthalpy of formation is often called **standard molar heat of formation** or, more simply, **heat of formation.** The superscript zero in ΔH_f^0 signifies standard pressure, 1 atmosphere. Negative values for ΔH_f^0 describe exothermic formation reactions, whereas positive values for ΔH_f^0 describe endothermic formation reactions.

The enthalpy change for a balanced equation that gives a compound from its elements does not necessarily give a molar enthalpy of formation for the compound. Consider the following exothermic reaction at standard conditions.

$$H_2(g) + Br_2(\ell) \longrightarrow 2HBr(g) \qquad \Delta H_{rxn}^0 = -72.8 \text{ kJ/mol rxn}$$
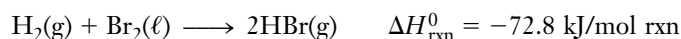
We see that *two* moles of HBr(g) are formed in the reaction as written. Half as much energy, 36.4 kJ, is liberated when *one mole* of HBr(g) is produced from its constituent elements in their standard states. For HBr(g), $\Delta H_f^0 = -36.4$ kJ/mol. This can be shown by dividing all coefficients in the balanced equation by 2.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(\ell) \longrightarrow HBr(g) \qquad \Delta H_{rxn}^0 = -36.4 \text{ kJ/mol rxn}$$
$$\Delta H_{f\,HBr(g)}^0 = -36.4 \text{ kJ/mol HBr(g)}$$

Standard heats of formation of some common substances are tabulated in Table 15-1. Appendix K contains a larger listing.

When referring to a thermodynamic quantity for a *substance*, we often omit the description of the substance from the units. Units for tabulated ΔH_f^0 values are given as "kJ/mol"; we must interpret this as "per mole of the substance in the specified state." For instance, for HBr(g) the tabulated ΔH_f^0 value of −36.4 kJ/mol should be interpreted as $\dfrac{-36.4 \text{ kJ}}{\text{mol HBr(g)}}$.

The coefficients $\tfrac{1}{2}$ preceding $H_2(g)$ and $Br_2(\ell)$ do *not* imply half a molecule of each. In thermochemical equations, the coefficients always refer to the number of *moles* under consideration.

EXAMPLE 15-6 *Interpretation of ΔH_f^0*

The standard molar enthalpy of formation of ethanol, $C_2H_5OH(\ell)$, is −277.7 kJ/mol. Write the thermochemical equation for the reaction for which $\Delta H_{rxn}^0 = -277.7$ kJ/mol rxn.

Plan

The definition of ΔH_f^0 of a substance refers to a reaction in which *one mole* of the substance is formed. We put one mole of $C_2H_5OH(\ell)$ on the right side of the chemical equation and put the appropriate elements in their standard states on the left. We balance the equation *without changing the coefficient of the product*, even if we must use fractional coefficients on the left.

Solution

$$2C(graphite) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(\ell) \qquad \Delta H = -277.7 \text{ kJ/mol rxn}$$

You should now work Exercise 26.

✓ Problem-Solving Tip: *How Do We Interpret Fractional Coefficients?*

Remember that we *always* interpret the coefficients in thermochemical equations as numbers of *moles* of reactants or products. The $\tfrac{1}{2}O_2(g)$ in the answer to Example 15-6 refers to $\tfrac{1}{2}$ *mole* of O_2 molecules, or

$$\tfrac{1}{2} \text{ mol } O_2 \times \frac{32.0 \text{ g } O_2}{\text{mol } O_2} = 16.0 \text{ g } O_2$$

It is important to realize that this is *not* the same as one mole of O atoms (though that would also weigh 16.0 g).

Similarly, the fractional coefficients in

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(\ell) \longrightarrow HBr(g)$$
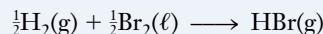
refer to

$$\tfrac{1}{2} \text{ mol } H_2 \times \frac{2.0 \text{ g } H_2}{\text{mol } H_2} = 1.0 \text{ g } H_2$$

and

$$\tfrac{1}{2} \text{ mol } Br_2 \times \frac{159.8 \text{ g } Br_2}{\text{mol } Br_2} = 79.9 \text{ g } Br_2$$

respectively.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 6.16, Hess's Law.

15-8 HESS'S LAW

In 1840, G. H. Hess (1802–1850) published his **law of heat summation,** which he derived on the basis of numerous thermochemical observations.

As an analogy, consider traveling from Kansas City (elevation 884 ft above sea level) to Denver (elevation 5280 ft). The change in elevation is (5280 − 884) ft = 4396 ft, regardless of the route taken.

> The enthalpy change for a reaction is the same whether it occurs by one step or by any series of steps.

Enthalpy is a state function. Its *change* is therefore independent of the pathway by which a reaction occurs. We do not need to know whether the reaction *does*, or even *can*, occur

by the series of steps used in the calculation. The steps must (if only "on paper") result in the overall reaction. Hess's Law lets us calculate enthalpy changes for reactions for which the changes could be measured only with difficulty, if at all. In general terms, Hess's Law of heat summation may be represented as

$$\Delta H^0_{rxn} = \Delta H^0_a + \Delta H^0_b + \Delta H^0_c + \cdots$$

Here a, b, c, . . . refer to balanced thermochemical equations that can be summed to give the equation for the desired reaction.

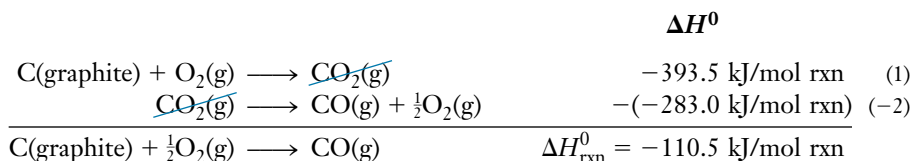Consider the following reaction.

$$C(graphite) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H^0_{rxn} = \underline{\ ?\ }$$
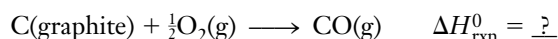
The enthalpy change for this reaction cannot be measured directly. Even though $CO(g)$ is the predominant product of the reaction of graphite with a *limited* amount of $O_2(g)$, some $CO_2(g)$ is always produced as well. The following reactions do go to completion with excess $O_2(g)$; therefore, ΔH^0 values have been measured experimentally for them. [Pure $CO(g)$ is readily available.]

$$C(graphite) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^0_{rxn} = -393.5 \text{ kJ/mol rxn} \qquad (1)$$
$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^0_{rxn} = -283.0 \text{ kJ/mol rxn} \qquad (2)$$

We can "work backward" to find out how to combine these two known equations to obtain the desired equation. We want one mole of CO on the right, so we reverse equation (2) [designated below as (−2)]; heat is then absorbed instead of released, so we must change the sign of its ΔH^0 value. Then we add it to equation (1), canceling equal numbers of moles of the same species on each side. This gives the equation for the reaction we want. Adding the corresponding enthalpy changes gives the enthalpy change we seek.
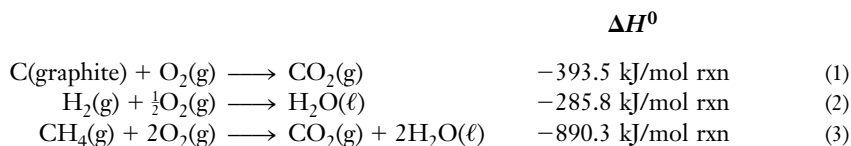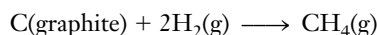
You are familiar with the addition and subtraction of algebraic equations. This method of combining thermochemical equations is analogous.

$$\Delta H^0$$

$$
\begin{array}{lll}
C(graphite) + O_2(g) \longrightarrow \cancel{CO_2(g)} & -393.5 \text{ kJ/mol rxn} & (1) \\
\cancel{CO_2(g)} \longrightarrow CO(g) + \tfrac{1}{2}O_2(g) & -(-283.0 \text{ kJ/mol rxn}) & (-2) \\
\hline
C(graphite) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) & \Delta H^0_{rxn} = -110.5 \text{ kJ/mol rxn} &
\end{array}
$$

This equation shows the formation of one mole of $CO(g)$ in its standard state from the elements in their standard states. In this way, we determine that ΔH^0_f for $CO(g)$ is −110.5 kJ/mol.
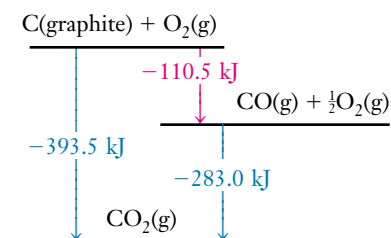
Above is a schematic representation of the enthalpy changes for the reaction $C(graphite) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$. The ΔH value for each step is based on the number of moles of each substance indicated.

EXAMPLE 15-7 *Combining Thermochemical Equations: Hess's Law*

Use the thermochemical equations shown here to determine ΔH^0_{rxn} at 25°C for the following reaction.

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

$$\Delta H^0$$

$$
\begin{array}{lll}
C(graphite) + O_2(g) \longrightarrow CO_2(g) & -393.5 \text{ kJ/mol rxn} & (1) \\
H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(\ell) & -285.8 \text{ kJ/mol rxn} & (2) \\
CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell) & -890.3 \text{ kJ/mol rxn} & (3)
\end{array}
$$

These are combustion reactions, for which ΔH^0_{rxn} values can be readily determined from calorimetry experiments.

Plan

(i) We want one mole of C(graphite) as reactant, so we write down equation (1).

(ii) We want two moles of $H_2(g)$ as reactants, so we multiply equation (2) by 2 [designated below as $2 \times (2)$].

(iii) We want one mole of $CH_4(g)$ as product, so we reverse equation (3) to give (-3).

(iv) We do the same operations on each ΔH^0 value.

(v) Then we add these equations term by term. The result is the desired thermochemical equation, with all unwanted substances canceling. The sum of the ΔH^0 values is the ΔH^0 for the desired reaction.
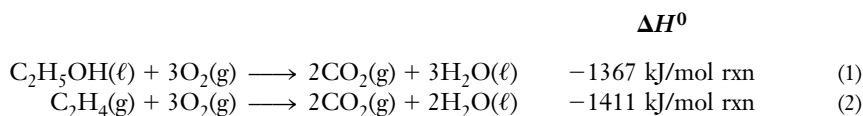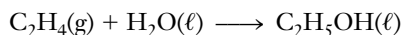
Solution

$$\Delta H^0$$
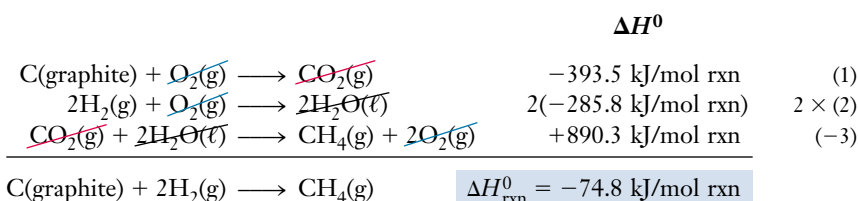
We have used a series of reactions for which ΔH^0 values can be easily measured to calculate ΔH^0 for a reaction that cannot be carried out.

C(graphite) + $O_2(g)$ ⟶ $CO_2(g)$	-393.5 kJ/mol rxn	(1)
$2H_2(g)$ + $O_2(g)$ ⟶ $2H_2O(\ell)$	$2(-285.8$ kJ/mol rxn$)$	$2 \times (2)$
$CO_2(g)$ + $2H_2O(\ell)$ ⟶ $CH_4(g)$ + $2O_2(g)$	$+890.3$ kJ/mol rxn	(-3)

C(graphite) + $2H_2(g)$ ⟶ $CH_4(g)$ $\Delta H^0_{rxn} = -74.8$ kJ/mol rxn
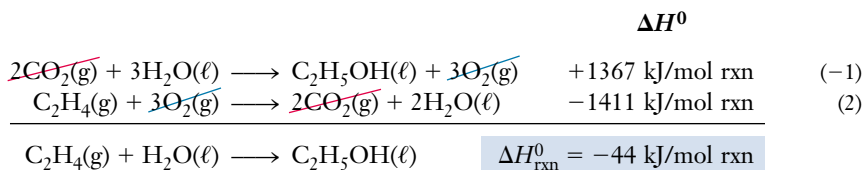
$CH_4(g)$ cannot be formed directly from C(graphite) and $H_2(g)$, so its ΔH^0_f value cannot be measured directly. The result of this example tells us that this value is -74.8 kJ/mol.

EXAMPLE 15-8   *Combining Thermochemical Equations: Hess's Law*

Given the following thermochemical equations, calculate the heat of reaction at 298 K for the reaction of ethylene with water to form ethanol.

$$C_2H_4(g) + H_2O(\ell) \longrightarrow C_2H_5OH(\ell)$$

$$\Delta H^0$$

$C_2H_5OH(\ell)$ + $3O_2(g)$ ⟶ $2CO_2(g)$ + $3H_2O(\ell)$	-1367 kJ/mol rxn	(1)
$C_2H_4(g)$ + $3O_2(g)$ ⟶ $2CO_2(g)$ + $2H_2O(\ell)$	-1411 kJ/mol rxn	(2)

Plan

We reverse equation (1) to give (-1); when the equation is reversed, the sign of ΔH^0 is changed because the reverse of an exothermic reaction is endothermic. Then we add it to equation (2).

Solution

$$\Delta H^0$$

$2CO_2(g)$ + $3H_2O(\ell)$ ⟶ $C_2H_5OH(\ell)$ + $3O_2(g)$	$+1367$ kJ/mol rxn	(-1)
$C_2H_4(g)$ + $3O_2(g)$ ⟶ $2CO_2(g)$ + $2H_2O(\ell)$	-1411 kJ/mol rxn	(2)

$C_2H_4(g)$ + $H_2O(\ell)$ ⟶ $C_2H_5OH(\ell)$ $\Delta H^0_{rxn} = -44$ kJ/mol rxn

You should now work Exercises 30 and 32.

✓ Problem-Solving Tip: ΔH_f^0 Refers to Specific Reaction

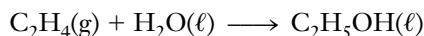The ΔH^0 for the reaction in Example 15-8 is -44 kJ for each mole of $C_2H_5OH(\ell)$ formed. This reaction, however, does not involve formation of $C_2H_5OH(\ell)$ from its constituent elements; therefore, ΔH_{rxn}^0 is *not* ΔH_f^0 for $C_2H_5OH(\ell)$. We have seen the reaction for ΔH_f^0 of $C_2H_5OH(\ell)$ in Example 15-6.

Similarly, the ΔH_{rxn}^0 for

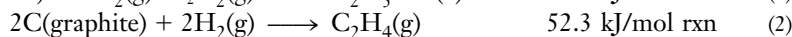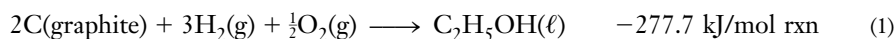$$CO(g) + \tfrac{1}{2}H_2(g) \longrightarrow CO_2(g)$$
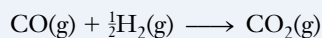
is *not* ΔH_f^0 for $CO_2(g)$.

Another interpretation of Hess's Law lets us use tables of ΔH_f^0 values to calculate the enthalpy change for a reaction. Let us consider again the reaction of Example 15-8.
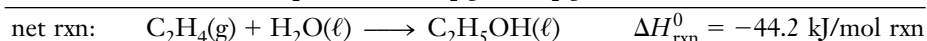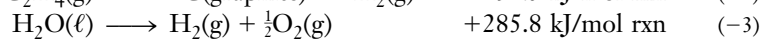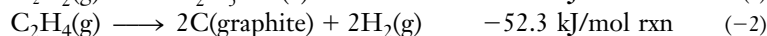
$$C_2H_4(g) + H_2O(\ell) \longrightarrow C_2H_5OH(\ell)$$

A table of ΔH_f^0 values (Appendix K) gives $\Delta H_{f\,C_2H_5OH(\ell)}^0 = -277.7$ kJ/mol, $\Delta H_{f\,C_2H_4(g)}^0 = 52.3$ kJ/mol, and $\Delta H_{f\,H_2O(\ell)}^0 = -285.8$ kJ/mol. We may express this information in the form of the following thermochemical equations.

$$\Delta H^0$$

$2C(\text{graphite}) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(\ell)$	-277.7 kJ/mol rxn	(1)
$2C(\text{graphite}) + 2H_2(g) \longrightarrow C_2H_4(g)$	52.3 kJ/mol rxn	(2)
$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$	-285.8 kJ/mol rxn	(3)

We may generate the equation for the desired net reaction by adding equation (1) to the reverse of equations (2) and (3). The value of ΔH^0 for the desired reaction is then the sum of the corresponding ΔH^0 values.

$$\Delta H^0$$

$2C(\text{graphite}) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(\ell)$	-277.7 kJ/mol rxn	(1)
$C_2H_4(g) \longrightarrow 2C(\text{graphite}) + 2H_2(g)$	-52.3 kJ/mol rxn	(-2)
$H_2O(\ell) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g)$	$+285.8$ kJ/mol rxn	(-3)
net rxn: $\quad C_2H_4(g) + H_2O(\ell) \longrightarrow C_2H_5OH(\ell)$	$\Delta H_{rxn}^0 = -44.2$ kJ/mol rxn	

We see that ΔH^0 for this reaction is given by

$$\Delta H_{rxn}^0 = \Delta H_{(1)}^0 + \Delta H_{(-2)}^0 + \Delta H_{(-3)}^0$$

or by

$$\Delta H_{rxn}^0 = \underset{\text{product}}{\Delta H_{f\,C_2H_5OH(\ell)}^0} - [\underset{\text{reactants}}{\Delta H_{f\,C_2H_4(g)}^0 + \Delta H_{f\,H_2O(\ell)}^0}]$$

In general terms this is a very useful form of Hess's Law.

$$\Delta H_{rxn}^0 = \Sigma\, n\, \Delta H_{f\,\text{products}}^0 - \Sigma\, n\, \Delta H_{f\,\text{reactants}}^0$$

The standard enthalpy change of a reaction is equal to the sum of the standard molar enthalpies of formation of the products, each multiplied by its coefficient, n, in the *balanced equation*, minus the corresponding sum of the standard molar enthalpies of formation of the reactants.

The capital Greek letter sigma (Σ) is read "the sum of." The $\Sigma\, n$ means that the ΔH_f^0 value of each product and reactant must be multiplied by its coefficient, n, in the balanced equation. The resulting values are then added.
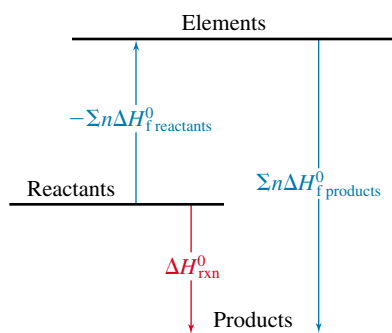
Figure 15-4 A schematic representation of Hess's Law. The red arrow represents the *direct* path from reactants to products. The series of blue arrows is a path (hypothetical) in which reactants are converted to elements, and they in turn are converted to products—all in their standard states.

In effect this form of Hess's Law supposes that the reaction occurs by converting reactants to the elements in their standard states, then converting these to products (Figure 15-4). Few, if any, reactions actually occur by such a pathway. Nevertheless, the ΔH^0 for this *hypothetical* pathway for *reactants → products* would be the same as that for any other pathway—including the one by which the reaction actually occurs.

EXAMPLE 15-9   *Using ΔH_f^0 Values: Hess's Law*

Calculate ΔH_{rxn}^0 for the following reaction at 298 K.

$$SiH_4(g) + 2O_2(g) \longrightarrow SiO_2(s) + 2H_2O(\ell)$$
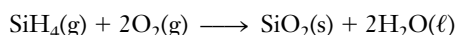
Plan

We apply Hess's Law in the form $\Delta H_{rxn}^0 = \Sigma\, n\, \Delta H_{f\,products}^0 - \Sigma\, n\, \Delta H_{f\,reactants}^0$, so we use the ΔH_f^0 values tabulated in Appendix K.

Solution

We can first list the ΔH_f^0 values we obtain from Appendix K:

	$SiH_4(g)$	$O_2(g)$	$SiO_2(g)$	$H_2O(\ell)$
ΔH_f^0, kJ/mol:	34.3	0	−910.9	−285.8

$O_2(g)$ is an element in its standard state, so its ΔH_f^0 is zero.

$$\Delta H_{rxn}^0 = \Sigma\, n\, \Delta H_{f\,products}^0 - \Sigma\, n\, \Delta H_{f\,reactants}^0$$

$$\Delta H_{rxn}^0 = [\Delta H_{f\,SiO_2(s)}^0 + 2\,\Delta H_{f\,H_2O(\ell)}^0] - [\Delta H_{f\,SiH_4(g)}^0 + 2\,\Delta H_{f\,O_2(g)}^0]$$

$$\Delta H_{rxn}^0 = \left[\frac{1\text{ mol } SiO_2(s)}{\text{mol rxn}} \times \frac{-910.9\text{ kJ}}{\text{mol } SiO_2(s)} + \frac{2\text{ mol } H_2O(\ell)}{\text{mol rxn}} \times \frac{-285.8\text{ kJ}}{\text{mol } H_2O(\ell)}\right]$$

$$- \left[\frac{1\text{ mol } SiH_4(g)}{\text{mol rxn}} \times \frac{+34.3\text{ kJ}}{\text{mol } SiH_4(g)} + \frac{2\text{ mol } O_2(g)}{\text{mol rxn}} \times \frac{0\text{ kJ}}{\text{mol } O_2(g)}\right]$$

$$\Delta H_{rxn}^0 = \boxed{-1515.7\text{ kJ/mol rxn}}$$

You should now work Exercise 36.

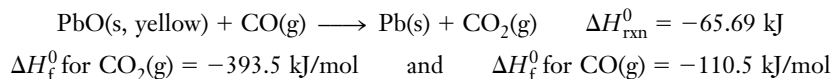Each term in the sums on the right-hand side of the solution in Example 15-9 has the units

$$\frac{\text{mol substance}}{\text{mol rxn}} \times \frac{\text{kJ}}{\text{mol substance}} \qquad \text{or} \qquad \frac{\text{kJ}}{\text{mol rxn}}$$

> For brevity, we shall omit units in the intermediate steps of calculations of this type, and just assign the proper units to the answer. Be sure that you understand how these units arise.

Suppose we measure ΔH_{rxn}^0 at 298 K and know all but one of the ΔH_f^0 values for reactants and products. We can then calculate the unknown ΔH_f^0 value.

EXAMPLE 15-10   *Using ΔH_f^0 Values: Hess's Law*

Use the following information to determine ΔH_f^0 for PbO(s, yellow).

$$\text{PbO(s, yellow)} + \text{CO(g)} \longrightarrow \text{Pb(s)} + \text{CO}_2\text{(g)} \qquad \Delta H_{rxn}^0 = -65.69 \text{ kJ}$$

$$\Delta H_f^0 \text{ for CO}_2\text{(g)} = -393.5 \text{ kJ/mol} \qquad \text{and} \qquad \Delta H_f^0 \text{ for CO(g)} = -110.5 \text{ kJ/mol}$$

We will consult Appendix K, only after working the problem, to check the answer.

Plan

We again use Hess's Law in the form $\Delta H_{rxn}^0 = \Sigma\, n\, \Delta H_{f\,products}^0 - \Sigma\, n\, \Delta H_{f\,reactants}^0$. The standard state of lead is Pb(s), so $\Delta H_{f\,Pb(s)}^0 = 0$ kJ/mol. Now we are given ΔH_{rxn}^0 and the ΔH_f^0 values for all substances *except* PbO(s, yellow). We can solve for this unknown.

Solution

We list the known ΔH_f^0 values:

	PbO(s, yellow)	CO(g)	Pb(s)	CO₂(g),
ΔH_f^0, kJ/mol:	$\Delta H_{f\,PbO_2(s,\,yellow)}^0$	-110.5	0	-393.5

$$\Delta H_{rxn}^0 = \Sigma\, n\, \Delta H_{f\,products}^0 \qquad - \Sigma\, n\, \Delta H_{f\,reactants}^0$$

$$\Delta H_{rxn}^0 = \Delta H_{f\,Pb(s)}^0 + \Delta H_{f\,CO_2(g)}^0 - [\Delta H_{f\,PbO(s,\,yellow)}^0 + \Delta H_{f\,CO(g)}^0]$$

$$-65.69 = 0 + (-393.5) \qquad - [\Delta H_{f\,PbO(s,\,yellow)}^0 + (-110.5)]$$

Rearranging to solve for $\Delta H_{f\,PbO(s,\,yellow)}^0$, we have

$$\Delta H_{f\,PbO(s,\,yellow)}^0 = 65.69 - 393.5 + 110.5 = \boxed{-217.3 \text{ kJ/mol of PbO}}$$

You should now work Exercise 42.

✓ Problem-Solving Tip: *Remember the Values of ΔH_f^0 for Elements*

In Example 15-10, we were not given the value of ΔH_f^0 for Pb(s). We should know without reference to tables that ΔH_f^0 for an *element* in its most stable form is exactly 0 kJ/mol. But the element *must* be in its most stable form. Thus, ΔH_f^0 for O_2(g) is zero, because ordinary oxygen is gaseous and diatomic. We would *not* assume that ΔH_f^0 would be zero for oxygen atoms, O(g), or for ozone, O_3(g). Similarly, ΔH_f^0 is zero for Cl_2(g) and for $Br_2(\ell)$, but not for Br_2(g). Recall that bromine is one of the few elements that is liquid at room temperature and 1 atm pressure.

15-9 BOND ENERGIES

Chemical reactions involve the breaking and making of chemical bonds. Energy is always required to break a chemical bond. Often this energy is supplied in the form of heat.

> The **bond energy (B.E.)** is the amount of energy necessary to break *one mole* of bonds in a gaseous covalent substance to form products in the gaseous state at constant temperature and pressure.

For all practical purposes, the bond energy is the same as bond enthalpy. Tabulated values of average bond energies are actually average bond enthalpies. We use the term "bond energy" rather than "bond enthalpy" because it is common practice to do so.

The greater the bond energy, the more stable (stronger) the bond is, and the harder it is to break. Thus bond energy is a measure of bond strengths.

TABLE 15-2			*Some Average Single Bond Energies (kJ/mol of bonds)*								
H	C	N	O	F	Si	P	S	Cl	Br	I	
436	413	391	463	565	318	322	347	432	366	299	H
	346	305	358	485			272	339	285	213	C
		163	201	283				192			N
			146		452	335		218	201	201	O
				155	565	490	284	253	249	278	F
					222		293	381	310	234	Si
						201		326		184	P
							226	255			S
								242	216	208	Cl
									193	175	Br
										151	I

Consider the following reaction.

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H^0_{rxn} = \Delta H_{H-H} = +436 \text{ kJ/mol H—H bonds}$$

The bond energy of the hydrogen–hydrogen bond is 436 kJ/mol of bonds. In other words, 436 kJ of energy must be absorbed for every mole of H—H bonds that are broken. This endothermic reaction (ΔH^0_{rxn} is positive) can be written

$$H_2(g) + 436 \text{ kJ} \longrightarrow 2H(g)$$
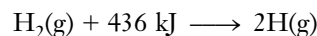
Some average bond energies are listed in Tables 15-2 and 15-3. We see from Table 15-3 that for any combination of elements, a triple bond is stronger than a double bond, which in turn is stronger than a single bond. Bond energies for double and triple bonds are *not* simply two or three times those for the corresponding single bonds. A single bond is a σ bond, whereas double and triple bonds involve a combination of σ and π bonding. The bond energy measures the difficulty of overcoming the orbital overlap, and we should not expect the strength of a π bond to be the same as that of a σ bond between the same two atoms.

We should keep in mind that each of the values listed is the average bond energy from a variety of compounds. The *average C—H bond energy* is 413 kJ/mol of bonds. Average

TABLE 15-3	*Comparison of Some Average Single and Multiple Bond Energies (kJ/mol of bonds)*				
Single Bonds		**Double Bonds**		**Triple Bonds**	
C—C	346	C=C	602	C≡C	835
N—N	163	N=N	418	N≡N	945
O—O	146	O=O	498		
C—N	305	C=N	615	C≡N	887
C—O	358	C=O	732*	C≡O	1072

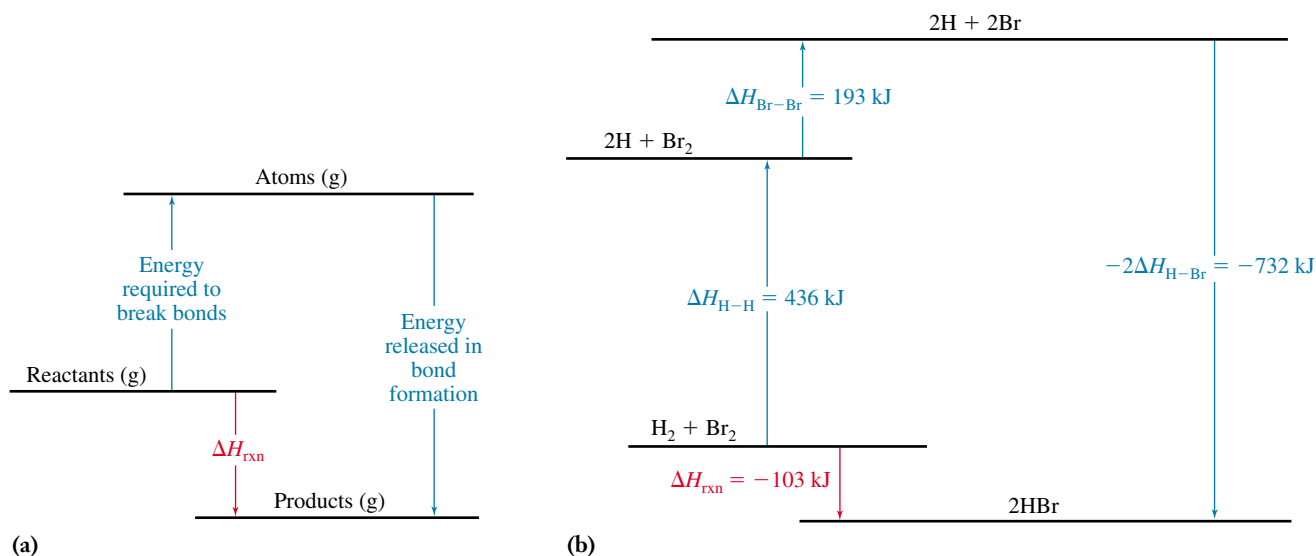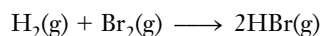*Except in CO_2, where it is 799 kJ/mol.

Figure 15-5 A schematic representation of the relationship between bond energies and ΔH_{rxn} for gas phase reactions. (a) For a general reaction (exothermic). (b) For the gas phase reaction

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

As usual for such diagrams, the value shown for each change refers to the number of moles of substances or bonds indicated in the diagram.

C—H bond energies differ slightly from compound to compound, as in CH_4, CH_3Cl, CH_3NO_2, and so on. Nevertheless, they are sufficiently constant to be useful in estimating thermodynamic data that are not readily available by another approach. Values of ΔH_{rxn}^0 estimated in this way are not as reliable as those obtained from ΔH_f^0 values for the substances involved in the reaction.

A special case of Hess's Law involves the use of bond energies to *estimate* heats of reaction. Consider the enthalpy diagrams in Figure 15-5. In general terms, ΔH_{rxn}^0 is related to the bond energies of the reactants and products in *gas phase reactions* by the following version of Hess's Law.

$$\Delta H_{rxn}^0 = \Sigma \text{ B.E.}_{reactants} - \Sigma \text{ B.E.}_{products} \qquad \text{in gas phase reactions only}$$

Note that this equation involves bond energies of *reactants* minus bond energies of *products*.

The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules *minus* the amount of energy required to break all the bonds in product molecules. Stated in another way, the amount of energy released when a bond is formed is equal to the amount absorbed when the same bond is broken. The heat of reaction for a gas phase reaction can be described as the amount of energy released in forming all the bonds in the products minus the amount of energy released in forming all the bonds in the reactants (see Figure 15-5). This heat of reaction can be estimated using the average bond energies in Tables 15-2 and 15-3.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 9.10, Bond Energy and ΔH_{rxn}^0.
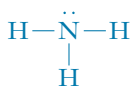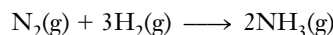
The definition of bond energies is limited to the bond-breaking process *only*, and does not include any provision for changes of state. Thus, it is valid only for substances in the gaseous state. The calculations of this section therefore apply *only* when all substances in the reaction are gases. If liquids or solids were involved, then additional information such as heats of vaporization and fusion would be needed to account for phase changes.

EXAMPLE 15-11　*Bond Energies*

Use the bond energies listed in Table 15-2 to estimate the heat of reaction at 298 K for the following reaction.

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

Plan

Each NH_3 molecule contains three N—H bonds, so two moles of NH_3 contain six moles of N—H bonds. Three moles of H_2 contain a total of three moles of H—H bonds, and one mole of N_2 contains one mole of N≡N bonds. Using the bond energy form of Hess's Law,
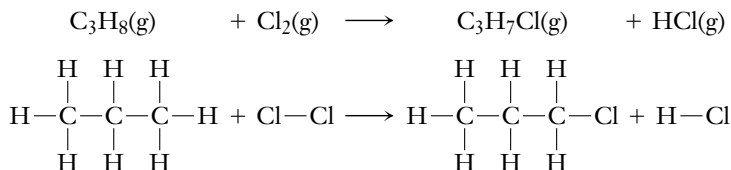
H—N—H
|
H

Solution

For each term in the sum, the units are

$$\frac{mol\ bonds}{mol\ rxn} \times \frac{kJ}{mol\ bonds}$$

$$\Delta H_{rxn}^0 = [\Delta H_{N≡N} + 3\Delta H_{H—H}] - [6\Delta H_{N—H}]$$

$$= 945 + 3(436) - 6(391) = \boxed{-93\ kJ/mol\ rxn}$$

You should now work Exercise 46.

EXAMPLE 15-12　*Bond Energies*

Use the bond energies listed in Table 15-2 to estimate the heat of reaction at 298 K for the following reaction.

$$C_3H_8(g) \quad\quad + Cl_2(g) \longrightarrow \quad C_3H_7Cl(g) \quad\quad + HCl(g)$$

H—C—C—C—H + Cl—Cl ⟶ H—C—C—C—Cl + H—Cl

Plan

We would get the same value for ΔH_{rxn}^0 if we used the full bond energy form of Hess's Law and assumed that *all* bonds in reactants were broken and then *all* bonds in products were formed. In such a calculation the bond energies for the unchanged bonds would cancel. Why? Try it!

Two moles of C—C bonds and seven moles of C—H bonds are the same before and after reaction, so we do not need to include them in the bond energy calculation. The only reactant bonds that are broken are one mole of C—H bonds and one mole of Cl—Cl bonds. On the product side, the only new bonds formed are one mole of C—Cl bonds and one mole of H—Cl bonds. We need to take into account only the bonds that are different on the two sides of the equation. As before, we add and subtract the appropriate bond energies, using values from Table 15-2.

Solution

$$\Delta H_{rxn}^0 = [\Delta H_{C—H} + \Delta H_{Cl—Cl}] - [\Delta H_{C—Cl} + \Delta H_{H—Cl}]$$

$$= [413 + 242] - [339 + 432] = \boxed{-116\ kJ/mol\ rxn}$$

You should now work Exercises 48 and 50.

15-10　CHANGES IN INTERNAL ENERGY, ΔE

Internal energy is a state function, so it is represented by a capital letter.

The **internal energy, E,** of a specific amount of a substance represents all the energy contained within the substance. It includes such forms as kinetic energies of the molecules; energies of attraction and repulsion among subatomic particles, atoms, ions, or molecules; and other forms of energy. The internal energy of a collection of molecules is

a state function. The difference between the internal energy of the products and the internal energy of the reactants of a chemical reaction or physical change, ΔE, is given by the equation

$$\Delta E = E_{final} - E_{initial} = E_{products} - E_{reactants} = q + w$$

The terms q and w represent heat and work, respectively. These are two ways in which energy can flow into or out of a system. **Work** involves a change of energy in which a body is moved through a distance, d, against some force, f; that is, $w = fd$.

$\Delta E =$ (amount of heat absorbed by system) + (amount of work done on system)

The following conventions apply to the signs of q and w.

q is positive:	Heat is *absorbed* by the system from the surroundings.
q is negative:	Heat is *released* by the system to the surroundings.
w is positive:	Work is done *on* the system by the surroundings.
w is negative:	Work is done *by* the system on the surroundings.

Whenever a given amount of energy is added to or removed from a system, either as heat or as work, the energy of the system changes by that same amount. Thus the equation $\Delta E = q + w$ is another way of expressing the First Law of Thermodynamics (see Section 15-1).

The only type of work involved in most chemical and physical changes is pressure–volume work. From dimensional analysis we can see that the product of pressure and volume is work. Pressure is the force exerted per unit area, where area is distance squared, d^2; volume is distance cubed, d^3. Thus, the product of pressure and volume is force times distance, which is work. An example of a physical change (a phase change) in which the system expands and thus does work as it absorbs heat is shown in Figure 15-6. Even if the weight of the book had not been present, the expanding system pushing against the atmosphere would have done work for the expansion.

When energy is released by a reacting system, ΔE is negative; energy can be written as a product in the equation for the reaction. When the system absorbs energy from the surroundings, ΔE is positive; energy can be written as a reactant in the equation.
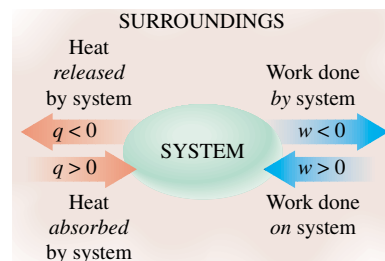
For example, the complete combustion of CH_4 at constant volume at 25°C *releases* energy.


Sign conventions for q and w.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 6.13, The First Law of Thermodynamics.

$$\frac{F}{d^2} \times d^3 = Fd = w$$
$$\quad\quad\quad P \quad V$$

Figure 15-6 A system that absorbs heat and does work. (a) Some powdered dry ice (solid CO_2) is placed into a flexible bag, which is then sealed. (b) As the dry ice absorbs heat from the surroundings, some solid CO_2 sublimes to form gaseous CO_2. The larger volume of the gas causes the bag to expand. The expanding gas does the work of raising a book that has been placed on the bag. Work would be done by the same amount of expansion, even if the book were not present, as the bag pushes against the surrounding atmosphere. The heat absorbed by such a process at constant pressure, q_p, is equal to ΔH for the process.

(a)

(b)

At 25°C the change in internal energy for the combustion of methane is −887 kJ/mol CH_4. The change in heat content is −890 kJ/mol CH_4 (see Section 15-1). The small difference is due to work done on the system as it is compressed by the atmosphere.
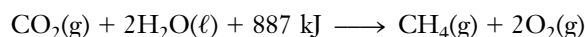
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell) + 887 \text{ kJ}$$

indicates release of energy
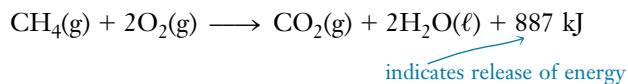
We can write the *change in energy* that accompanies this reaction as

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell) \qquad \Delta E = -887 \text{ kJ/mol rxn}$$
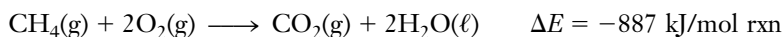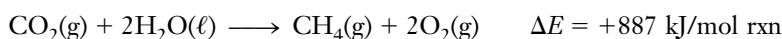
As discussed in Section 15-2, the negative sign indicates a *decrease* in energy of the system, or a *release* of energy by the system.

The reverse of this reaction *absorbs* energy. It can be written as

$$CO_2(g) + 2H_2O(\ell) + 887 \text{ kJ} \longrightarrow CH_4(g) + 2O_2(g)$$

indicates absorption of energy

or

$$CO_2(g) + 2H_2O(\ell) \longrightarrow CH_4(g) + 2O_2(g) \qquad \Delta E = +887 \text{ kJ/mol rxn}$$

If the latter reaction could be forced to occur, the system would have to absorb 887 kJ of energy per mole of reaction from its surroundings.

When a gas is produced against constant external pressure, such as in an open vessel at atmospheric pressure, the gas does work as it expands against the pressure of the atmosphere. If no heat is absorbed during the expansion, the result is a decrease in the internal energy of the system. On the other hand, when a gas is consumed in a process, the atmosphere does work on the reacting system.

Let us illustrate the latter case. Consider the complete reaction of a 2:1 mole ratio of H_2 and O_2 to produce steam at some constant temperature above 100°C and at one atmosphere pressure (Figure 15-7).

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) + \text{heat}$$
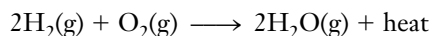
Assume that the constant-temperature bath surrounding the reaction vessel completely absorbs all the evolved heat so that the temperature of the gases does not change. The volume of the system decreases by one third (3 mol gaseous reactants → 2 mol gaseous
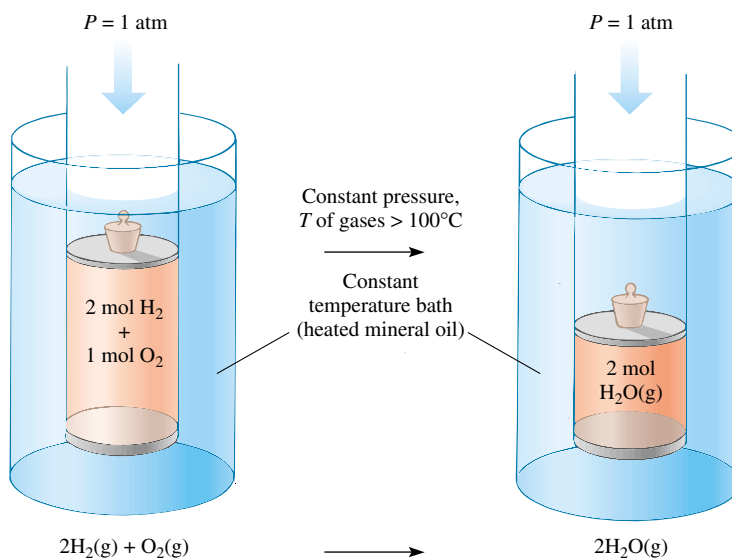

Figure 15-7 An illustration of the one-third decrease in volume that accompanies the reaction of H_2 with O_2 at constant temperature. The temperature is above 100°C.

products). The surroundings exert a constant pressure of one atmosphere and do work on the system by compressing it. The internal energy of the system increases by an amount equal to the amount of work done on it.

The work done on or by a system depends on the *external* pressure and the volume. When the external pressure is constant during a change, the amount of work done is equal to this pressure times the change in volume. The work done *on* a system equals $-P\,\Delta V$ or $-P(V_2 - V_1)$.

V_2 is the final volume, and V_1 is the initial volume.

Compression (volume decreases)	Expansion (volume increases)
Work is done *by* the surroundings *on* the system, so the sign of w is positive	Work is done *by* the system *on* the surroundings, so the sign of w is negative
V_2 is less than V_1, so $\Delta V = (V_2 - V_1)$ is negative	V_2 is greater than V_1, so $\Delta V = (V_2 - V_1)$ is positive
$w = -P\,\Delta V$ is positive $$(-) \times (+) \times (-) = +$$	$w = -P\,\Delta V$ is negative $$(-) \times (+) \times (+) = -$$
Can be due to a *decrease* in number of moles of gas (Δn negative)	Can be due to an *increase* in number of moles of gas (Δn positive)

We substitute $-P\,\Delta V$ for w in the equation $\Delta E = q + w$ to obtain

$$\Delta E = q - P\,\Delta V$$

In constant-volume reactions, no $P\,\Delta V$ work is done. Volume does not change, so nothing "moves through a distance," and $d = 0$ and $fd = 0$. The change in internal energy of the system is just the amount of heat absorbed or released at constant volume, q_v.

Do not make the error of setting work equal to $V\,\Delta P$.

A subscript v indicates a constant-volume process; a subscript p indicates a constant-pressure process.

$$\Delta E = q_v$$

Figure 15-8 shows the same phase change process as in Figure 15-6, but at constant volume condition, so no work is done.

Solids and liquids do not expand or contract significantly when the pressure changes ($\Delta V \approx 0$). In reactions in which equal numbers of moles of gases are produced and consumed at constant temperature and pressure, essentially no work is done. By the ideal gas law, $P\,\Delta V = (\Delta n)RT$ and $\Delta n = 0$, where Δn equals the number of moles of gaseous products minus the number of moles of gaseous reactants. Thus, the work term w has a significant value at constant pressure only when there are different numbers of moles of gaseous products and reactants so that the volume of the system changes.

Figure 15-8 A system that absorbs heat at constant volume. Some dry ice [CO_2(s)] is placed into a rigid flask, which is then sealed. As the dry ice absorbs heat from the surroundings, some CO_2(s) sublimes to form CO_2(g). In contrast to the case in Figure 15-6, this system cannot expand ($\Delta V = 0$), so no work is done, and the pressure in the flask increases. Thus, the heat absorbed at constant volume, q_v, is equal to ΔE for the process.

## EXAMPLE 15-13 *Predicting the Sign of Work*

For each of the following chemical reactions carried out at constant temperature and constant pressure, predict the sign of w and tell whether work is done *on* or *by* the system. Consider the reaction mixture to be the system.

(a) Ammonium nitrate, commonly used as a fertilizer, decomposes explosively.

$$2NH_4NO_3(s) \longrightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$$

This reaction was responsible for an explosion in 1947 that destroyed nearly the entire port of Texas City, Texas, and killed 576 people.

(b) Hydrogen and chlorine combine to form hydrogen chloride gas.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
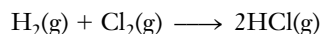
The decomposition of NH_4NO_3 produces large amounts of gas, which expands rapidly as the very fast reaction occurs. This explosive reaction was the main cause of the damage to New York's World Trade Center in 1993 and the destruction of the Federal Building in Oklahoma City (shown here) in 1995.

(c) Sulfur dioxide is oxidized to sulfur trioxide, one step in the production of sulfuric acid.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$
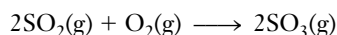
Plan

Δn refers to the balanced equation.

For a process at constant pressure, $w = -P\,\Delta V = -(\Delta n)RT$. For each reaction, we evaluate Δn, the change in the number of moles of *gaseous* substances in the reaction.

$$\Delta n = \text{(no. of moles of gaseous products)} - \text{(no. of moles of gaseous reactants)}$$

Because both R and T (on the Kelvin scale) are positive quantities, the sign of w is opposite from that of Δn; it tells us whether the work is done *on* ($w = +$) or *by* ($w = -$) the system.

Here there are no gaseous reactants.

Solution

(a) $\Delta n = [2 \text{ mol } N_2(g) + 4 \text{ mol } H_2O(g) + 1 \text{ mol } O_2(g)] - 0 \text{ mol}$
$\qquad = 7 \text{ mol} - 0 \text{ mol} = +7 \text{ mol}$

Δn is positive, so w is negative. This tells us that work is done *by* the system. The large amount of gas formed by the reaction pushes against the surroundings (as happened with devastating effect in the Texas City disaster).

(b) $\Delta n = [2 \text{ mol } HCl(g)] - [1 \text{ mol } H_2(g) + 1 \text{ mol } Cl_2(g)]$
$\qquad = 2 \text{ mol} - 2 \text{ mol} = 0 \text{ mol}$

Thus, w = 0, and no work is done as the reaction proceeds. We can see from the balanced equation that for every two moles (total) of gas that react, two moles of gas are formed, so the volume neither expands nor contracts as the reaction occurs.

(c) $\Delta n = [2 \text{ mol } SO_3(g)] - [2 \text{ mol } SO_2(g) + 1 \text{ mol } O_2(g)]$
$\qquad = 2 \text{ mol} - 3 \text{ mol} = -1 \text{ mol}$

Δn is negative, so w is positive. This tells us that work is done *on* the system as the reaction proceeds. The surroundings push against the diminishing volume of gas.

You should now work Exercises 75 and 76.

The "calorie content" of a food can be determined by burning it in excess oxygen inside a bomb calorimeter and determining the heat released. 1 "nutritional Calorie" = 1 kcal = 4.184 kJ.

A bomb calorimeter is a device that measures the amount of heat evolved or absorbed by a reaction occurring at constant volume (Figure 15-9). A strong steel vessel (the bomb) is immersed in a large volume of water. As heat is produced or absorbed by a reaction inside the steel vessel, the heat is transferred to or from the large volume of water. Thus, only rather small temperature changes occur. For all practical purposes, the energy changes associated with the reactions are measured at constant volume and constant temperature.

No work is done when a reaction is carried out in a bomb calorimeter, even if gases are involved, because $\Delta V = 0$. Therefore,

$$\Delta E = q_v \qquad \text{(constant volume)}$$

EXAMPLE 15-14 *Bomb Calorimeter*

A 1.000-gram sample of ethanol, C_2H_5OH, was burned in a bomb calorimeter whose heat capacity had been determined to be 2.71 kJ/°C. The temperature of 3000 grams of water rose from 24.284°C to 26.225°C. Determine ΔE for the reaction in joules per gram of ethanol, and then in kilojoules per mole of ethanol. The specific heat of water is 4.184 J/g·°C. The combustion reaction is

$$C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$$
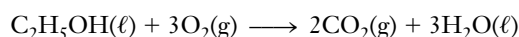
Plan

The amount of heat given off by the system (in the sealed compartment) raises the temperature of the calorimeter and its water. The amount of heat absorbed by the water can be calculated using the specific heat of water; similarly, we use the heat capacity of the calorimeter to find the amount of heat absorbed by the calorimeter. The sum of these two amounts of heat is the total amount of heat released by the combustion of 1.000 gram of ethanol. We must then scale that result to correspond to one mole of ethanol.

Solution

The increase in temperature is

$$\underline{?}\,°C = 26.225°C - 24.284°C = 1.941°C \text{ rise}$$

The amount of heat responsible for this increase in temperature of 3000 grams of water is

$$\text{Heat to warm water} = 1.941°C \times \frac{4.184 \text{ J}}{\text{g}\cdot°C} \times 3000 \text{ g} = 2.436 \times 10^4 \text{ J} = 24.36 \text{ kJ}$$

The amount of heat responsible for the warming of the calorimeter is

$$\text{Heat to warm calorimeter} = 1.941°C \times \frac{2.71 \text{ kJ}}{°C} = 5.26 \text{ kJ}$$

The total amount of heat absorbed by the calorimeter *and* by the water is

$$\text{Total amount of heat} = 24.36 \text{ kJ} + 5.26 \text{ kJ} = 29.62 \text{ kJ}$$

Combustion of one gram of C_2H_5OH liberates 29.62 kJ of energy in the form of heat, that is

$$\Delta E = q_v = \boxed{-29.62 \text{ kJ/g ethanol}}$$

The negative sign indicates that energy is released by the system to the surroundings. Now we may evaluate ΔE in kJ/mol of ethanol by converting grams of C_2H_5OH to moles.

$$\frac{?\text{ kJ}}{\text{mol ethanol}} = \frac{-29.62 \text{ kJ}}{\text{g}} \times \frac{46.07 \text{ g } C_2H_5OH}{1 \text{ mol } C_2H_5OH} = -1365 \text{ kJ/mol ethanol}$$

$$\Delta E = \boxed{-1365 \text{ kJ/mol ethanol}}$$

This calculation shows that for the combustion of ethanol at constant temperature and constant volume, the change in internal energy is -1365 kJ/mol ethanol.

You should now work Exercises 64 and 65.

Benzoic acid, C_6H_5COOH, is often used to determine the heat capacity of a calorimeter. It is a solid that can be compressed into pellets. Its heat of combustion is accurately known: 3227 kJ/mol benzoic acid, or 26.46 kJ/g benzoic acid. Another way to measure the heat capacity of a calorimeter is to add a known amount of heat electrically.
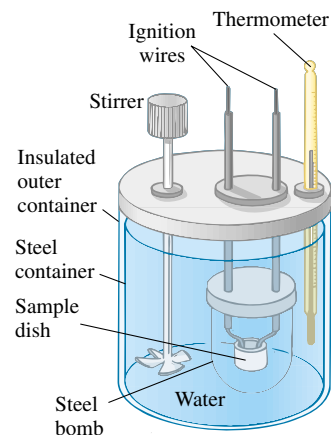

Figure 15-9 A bomb calorimeter measures q_v, the amount of heat given off or absorbed by a reaction occurring at constant *volume*. The amount of energy introduced via the ignition wires is measured and taken into account.

(a)

(a) This small piece of candy is mostly sucrose, $C_{12}H_{22}O_{11}$, a sugar. (b) When the piece of candy is heated together with potassium chlorate, $KClO_3$ (a good oxidizing agent), a highly product-favored reaction occurs.

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(g)$$
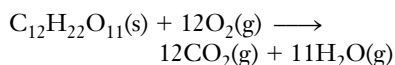
If that amount of sucrose is completely metabolized to carbon dioxide and water vapor in your body, the same amount of energy is released, though more slowly.
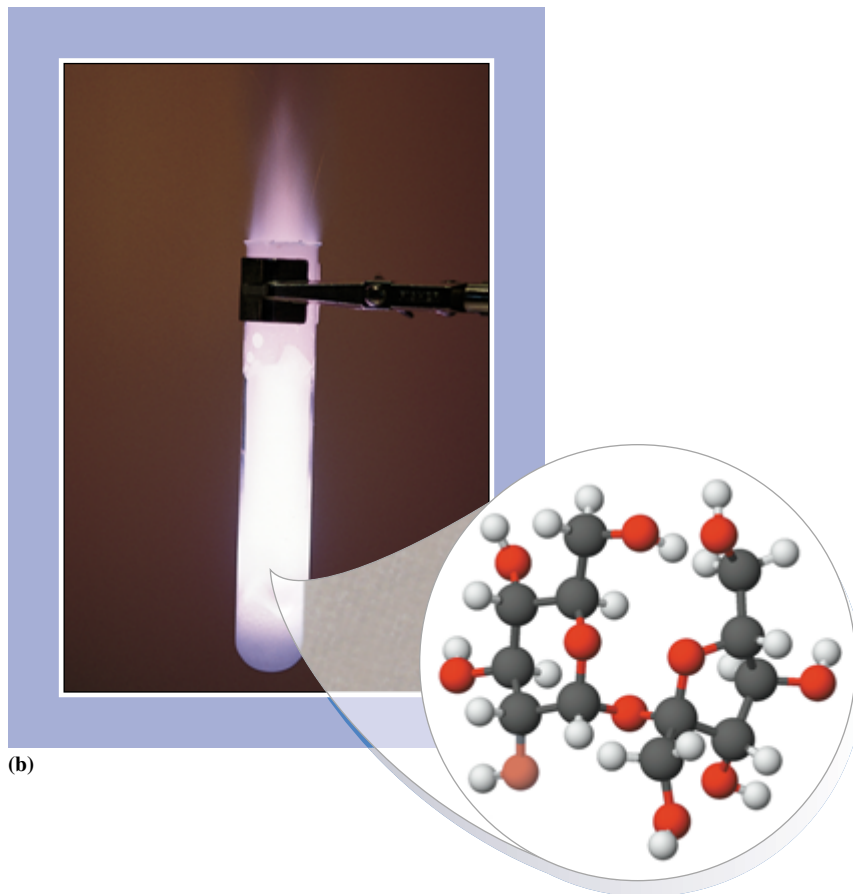
(b)

The balanced chemical equation involves one mole of ethanol, so we can write the unit factor $\dfrac{1 \text{ mol ethanol}}{1 \text{ mol rxn}}$. Then we express the result of Example 15-14 as

$$\Delta E = \frac{-1365 \text{ kJ}}{\text{mol ethanol}} \times \frac{1 \text{ mol ethanol}}{1 \text{ mol rxn}} = -1365 \text{ kJ/mol rxn}$$

15-11 RELATIONSHIP BETWEEN ΔH AND ΔE

The fundamental definition of enthalpy, H, is

$$H = E + PV$$

For a process at constant temperature and pressure,

$$\Delta H = \Delta E + P \, \Delta V \qquad \text{(constant } T \text{ and } P)$$

From Section 15-10, we know that $\Delta E = q + w$, so

$$\Delta H = q + w + P \, \Delta V \qquad \text{(constant } T \text{ and } P)$$

At constant pressure, $w = -P \Delta V$, so

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

$$\Delta H = q_p \qquad \text{(constant } T \text{ and } P)$$

The difference between ΔE and ΔH is the amount of expansion work ($P \Delta V$ work) that the system can do. Unless there is a change in the number of moles of gas present, this difference is extremely small and can usually be neglected. For an ideal gas, $PV = nRT$. At constant temperature and constant pressure, $P \Delta V = (\Delta n)RT$, a work term. Substituting gives

As usual, Δn refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

$$\Delta H = \Delta E + (\Delta n)RT \qquad \text{or} \qquad \Delta E = \Delta H - (\Delta n)RT \qquad \text{(constant } T \text{ and } P)$$

✔ **Problem-Solving Tip:** *Two Equations Relate ΔH and ΔE—Which One Should Be Used?*

The relationship $\Delta H = \Delta E + P \Delta V$ is valid for *any* process that takes place at constant temperature and pressure. It is very useful for physical changes that involve volume changes, such as expansion or compression of a gas. When a chemical reaction occurs and causes a change in the number of moles of gas, it is more convenient to use the relationship in the form $\Delta H = \Delta E + (\Delta n)RT$. You should always remember that Δn refers to the change in number of moles of *gas* in the balanced chemical equation.

In Example 15-14 we found that the change in internal energy, ΔE, for the combustion of ethanol is -1365 kJ/mol ethanol at 298 K. Combustion of one mole of ethanol at 298 K and constant pressure releases 1367 kJ of heat. Therefore (see Section 15-5)

$$\Delta H = -1367 \, \frac{\text{kJ}}{\text{mol ethanol}}$$

The difference between ΔH and ΔE is due to the work term, $-P \Delta V$ or $-(\Delta n)RT$. In this balanced equation there are fewer moles of gaseous products than of gaseous reactants: $\Delta n = 2 - 3 = -1$.

$$C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$$
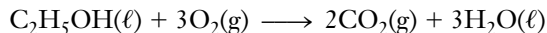
Thus, the atmosphere does work on the system (compresses it). Let us find the work done on the system per mole of reaction.

$$w = -P \Delta V = -(\Delta n)RT$$

$$= -(-1 \text{ mol}) \left(\frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K}) = +2.48 \times 10^3 \text{ J}$$

$$w = +2.48 \text{ kJ} \qquad \text{or} \qquad (\Delta n)RT = -2.48 \text{ kJ}$$

We can now calculate ΔE for the reaction from ΔH and $(\Delta n)RT$ values.

$$\Delta E = \Delta H - (\Delta n)RT = [-1367 - (-2.48)] = -1365 \text{ kJ/mol rxn}$$

The positive sign is consistent with the fact that work is done on the system. The balanced equation involves one mole of ethanol, so this is the amount of work done when one mole of ethanol undergoes combustion.

This value agrees with the result that we obtained in Example 15-14. The size of the work term (+2.48 kJ) is very small compared with ΔH (-1367 kJ/mol rxn). This is true for

many reactions. Of course, if $\Delta n = 0$, then $\Delta H = \Delta E$, and the same amount of heat would be absorbed or given off by the reaction whether it is carried out at constant pressure or at constant volume.

SPONTANEITY OF PHYSICAL AND CHEMICAL CHANGES

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 6.2, Product-Favored Systems, and Screen 20.3, Directionality of Reactions: Matter and Energy Dispersal.

Another major concern of thermodynamics is predicting *whether* a particular process can occur under specified conditions to give predominantly products. We may summarize this concern in the question "Which would be more stable at the given conditions—the reactants or the products?" A change for which the collection of products is thermodynamically *more stable* than the collection of reactants under the given conditions is said to be **product-favored,** or **spontaneous,** under those conditions. A change for which the products are thermodynamically *less stable* than the reactants under the given conditions is described as **reactant-favored,** or **nonspontaneous,** under those conditions. Some changes are spontaneous under all conditions; others are nonspontaneous under all conditions. The great majority of changes, however, are spontaneous under some conditions but not under others. We use thermodynamics to predict conditions for which the latter type of reactions can occur to give predominantly products.

The concept of spontaneity has a very specific interpretation in thermodynamics. A spontaneous chemical reaction or physical change is one that can happen without any continuing outside influence. Any spontaneous change has a natural direction, like the rusting of a piece of iron, the burning of a piece of paper, or the melting of ice at room temperature. We can think of a spontaneous process as one for which products are favored over reactants at the specified conditions. Although a spontaneous reaction *might* occur rapidly, thermodynamic spontaneity is not related to speed. The fact that a process is spontaneous does not mean that it will occur at an observable rate. It may occur rapidly, at a moderate rate, or very slowly. The rate at which a spontaneous reaction occurs is addressed by kinetics (Chapter 16). We now study the factors that influence spontaneity of a physical or chemical change.

15-12 THE TWO ASPECTS OF SPONTANEITY

Many product-favored reactions are exothermic. For instance, the combustion (burning) reactions of hydrocarbons such as methane and octane are all exothermic and highly product-favored (spontaneous). The enthalpy contents of the products are lower than those of the reactants. Not all exothermic changes are spontaneous, however, nor are all spontaneous changes exothermic. As an example, consider the freezing of water, which is an exothermic process (heat is released). This process is spontaneous at temperatures below $0°C$, but it certainly is not spontaneous at temperatures above $0°C$. Likewise, we can find conditions at which the melting of ice, an endothermic process, is spontaneous. Spontaneity is *favored* but not required when heat is released during a chemical reaction or a physical change.

Another factor, related to the disorder of reactants and products, also plays a role in determining spontaneity. The dissolution of ammonium nitrate, NH_4NO_3, in water is spontaneous. Yet a beaker in which this process occurs becomes colder (see Figure 15-2).

The system (consisting of the water, the solid NH_4NO_3, and the resulting hydrated NH_4^+ and NO_3^- ions) absorbs heat from the surroundings as the endothermic process occurs. Nevertheless, the process is spontaneous because the system becomes more disordered as the regularly arranged ions of crystalline ammonium nitrate become more randomly distributed hydrated ions in solution (Figure 15-10). An increase in disorder in the system favors the spontaneity of a reaction. In this particular case, the increase in disorder overrides the effect of endothermicity.

> Two factors affect the spontaneity of any physical or chemical change:
>
> 1. Spontaneity is *favored* when *heat is released* during the change (exothermic).
> 2. Spontaneity is *favored* when the change causes an *increase in disorder*.

The balance of these two effects is considered in Section 15-15.

15-13 THE SECOND LAW OF THERMODYNAMICS

We now know that two factors determine whether a reaction is spontaneous under a given set of conditions. The effect of one factor, the enthalpy change, is that spontaneity is favored (but not required) by exothermicity, and nonspontaneity is favored (but not required) by endothermicity. The effect of the other factor is summarized by the **Second Law of Thermodynamics.**

> In spontaneous changes, the universe tends toward a state of greater disorder.

The Second Law of Thermodynamics is based on our experiences. Some examples illustrate this law in the macroscopic world. When a mirror is dropped, it can shatter. When a drop of food coloring is added to a glass of water, it diffuses until a homogeneously colored solution results. When a truck is driven down the street, it consumes fuel and oxygen, producing carbon dioxide, water vapor, and other emitted substances.

The reverse of any spontaneous change is nonspontaneous, because if it did occur, the universe would tend toward a state of greater order. This is contrary to our experience. We would be very surprised if we dropped some pieces of silvered glass on the floor and a mirror spontaneously assembled. A truck cannot be driven along the street, even in reverse gear, so that it sucks up CO_2, water vapor, and other substances and produces fuel and oxygen.

15-14 ENTROPY, *S*

The thermodynamic state function **entropy, *S*,** is a measure of the disorder of the system. The greater the disorder of a system, the higher is its entropy. For any substance, the particles are more highly ordered in the solid state than in the liquid state. These, in turn,
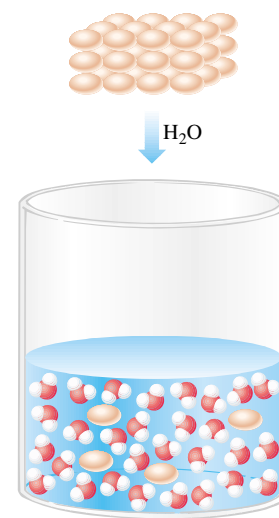

Figure 15-10   As particles leave a crystal to go into solution, they become more disordered. This increase in disorder favors the dissolution of the crystal.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 20.6, The Second Law of Thermodynamics.

Suppose we shake a beaker containing marbles. A disordered arrangement (*left*) is more likely than an ordered arrangement (*right*), in which all marbles of the same color remain together.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 20.4, Entropy: Matter Dispersal or Disorder.

Figure 15-11   As a sample changes from solid to liquid to gas, its particles become increasingly less ordered (more disordered), so its entropy increases.

Solid

Liquid

Gas

Increasing disorder
Increasing entropy, S

(a) Stopcock closed

(b) Stopcock open

Figure 15-12   (a) A sample of gas in which all molecules of one gas are in one bulb and all molecules of the other gas are in the other bulb. (b) A sample of gas that contains the same number of each kind of molecule as in (a), but with the two kinds randomly mixed in the two bulbs. Sample (b) has greater disorder (higher entropy), and is thus more probable.

are more highly ordered than in the gaseous state. Thus, the entropy of any substance increases as the substance goes from solid to liquid to gas (Figure 15-11).

If the entropy of a system increases during a process, the spontaneity of the process is favored but not required. The Second Law of Thermodynamics says that the entropy of the *universe* (not the system) increases during a spontaneous process, that is,

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0 \qquad \text{(spontaneous process)}$$

Of the two ideal gas samples in Figure 15-12, the more ordered arrangement (Figure 15-12a) has lower entropy than the randomly mixed arrangement with the same volume (Figure 15-12b). Because these ideal gas samples mix without absorbing or releasing heat and without a change in total volume, they do not interact with the surroundings, so the entropy of the surroundings does not change. In this case

$$\Delta S_{universe} = \Delta S_{system}$$

If we open the stopcock between the two bulbs in Figure 15-12a, we expect the gases to mix spontaneously, with an increase in the disorder of the system, that is, ΔS_{system} is positive.

$$\text{unmixed gases} \longrightarrow \text{mixed gases} \qquad \Delta S_{universe} = \Delta S_{system} > 0$$

We do not expect the more homogeneous sample in Figure 15-12b to spontaneously "unmix" to give the arrangement in Figure 15-12a (which would correspond to a decrease in ΔS_{system}).

$$\text{mixed gases} \longrightarrow \text{unmixed gases} \qquad \Delta S_{universe} = \Delta S_{system} < 0$$

The ideas of entropy, order, and disorder are related to probability. The more ways an event can happen, the more probable that event is. In Figure 15-12b each individual red molecule is equally likely to be in either container, as is each individual blue molecule. As a result, there are many ways in which the mixed arrangement of Figure 15-12b can occur, so the probability of its occurrence is high, and so its entropy is high. In contrast, there is only one way the unmixed arrangement in Figure 15-12a can occur. The resulting probability is extremely low, and the entropy of this arrangement is low.

The entropy of a system can decrease during a spontaneous process or increase during a nonspontaneous process, depending on the accompanying ΔS_{surr}. If ΔS_{sys} is negative

(decrease in disorder), then ΔS_{univ} may still be positive (overall increase in disorder) *if* ΔS_{surr} is more positive than ΔS_{sys} is negative. A refrigerator provides an illustration. It removes heat from inside the box (the system) and ejects that heat, *plus* the heat generated by the compressor, into the room (the surroundings). The entropy of the system decreases because the air molecules inside the box move more slowly. The increase in the entropy of the surroundings more than makes up for that, however, so the entropy of the universe (refrigerator + room) increases.

Similarly, if ΔS_{sys} is positive but ΔS_{surr} is even more negative, then ΔS_{univ} is still negative. Such a process will be nonspontaneous.

Let's consider the entropy changes that occur when a liquid solidifies at a temperature *below* its freezing (melting) point (Figure 15-13a). ΔS_{sys} is negative because a solid forms from its liquid, yet we know that this is a spontaneous process. A liquid releases heat to its surroundings (atmosphere) as it crystallizes. The released heat increases the motion (disorder) of the molecules of the surroundings, so ΔS_{surr} is positive. As the temperature decreases, the ΔS_{surr} contribution becomes more important. When the temperature is low enough (below the freezing point), the positive ΔS_{surr} outweighs the negative ΔS_{sys}. Then ΔS_{univ} becomes positive, and the freezing process becomes spontaneous.

The situation is reversed when a liquid is boiled or a solid is melted (Figure 15-13b). For example, at temperatures above its melting point, a solid spontaneously melts, and ΔS_{sys} is positive. The heat absorbed when the solid (system) melts comes from its surroundings. This decreases the motion of the molecules of the surroundings. Thus, ΔS_{surr} is negative (the surroundings become less disordered). The positive ΔS_{sys} is greater in magnitude than the negative ΔS_{surr}, however, so ΔS_{univ} is positive and the process is spontaneous.

Above the melting point, ΔS_{univ} is positive for melting. Below the melting point, ΔS_{univ} is positive for freezing. At the melting point, ΔS_{surr} is equal in magnitude and opposite in sign to ΔS_{sys}. Then ΔS_{univ} is zero for both melting and freezing; the system is at *equilibrium*. Table 15-4 lists the entropy effects for these changes of physical state.

We have said that ΔS_{univ} is positive for all spontaneous (product-favored) processes. Unfortunately, it is not possible to make direct measurements of ΔS_{univ}. Consequently, entropy changes accompanying physical and chemical changes are reported in terms of ΔS_{sys}. The subscript "sys" for system is usually omitted. The symbol ΔS refers to the change in enthalpy of the reacting system, just as ΔH refers to the change in enthalpy of the reacting system.

We abbreviate these subscripts as follows: system = sys, surroundings = surr, and universe = univ.

Can you develop a comparable table for boiling (liquid → gas) and condensation (gas → liquid)? (Study Table 15-4 carefully.)
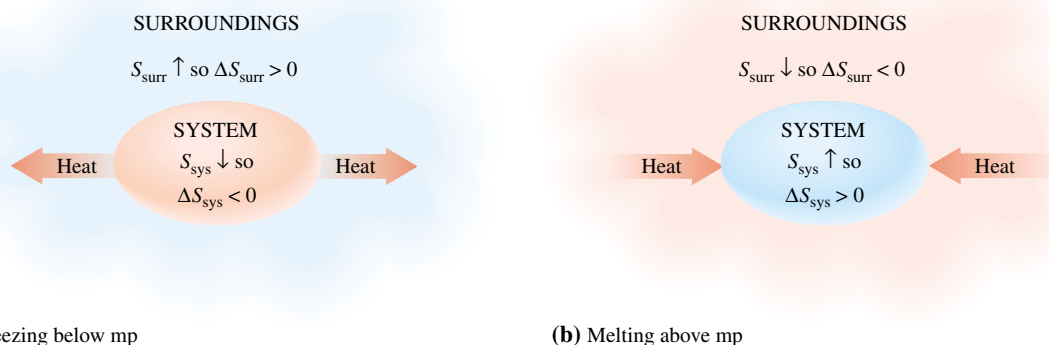
(a) Freezing below mp   **(b)** Melting above mp

Figure 15-13   A schematic representation of heat flow and entropy changes for (a) freezing and (b) melting of a pure substance.

TABLE 15-4	*Entropy Effects Associated with Melting and Freezing*					
		Sign of		(Magnitude of ΔS_{sys}) Compared with (Magnitude of ΔS_{surr})	$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$	
Change	**Temperature**	ΔS_{sys}	ΔS_{surr}			**Spontaneity**
1. Melting (solid → liquid)	(a) > mp	+	−	>	> 0	Spontaneous
	(b) = mp	+	−	=	= 0	Equilibrium
	(c) < mp	+	−	<	< 0	Nonspontaneous
2. Freezing (liquid → solid)	(a) > mp	−	+	>	< 0	Nonspontaneous
	(b) = mp	−	+	=	= 0	Equilibrium
	(c) < mp	−	+	<	> 0	Spontaneous

The **Third Law of Thermodynamics** establishes the zero of the entropy scale.

> The entropy of a pure, perfect crystalline substance (perfectly ordered) is zero at absolute zero (0 K).

As the temperature of a substance increases, the particles vibrate more vigorously, so the entropy increases (Figure 15-14). Further heat input causes either increased temperature (still higher entropy) or phase transitions (melting, sublimation, or boiling) that also result in higher entropy. The entropy of a substance at any condition is its **absolute entropy,** also called standard molar entropy. Consider the absolute entropies at 298 K listed in Table 15-5. At 298 K, *any* substance is more disordered than if it were in a perfect crystalline state at absolute zero, so tabulated S_{298}^{0} values for compounds and elements are *always positive*. Notice especially that S_{298}^{0} of an element, unlike its ΔH_{f}^{0}, is *not* equal to zero. The reference state for absolute entropy is specified by the Third Law of Ther-

Enthalpies are measured only as differences with respect to an arbitrary standard state. Entropies, in contrast, are defined relative to an absolute zero level. In either case, the per mole designation means per mole of substance in the specified state.

(a)　　　　　　　　　(b)

Figure 15-14 (a) A simplified representation of a side view of a "perfect" crystal of a polar substance of 0 K. Note the perfect alignment of the dipoles in all molecules in a perfect crystal. This causes its entropy to be zero at 0 K. There are no perfect crystals, however, because even the purest substances that scientists have prepared are contaminated by traces of impurities that occupy a few of the positions in the crystal structure. Additionally, there are some vacancies in the crystal structures of even very highly purified substances such as those used in semiconductors (see Section 13-17). (b) A simplified representation of the same "perfect" crystal at a temperature above 0 K. Vibrations of the individual molecules within the crystal cause some dipoles to be oriented in directions other than those in a perfect arrangement. The entropy of such a crystalline solid is greater than zero, because there is disorder in the crystal.

TABLE 15-5	*Absolute Entropies at 298 K for a Few Common Substances*
Substance	S^{0} **(J/mol·K)**
C(diamond)	2.38
C(g)	158.0
$H_2O(\ell)$	69.91
$H_2O(g)$	188.7
$I_2(s)$	116.1
$I_2(g)$	260.6

modynamics. It is different from the reference state for ΔH_f^0 (see Section 15-7). The absolute entropies, S_{298}^0, of various substances under standard conditions are tabulated in Appendix K.

The **standard entropy change, ΔS^0,** of a reaction can be determined from the absolute entropies of reactants and products. The relationship is analogous to Hess's Law.

$$\Delta S_{rxn}^0 = \Sigma\, n\, S_{products}^0 - \Sigma\, n\, S_{reactants}^0$$

The $\Sigma\, n$ means that each S^0 value must be multiplied by the appropriate coefficient, n, from the balanced equation. These values are then added.

S^0 values are tabulated in units of *J/mol·K* rather than the larger units involving kilojoules that are used for enthalpy changes. The "mol" term in the units for a *substance* refers to a mole of the substance, whereas for a *reaction* it refers to a mole of reaction. Each term in the sums on the right-hand side of the equation has the units

$$\frac{\text{mol substance}}{\text{mol rxn}} \times \frac{\text{J}}{(\text{mol substance}) \cdot \text{K}} = \frac{\text{J}}{(\text{mol rxn}) \cdot \text{K}}$$

S ee the *Saunders Interactive General Chemistry CD-ROM,* Screen 20.5, Calculating ΔS for a Chemical Reaction.

The result is usually abbreviated as J/mol·K, or sometimes even as J/K. As before, we will usually omit units in intermediate steps and then apply appropriate units to the result.

EXAMPLE 15-15   *Calculation of ΔS_{rxn}^0*

Use the values of standard molar entropies in Appendix K to calculate the entropy change at 25°C and one atmosphere pressure for the reaction of hydrazine with hydrogen peroxide. This explosive reaction has been used for rocket propulsion. Do you think the reaction is spontaneous? The balanced equation for the reaction is

$$\text{N}_2\text{H}_4(\ell) + 2\text{H}_2\text{O}_2(\ell) \longrightarrow \text{N}_2(g) + 4\text{H}_2\text{O}(g) \qquad \Delta H_{rxn}^0 = -642.2 \text{ kJ/mol reaction}$$
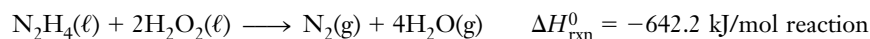
Plan

We use the equation for standard entropy change to calculate ΔS_{rxn}^0 from the tabulated values of standard molar entropies, S_{298}^0, for the substances in the reaction.

Solution

We can list the S_{298}^0 values that we obtain from Appendix K for each substance:

	$\text{N}_2\text{H}_4(\ell)$	$\text{H}_2\text{O}_2(\ell)$	$\text{N}_2(g)$	$\text{H}_2\text{O}(g)$
S^0, J/mol·K:	121.2	109.6	191.5	188.7

$$\Delta S_{rxn}^0 = \Sigma\, n\, S_{products}^0 - \Sigma\, n\, S_{reactants}^0$$
$$= [S_{\text{N}_2(g)}^0 + 4S_{\text{H}_2\text{O}(g)}^0] - [S_{\text{N}_2\text{H}_4(\ell)}^0 + 2S_{\text{H}_2\text{O}_2(\ell)}^0]$$
$$= [1\,(191.5) + 4\,(188.7)] - [1\,(121.2) + 2\,(109.6)]$$

$$\Delta S_{rxn}^0 = +605.9 \text{ J/mol·K}$$

Small booster rockets adjust the course of a satellite in orbit. Some of these small rockets are powered by the N_2H_4–H_2O_2 reaction.

The "mol" designation for ΔS_{rxn}^0 refers to a mole of reaction, that is, one mole of $\text{N}_2\text{H}_4(\ell)$, two moles of $\text{H}_2\text{O}_2(\ell)$, and so on. Although it may not appear to be, +605.9 J/mol·K is a relatively large value of ΔS_{sys}^0. The positive entropy change favors spontaneity. This reaction is also exothermic (ΔH^0 is negative). As we shall see, this reaction *must* be spontaneous, because both factors are favorable: the reaction is exothermic (ΔH_{rxn}^0 is negative) and the disorder of the system increases (ΔS_{rxn}^0 is positive).

You should now work Exercise 92.

Because changes in the thermodynamic quantity *entropy* may be understood in terms of changes in *molecular disorder*, we can often predict the sign of ΔS_{sys}. The following illustrations emphasize several common types of processes that result in predictable entropy changes for the system.

1. *Phase changes.* When melting occurs, the molecules or ions are taken from their quite ordered crystalline arrangement to a more disordered one in which they are able to move past one another in the liquid. Thus, a melting process is always accompanied by an entropy increase ($\Delta S_{sys} > 0$). Likewise, vaporization and sublimation both take place with large increases in disorder, and hence with increases in entropy. For the reverse processes of freezing, condensation, and deposition, entropy decreases because order increases.

2. *Temperature changes*—for example, warming a gas from 25°C to 50°C. As any sample is warmed, the molecules undergo more (random) motion; hence entropy increases ($\Delta S_{sys} > 0$) as temperature increases. Likewise, as we raise the temperature of a solid, the particles vibrate more vigorously about their positions in the crystal, so that at any instant there is a larger average displacement from their mean positions; this results in an increase in entropy.

3. *Volume changes.* When the volume of a sample of gas increases, the molecules can occupy more positions, and hence are more randomly arranged than when they are closer together in a smaller volume. Hence, an expansion is accompanied by an increase in entropy ($\Delta S_{sys} > 0$). Conversely, as a sample is compressed, the molecules are more restricted in their locations, and a situation of greater order (lower entropy) results.

4. *Mixing of substances*, even without chemical reaction. Situations in which the molecules are more "mixed up" are more disordered, and hence are at higher entropy. We pointed out that the mixed gases of Figure 15-12b were more disordered than the separated gases of Figure 15-12a, and that the former was a situation of higher entropy. We see that mixing of gases by diffusion is a process for which $\Delta S_{sys} > 0$; we know from experience that it is always spontaneous. We have already pointed
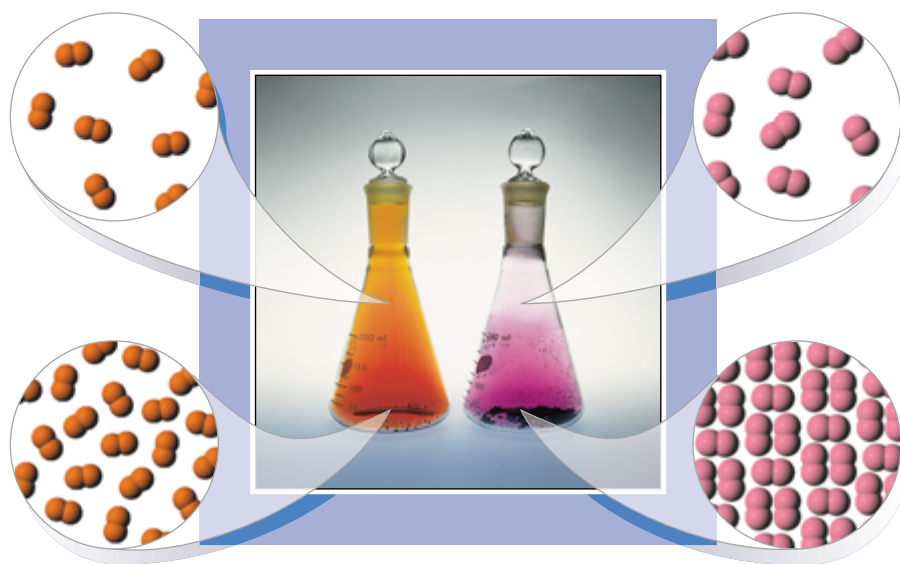
The vaporization of bromine, $Br_2(\ell) \rightarrow Br_2(g)$ (*left*) and the sublimation of iodine, $I_2(s) \rightarrow I_2(g)$ (*right*) both lead to an increase in disorder, so $\Delta S_{sys} > 0$ for each process. Which do you think results in the more positive ΔS? Carry out the calculation using values from Appendix K to check whether your prediction was correct.
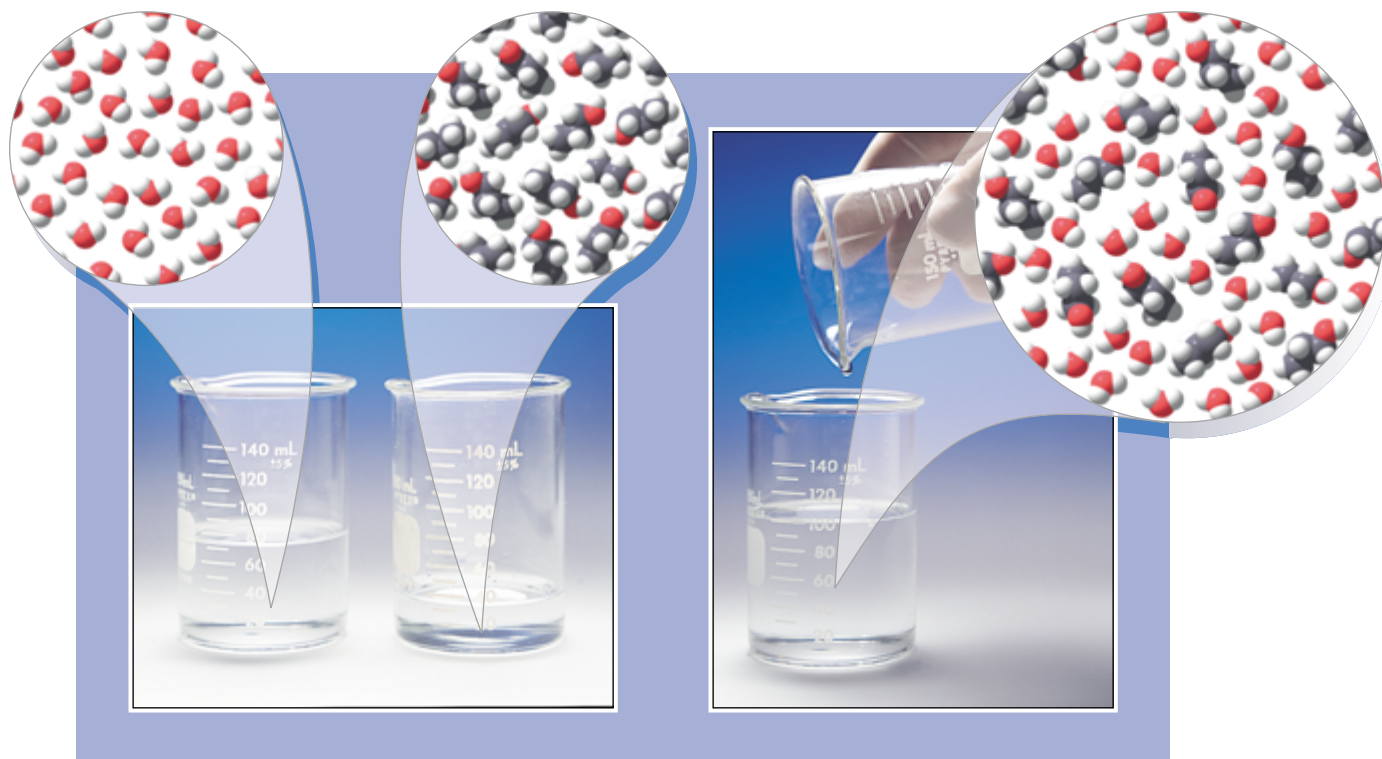
When water, H_2O, and propyl alcohol, $CH_3CH_2CH_2OH$ (*left*) are mixed to form a solution (*right*), disorder increases. $\Delta S > 0$ for the mixing of any two molecular substances.

out (Section 14-2) that the increase in disorder (entropy increase) that accompanies mixing often provides the driving force for solubility of one substance in another. For example, when one mole of solid NaCl dissolves in water, $NaCl(s) \rightarrow NaCl(aq)$, the entropy (Appendix K) increases from 72.4 J/mol·K to 115.5 J/mol·K, or $\Delta S^0 = +43.1$ J/mol·K. The term "mixing" can be interpreted rather liberally. For example, the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ has $\Delta S^0 > 0$; in the reactants, each atom is bonded to an identical atom, a less "mixed-up" situation than in the products, where unlike atoms are bonded together.

5. *Increase in the number of particles*, as in the dissociation of a diatomic gas such as $F_2(g) \rightarrow 2F(g)$. Any process in which the number of particles increases results in an increase in entropy, $\Delta S_{sys} > 0$. Values of ΔS^0 calculated for several reactions of this type are given in Table 15-6. As you can see, the ΔS^0 values for the dissociation process $X_2 \rightarrow 2X$ are all similar for X = H, F, Cl, and N. Why is the value given in Table 15-6 so much larger for X = Br? This process starts with *liquid* Br_2. The total process $Br_2(\ell) \rightarrow 2Br(g)$, for which $\Delta S^0 = 197.5$ J/mol·K, can be treated as the result of *two* processes. The first of these is *vaporization*, $Br_2(\ell) \rightarrow Br_2(g)$, for which $\Delta S^0 = 93.1$ J/mol·K. The second step is the dissociation of gaseous bromine, $Br_2(g) \rightarrow 2Br(g)$, for which $\Delta S^0 = 104.4$ J/mol·K; this entropy increase is about the same as for the other processes that involve *only* dissociation of a gaseous diatomic species. Can you rationalize the even higher value given in the table for the process $I_2(s) \rightarrow 2I(g)$?

TABLE 15-6 *Entropy Changes for Some Processes $X_2 \rightarrow 2X$*

Reaction	ΔS^0 (J/mol·K)
$H_2(g) \longrightarrow 2H(g)$	98.0
$N_2(g) \longrightarrow 2N(g)$	114.9
$O_2(g) \longrightarrow 2O(g)$	117.0
$F_2(g) \longrightarrow 2F(g)$	114.5
$Cl_2(g) \longrightarrow 2Cl(g)$	107.2
$Br_2(\ell) \longrightarrow 2Br(g)$	197.5
$I_2(s) \longrightarrow 2I(g)$	245.3

Do you think that the reaction

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

would have a higher or lower value of ΔS^0 than when the water is in the gas phase? Confirm by calculation.

6. *Changes in the number of moles of gaseous substances.* Processes that result in an increase in the number of moles of gaseous substances have $\Delta S_{sys} > 0$. Example 15-15 illustrates this. There are no gaseous reactants, but the products include five moles of gas. Conversely, we would predict that the process $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ has a negative ΔS^0 value; here, three moles of gas is consumed while only two moles is produced, for a net decrease in the number of moles in the gas phase. You should be able to calculate the value of ΔS^0 for this reaction from the values in Appendix K.

15-15 FREE ENERGY CHANGE, ΔG, AND SPONTANEITY

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 20.7, Gibbs Free Energy.

Energy is the capacity to do work. If heat is released in a chemical reaction (ΔH is negative), *some* of the heat may be converted into useful work. Some of it may be expended to increase the order of the system (if ΔS is negative). If a system becomes more disordered ($\Delta S > 0$), however, more useful energy becomes available than indicated by ΔH alone. J. Willard Gibbs (1839–1903), a prominent nineteenth-century American professor of mathematics and physics, formulated the relationship between enthalpy and entropy in terms of another state function that we now call the **Gibbs free energy, G.** It is defined as

$$G = H - TS$$

The **Gibbs free energy change, ΔG,** at constant temperature and pressure, is

This is often called simply the *Gibbs energy change* or the *free energy change.*

$$\Delta G = \Delta H - T\,\Delta S \qquad \text{(constant } T \text{ and } P\text{)}$$

The amount by which the Gibbs free energy decreases is the *maximum useful energy* obtainable in the form of work from a given process at constant temperature and pressure. It is also the *indicator of spontaneity of a reaction or physical change* at constant T and P. If there is a net decrease of useful energy, ΔG is negative and the process is sponta-

(a) The entropy of an organism decreases (unfavorable) when new cells are formed. The energy to sustain animal life is provided by the metabolism of food. This energy is released when the chemical bonds in the food are broken. Exhalation of gases and excretion of waste materials increase the entropy of the surroundings enough so that the entropy of the universe increases and the overall process can occur. (b) Stored chemical energy can later be transformed by the organism to the mechanical energy for muscle contraction, to the electrical energy for brain function, or to another needed form.

(a)

(b)

neous (product-favored). We see from the equation that ΔG becomes more negative as (1) ΔH becomes more negative (the process gives off more heat) and (2) ΔS becomes more positive (the process results in greater disorder). If there is a net increase in free energy of the system during a process, ΔG is positive and the process is nonspontaneous (reactant-favored). This means that the reverse process is spontaneous under the given conditions. When $\Delta G = 0$, there is no net transfer of free energy; both the forward and reverse processes are equally favorable. Thus, $\Delta G = 0$ describes a system at *equilibrium*.

The relationship between ΔG and spontaneity may be summarized as follows.

ΔG	Spontaneity of Reaction (constant T and P)
ΔG is positive	Reaction is nonspontaneous (reactant-favored)
ΔG is zero	System is at equilibrium
ΔG is negative	Reaction is spontaneous (product-favored)

$-$	0	$+$
$\Delta G < 0$		$\Delta G > 0$
Reaction is spontaneous		Reaction is not spontaneous
Product-favored reaction		Reactant-favored reaction
Forward reaction is favored		Reverse reaction is favored

The free energy content of a system depends on temperature and pressure (and, for mixtures, on concentrations). The value of ΔG for a process depends on the states and the concentrations of the various substances involved. It also depends strongly on temperature, because the equation $\Delta G = \Delta H - T\,\Delta S$ includes temperature. Just as for other thermodynamic variables, we choose some set of conditions as a standard state reference. The standard state for ΔG^0 is the same as for ΔH^0—1 atm and the specified temperature, usually 25°C (298 K). Values of standard molar free energy of formation, ΔG_f^0, for many substances are tabulated in Appendix K. For *elements* in their standard states, $\Delta G_f^0 = 0$. The values of ΔG_f^0 may be used to calculate the standard free energy change of a reaction *at 298 K* by using the following relationship.

$$\Delta G_{rxn}^0 = \Sigma\, n\, \Delta G_{f\ products}^0 - \Sigma\, n\, \Delta G_{f\ reactants}^0 \qquad \text{(1 atm and 298 K \textit{only})}$$

The value of ΔG_{rxn}^0 allows us to predict the spontaneity of a very special hypothetical reaction that we call the *standard reaction*.

In the **standard reaction,** the numbers of moles of reactants shown in the balanced equation, all at standard conditions, are *completely* converted to the numbers of moles of products shown in the balanced equation, all at standard conditions.

In other words, are the reactants or the products more stable at standard conditions?

We must remember that it is ΔG, and not ΔG^0, that is the general criterion for spontaneity. ΔG depends on concentrations of reactants and products in the mixture. For most reactions, there is an *equilibrium mixture* of reactants and products that is more stable than either all reactants or all products. In Chapter 17 we will study the concept of equilibrium and see how to find ΔG for mixtures.

EXAMPLE 15-16   *Spontaneity of Standard Reaction*

Diatomic nitrogen and oxygen molecules make up about 99% of all the molecules in reason-
ably "unpolluted" dry air. Evaluate ΔG^0 for the following reaction at 298 K, using ΔG_f^0 values
from Appendix K. Is the standard reaction spontaneous?

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \text{(nitrogen oxide)}$$

Plan

The reaction conditions are 1 atm and 298 K, so we can use the tabulated values of ΔG_f^0 for
each substance in Appendix K to evaluate ΔG_{rxn}^0 in the preceding equation. The treatment of
units for calculation of ΔG^0 is the same as that for ΔH^0 in Example 15-9.

Solution

We obtain the following values of ΔG_f^0 from Appendix K:

	$N_2(g)$	$O_2(g)$	$NO(g)$
ΔG_f^0, kJ/mol:	0	0	86.57

$$\Delta G_{rxn}^0 = \Sigma\, n\, \Delta G_{f\ products}^0 - \Sigma\, n\, \Delta G_{f\ reactants}^0$$
$$= 2\, \Delta G_{f\ NO(g)}^0 - [\Delta G_{f\ N_2(g)}^0 + \Delta G_{f\ O_2(g)}^0]$$
$$= 2(86.57) - [0 + 0]$$

$$\Delta G_{rxn}^0 = +173.1 \text{ kJ/mol rxn} \qquad \text{for the reaction as written}$$

For the reverse reaction at 298 K, $\Delta G_{rxn}^0 = -173.1$ kJ/mol. It is product-favored but very slow at room temperature. The NO formed in automobile engines is oxidized to even more harmful NO_2 much more rapidly than it decomposes to N_2 and O_2. Thermodynamic spontaneity does not guarantee that a process occurs at an observable rate. The oxides of nitrogen in the atmosphere represent a major environmental problem.

Because ΔG^0 is positive, the reaction is nonspontaneous at 298 K under standard state condi-
tions.

You should now work Exercise 99.

The value of ΔG^0 can also be calculated by the equation

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \qquad \text{(constant } T \text{ and } P\text{)}$$

Strictly, this last equation applies to standard conditions; however, ΔH^0 and ΔS^0 often do
not vary much with temperature, so the equation can often be used to *estimate* free energy
changes at other temperatures.

✓ Problem-Solving Tip: *Some Common Pitfalls in Calculating ΔG_{rxn}^0*

Be careful of these points when you carry out calculations that involve ΔG^0:

1. The calculation of ΔG_{rxn}^0 from tabulated values of ΔG_f^0 is valid *only* if the reaction is
   at 25°C (298 K) and one atmosphere.
2. Calculations with the equation $\Delta G^0 = \Delta H^0 - T\,\Delta S^0$ must be carried out with the
   temperature in kelvins.
3. The energy term in ΔS^0 is usually in joules, whereas that in ΔH^0 is usually in kilo-
   joules; remember to convert one of these so that units are consistent before you
   combine them.

EXAMPLE 15-17 *Spontaneity of Standard Reaction*

Make the same determination as in Example 15-16, using heats of formation and absolute entropies rather than free energies of formation.

Plan

First we calculate ΔH^0_{rxn} and ΔS^0_{rxn}. We use the relationship $\Delta G^0 = \Delta H^0 - T\Delta S^0$ to evaluate the free energy change under standard state conditions at 298 K.

Solution

The values we obtain from Appendix K are:

	$N_2(g)$	$O_2(g)$	$NO(g)$
ΔH^0_f kJ/mol:	0	0	90.25
S^0, J/mol·K:	191.5	205.0	210.7

$$\Delta H^0_{rxn} = \Sigma\, n\, \Delta H^0_{f\,products} - \Sigma\, n\, \Delta H^0_{f\,reactants}$$
$$= 2\, \Delta H^0_{f\,NO(g)} - [\Delta H^0_{f\,N_2(g)} + \Delta H^0_{f\,O_2(g)}]$$
$$= [2(90.25) - (0 + 0)] = 180.5 \text{ kJ/mol}$$

$$\Delta S^0_{rxn} = \Sigma\, nS^0_{products} - \Sigma\, nS^0_{reactants}$$
$$= 2S^0_{NO(g)} - [S^0_{N_2(g)} + S^0_{O_2(g)}]$$
$$= [2\,(210.7) - (191.5 + 205.0)] = 24.9 \text{ J/mol·K} = 0.0249 \text{ kJ/mol·K}$$

Now we use the relationship $\Delta G^0 = \Delta H^0 - T\Delta S^0$, with $T = 298$ K, to evaluate the free energy change under standard state conditions at 298 K.

$$\Delta G^0_{rxn} = \Delta H^0_{rxn} - T\Delta S^0_{rxn}$$
$$= 180.5 \text{ kJ/mol} - (298 \text{ K})(0.0249 \text{ kJ/mol·K})$$
$$= 180.5 \text{ kJ/mol} - 7.42 \text{ kJ/mol}$$

$\Delta G^0_{rxn} = +173.1$ kJ/mol rxn, the same value obtained in Example 15-16.

You should now work Exercise 100.

15-16 THE TEMPERATURE DEPENDENCE OF SPONTANEITY

The methods developed in Section 15-15 can also be used to estimate the temperature at which a process is in equilibrium. When a system is at equilibrium, $\Delta G = 0$. Thus,

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} \qquad \text{or} \qquad 0 = \Delta H_{rxn} - T\Delta S_{rxn}$$

so

$$\Delta H_{rxn} = T\Delta S_{rxn} \qquad \text{or} \qquad T = \frac{\Delta H_{rxn}}{\Delta S_{rxn}} \qquad \text{(at equilibrium)}$$

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 20.8, Free Energy and Temperature.

EXAMPLE 15-18 *Estimation of Boiling Point*

Use the thermodynamic data in Appendix K to estimate the normal boiling point of bromine, Br_2. Assume that ΔH and ΔS do not change with temperature.

Plan

The process we must consider is

$$Br_2(\ell) \longrightarrow Br_2(g)$$
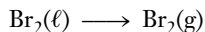
Actually, both ΔH^0_{rxn} and ΔS^0_{rxn} vary with temperature, but usually not enough to introduce significant errors for modest temperature changes. The value of ΔG^0_{rxn}, on the other hand, is strongly dependent on the temperature.

By definition, the normal boiling point of a liquid is the temperature at which pure liquid and pure gas coexist in equilibrium at 1 atm. Therefore, $\Delta G = 0$. We assume that $\Delta H_{rxn} = \Delta H^0_{rxn}$ and $\Delta S_{rxn} = \Delta S^0_{rxn}$. We can evaluate these two quantities, substitute them in the relationship $\Delta G = \Delta H - T \Delta S$, and then solve for T.

Solution

The required values (Appendix K) are as follows:

	$Br_2(\ell)$	$Br_2(g)$
ΔH^0_f, kJ/mol:	0	30.91
S^0, J/mol·K:	152.2	245.4

$$\Delta H_{rxn} = \Delta H^0_{f\,Br_2(g)} - \Delta H^0_{f\,Br_2(\ell)}$$

$$= 30.91 \quad - 0 = 30.91 \text{ kJ/mol}$$

$$\Delta S_{rxn} = S^0_{Br_2(g)} \quad - S^0_{Br_2(\ell)}$$

$$= (245.4 \quad - 152.2) = 93.2 \text{ J/mol·K} = 0.0932 \text{ kJ/mol·K}$$

We can now solve for the temperature at which the system is in equilibrium, that is, the boiling point of Br_2.

$$\Delta G_{rxn} = \Delta H_{rxn} - T \Delta S_{rxn} = 0 \quad \text{so} \quad \Delta H_{rxn} = T \Delta S_{rxn}$$

$$T = \frac{\Delta H_{rxn}}{\Delta S_{rxn}} = \frac{30.91 \text{ kJ/mol}}{0.0932 \text{ kJ/mol·K}} = \boxed{332 \text{ K (59°C)}}$$

This is the temperature at which the system is in equilibrium, that is, the boiling point of Br_2. The value listed in a handbook of chemistry and physics is 58.78°C.

You should now work Exercise 110.

The free energy change and spontaneity of a reaction depend on both enthalpy and entropy changes. Both ΔH and ΔS may be either positive or negative, so we can group reactions in four classes with respect to spontaneity (Figure 15-15).

$\Delta G = \Delta H - T \Delta S$		(constant temperature and pressure)
1. $\Delta H = -$ (favorable)	$\Delta S = +$ (favorable)	Reactions are product-favored at all temperatures
2. $\Delta H = -$ (favorable)	$\Delta S = -$ (unfavorable)	Reactions become product-favored below a definite temperature
3. $\Delta H = +$ (unfavorable)	$\Delta S = +$ (favorable)	Reactions become product-favored above a definite temperature
4. $\Delta H = +$ (unfavorable)	$\Delta S = -$ (unfavorable)	Reactions are reactant-favored at all temperatures
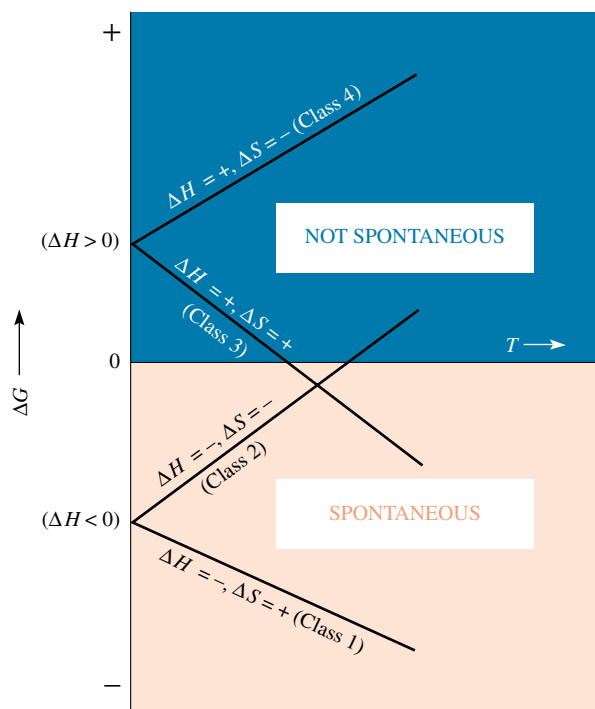
Figure 15-15 A graphical representation of the dependence of ΔG and spontaneity on temperature for each of the four classes of reactions listed in the text and in Table 15-7.

When ΔH and ΔS have opposite signs (classes 1 and 4), they act in the same direction, so the direction of spontaneous change does not depend on temperature. When ΔH and ΔS have the same signs (classes 2 and 3), their effects oppose one another, so changes in temperature can cause one factor or the other to dominate, and spontaneity depends on temperature. For class 2, decreasing the temperature decreases the importance of the *unfavorable* $T\,\Delta S$ term, so the reaction becomes product-favored at lower temperatures. For class 3, increasing the temperature increases the importance of the *favorable* $T\,\Delta S$ term, so the reaction becomes product-favored at higher temperatures.

We can estimate the temperature range over which a chemical reaction in class 2 or 3 is spontaneous by evaluating ΔH^0_{rxn} and ΔS^0_{rxn} from tabulated data. The temperature at which $\Delta G^0_{rxn} = 0$ is the temperature limit of spontaneity. The sign of ΔS^0_{rxn} tells us whether the reaction is spontaneous *below* or *above* this limit (Table 15-7).

TABLE 15-7	***Thermodynamic Classes of Reactions***			
Class	**Examples**	**ΔH (kJ/mol)**	**ΔS (J/mol·K)**	**Temperature Range of Spontaneity**
1	$\begin{cases} 2H_2O_2(\ell) \longrightarrow 2H_2O(\ell) + O_2(g) \\ H_2(g) + Br_2(\ell) \longrightarrow 2HBr(g) \end{cases}$	-196 -72.8	$+126$ $+114$	All temperatures All temperatures
2	$\begin{cases} NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \\ 2H_2S(g) + SO_2(g) \longrightarrow 3S(s) + 2H_2O(\ell) \end{cases}$	-176 -233	-285 -424	Lower temperatures (<619 K) Lower temperatures (<550 K)
3	$\begin{cases} NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g) \\ CCl_4(\ell) \longrightarrow C(graphite) + 2Cl_2(g) \end{cases}$	$+176$ $+135$	$+285$ $+235$	Higher temperatures (>619 K) Higher temperatures (>517 K)
4	$\begin{cases} 2H_2O(\ell) + O_2(g) \longrightarrow 2H_2O_2(\ell) \\ 3O_2(g) \longrightarrow 2O_3(g) \end{cases}$	$+196$ $+285$	-126 -137	Nonspontaneous, all temperatures Nonspontaneous, all temperatures

EXAMPLE 15-19   *Temperature Range of Spontaneity*

Mercury(II) sulfide is a dark red mineral called cinnabar. Metallic mercury is obtained by roasting the sulfide in a limited amount of air. Estimate the temperature range in which the *standard* reaction is product-favored.
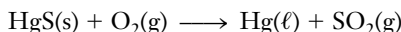
$$HgS(s) + O_2(g) \longrightarrow Hg(\ell) + SO_2(g)$$

Plan

We evaluate ΔH^0_{rxn} and ΔS^0_{rxn} and assume that their values are independent of temperature. We find that both factors are favorable to spontaneity.

Solution

From Appendix K:

	HgS(s)	O_2	Hg(ℓ)	$SO_2(g)$
ΔH^0_f, kJ/mol:	−58.2	0	0	−296.8
S^0, J/mol·K:	82.4	205.0	76.0	248.1

$$\Delta H^0_{rxn} = \Delta H^0_{f\,Hg(\ell)} + \Delta H^0_{f\,SO_2(g)} - [\Delta H^0_{f\,HgS(s)} + \Delta H^0_{f\,O_2(g)}]$$
$$= 0 - 296.8 + 58.2 - 0 = -238.6 \text{ kJ/mol}$$

$$\Delta S^0_{rxn} = S^0_{Hg(\ell)} + S^0_{SO_2(g)} - [S^0_{HgS(s)} + S^0_{O_2(g)}]$$
$$= 76.02 + 248.1 - [82.4 + 205.0] = +36.7 \text{ J/mol·K}$$

ΔH^0_{rxn} is negative and ΔS^0_{rxn} is positive, so the reaction is product-favored at all temperatures. The reverse reaction is, therefore, nonspontaneous at all temperatures.

Heating red HgS in air produces liquid Hg. The gaseous SO_2 escapes. Cinnabar, an important ore of mercury, contains HgS.

The fact that a reaction is product-favored at all temperatures does not mean that the reaction occurs rapidly enough to be useful at all temperatures. As a matter of fact, Hg(ℓ) can be obtained from HgS(s) by this reaction at a reasonable rate only at high temperatures.

EXAMPLE 15-20   *Temperature Range of Spontaneity*

Estimate the temperature range for which the following standard reaction is product-favored.

$$SiO_2(s) + 2C(graphite) + 2Cl_2(g) \longrightarrow SiCl_4(g) + 2CO(g)$$
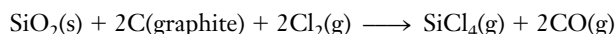
Plan

When we proceed as in Example 15-19, we find that ΔS^0_{rxn} is favorable to spontaneity, whereas ΔH^0_{rxn} is unfavorable. Thus, we know that the reaction becomes product-favored *above* some temperature. We can set ΔG^0 equal to zero in the equation $\Delta G^0 = \Delta H^0 - T\Delta S^0$ and solve for the temperature at which the system is *at equilibrium*. This will represent the temperature above which the reaction would be product-favored.

Solution

From Appendix K:

	$SiO_2(s)$	C(graphite)	$Cl_2(g)$	$SiCl_4(g)$	CO(g)
ΔH^0_f, kJ/mol:	−910.9	0	0	−657.0	−110.5
S^0, J/mol·K:	41.84	5.740	223.0	330.6	197.6

$$\Delta H^0_{rxn} = [\Delta H^0_{f\ SiCl_4(g)} + 2\ \Delta H^0_{f\ CO(g)}] - [\Delta H^0_{f\ SiO_2(s)} + 2\ \Delta H^0_{f\ C(graphite)} + 2\ \Delta H^0_{f\ Cl_2(g)}]$$
$$= [(-657.0) + 2(-110.5)] - [(-910.9) + 2(0) + 2(0)]$$
$$= +32.9\ kJ/mol$$

$$\Delta S^0_{rxn} = S^0_{SiCl_4(g)} + 2S^0_{CO(g)} - [S^0_{SiO_2(s)} + 2S^0_{C(graphite)} + 2S^0_{Cl_2(g)}]$$
$$= [330.6 + 2(197.6)] - [41.84 + 2(5.740) + 2(223.0)]$$
$$= 226.5\ J/mol\cdot K = 0.2265\ kJ/mol\cdot K$$

When $\Delta G^0 = 0$, neither the forward nor the reverse reaction is favored. Let's find the temperature at which $\Delta G^0 = 0$ and the system is at equilibrium.

$$0 = \Delta G^0 = \Delta H^0 - T\,\Delta S^0$$
$$\Delta H^0 = T\,\Delta S^0$$
$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{+32.9\ kJ/mol}{+0.2265\ kJ/mol\cdot K}$$
$$= 145\ K$$

At temperatures above 145 K, the $T\,\Delta S^0$ term would be greater ($-T\,\Delta S^0$ would be more negative) than the ΔH^0 term, which would make ΔG^0 negative; so the reaction would be product-favored above 145 K. At temperatures below 145 K, the $T\,\Delta S^0$ term would be smaller than the ΔH^0 term, which would make ΔG^0 positive; so the reaction would be reactant-favored below 145 K.

However, 145 K ($-128°C$) is a very low temperature. For all practical purposes, the reaction is product-favored at all but very low temperatures. In practice, it is carried out at 800°C to 1000°C because of the greater reaction rate at these higher temperatures. This gives a useful and economical rate of production of $SiCl_4$, an important industrial chemical.

You should now work Exercises 104 and 108.

Key Terms

Absolute entropy (of a substance) The entropy of a substance relative to its entropy in a perfectly ordered crystalline form at 0 K (where its entropy is zero).

Bomb calorimeter A device used to measure the heat transfer between system and surroundings at constant volume.

Bond energy The amount of energy necessary to break one mole of bonds in a gaseous substance, to form gaseous products at the same temperature and pressure.

Calorimeter A device used to measure the heat transfer that accompanies a physical or chemical change.

Endothermic process A process that absorbs heat.

Enthalpy change, ΔH The quantity of heat transferred into or out of a system as it undergoes a chemical or physical change at constant temperature and pressure.

Entropy, S A thermodynamic state property that measures the degree of disorder or randomness of a system.

Equilibrium A state of dynamic balance in which the rates of forward and reverse processes (reactions) are equal; the state of a system when neither the forward nor the reverse process is thermodynamically favored.

Exothermic process A process that gives off (releases) heat.

First Law of Thermodynamics The total amount of energy in the universe is constant (also known as the Law of Conservation of Energy); energy is neither created nor destroyed in ordinary chemical reactions and physical changes.

Gibbs free energy, G The thermodynamic state function of a system that indicates the amount of energy available for the system to do useful work at constant T and P. It is defined as $G = H - TS$.

Gibbs free energy change, ΔG The indicator of spontaneity of a process at constant T and P. $\Delta G = \Delta H - T\,\Delta S$. If ΔG is negative, the process is product-favored (spontaneous).

Hess's Law of heat summation The enthalpy change for a reaction is the same whether it occurs in one step or a series of steps.

Internal energy, E All forms of energy associated with a specific amount of a substance.

Mole of reaction (mol rxn) The amount of reaction that corresponds to the number of moles of each substance shown in the balanced equation.

Nonspontaneous change   See *Reactant-favored change.*

Pressure–volume work   Work done by a gas when it expands against an external pressure or work done on a system as gases are compressed or consumed in the presence of an external pressure.

Product-favored change   A change for which the collection of products is more stable than the collection of reactants under the given conditions; also called *spontaneous change.*

Reactant-favored change   A change for which the collection of reactants is more stable than the collection of products under the given conditions; also called *nonspontaneous change.*

Second Law of Thermodynamics   The universe tends toward a state of greater disorder in spontaneous processes.

Spontaneous change   See *Product-favored change.*

Standard enthalpy change, ΔH^0   The enthalpy change in which the number of moles of reactants specified in the balanced chemical equation, all at standard states, is converted completely to the specified number of moles of products, all at standard states.

Standard entropy, S^0 (of a substance)   The absolute entropy of a substance in its standard state at 298 K.

Standard entropy change, ΔS^0   The entropy change in which the number of moles of reactants specified in the balanced chemical equation, all at standard states, is converted completely to the specified number of moles of products, all at standard states.

Standard molar enthalpy of formation, ΔH_f^0 (of a substance)   The enthalpy change for the formation of one mole of a substance in a specified state from its elements in their standard states.

Standard reaction   A reaction in which the numbers of moles of reactants shown in the balanced equation, all in their standard states, are *completely* converted to the numbers of moles of products shown in the balanced equation, also all at their standard states.

Standard state (of a substance)   See *Thermodynamic standard state of a substance.*

State function   A variable that defines the state of a system; a function that is independent of the pathway by which a process occurs.

Surroundings   Everything in the environment of the system.

System   The substances of interest in a process; the part of the universe under investigation.

Thermochemical equation   A balanced chemical equation together with a designation of the corresponding value of ΔH_{rxn}. Sometimes used with changes in other thermodynamic quantities.

Thermodynamics   The study of the energy transfers accompanying physical and chemical processes.

Thermodynamic state of a system   A set of conditions that completely specifies all of the properties of the system.

Thermodynamic standard state of a substance   The most stable state of the substance at one atmosphere pressure and at some specific temperature (25°C unless otherwise specified).

Third Law of Thermodynamics   The entropy of a hypothetical pure, perfect, crystalline substance at absolute zero temperature is zero.

Universe   The system plus the surroundings.

Work   The application of a force through a distance; for physical changes or chemical reactions at constant external pressure, the work done on the system is $-P\,\Delta V$.

Exercises

General Concepts

1. State precisely the meaning of each of the following terms. You may need to review Chapter 1 to refresh your memory concerning terms introduced there. (a) energy; (b) kinetic energy; (c) potential energy; (d) joule.

2. State precisely the meaning of each of the following terms. You may need to review Chapter 1 to refresh your memory about terms introduced there. (a) heat; (b) temperature; (c) system; (d) surroundings; (e) thermodynamic state of system; (f) work.

3. (a) Give an example of the conversion of heat into work. (b) Give an example of the conversion of work into heat.

4. Distinguish between endothermic and exothermic processes. If we know that a reaction is endothermic in one direction, what can be said about the reaction in the reverse direction?

5. According to the First Law of Thermodynamics, the total amount of energy in the universe is constant. Why, then, do we say that we are experiencing a declining supply of energy?

6. Use the First Law of Thermodynamics to describe what occurs when an incandescent light is turned on.

7. Use the First Law of Thermodynamics to describe what occurs when sunlight strikes a black surface.

8. Which of the following are examples of state functions? (a) your bank balance; (b) your mass; (c) your weight; (d) the heat lost by perspiration during a climb up a mountain along a fixed path.

9. What is a state function? Would Hess's Law be a law if enthalpy were not a state function?

Enthalpy and Changes in Enthalpy

10. (a) Distinguish between ΔH and ΔH^0 for a reaction. (b) Distinguish between ΔH_{rxn}^0 and ΔH_f^0.

11. A reaction is characterized by $\Delta H_{rxn} = -500$ kJ/mol.

Does the reaction mixture absorb heat from the surroundings or release heat to them?

12. For each of the following reactions, (a) does the enthalpy increase or decrease; (b) is $H_{reactant} > H_{product}$ or is $H_{product} > H_{reactant}$; (c) is ΔH positive or negative?
(i) $Al_2O_3(s) \longrightarrow 2Al(s) + \frac{3}{2}O_2(g)$ (endothermic)
(ii) $Sn(s) + Cl_2(g) \longrightarrow SnCl_2(s)$ (exothermic)

13. (a) The combustion of 0.0222 g of isooctane vapor, $C_8H_{18}(g)$, at constant pressure raises the temperature of a calorimeter 0.400°C. The heat capacity of the calorimeter and water combined is 2.48 kJ/°C. Find the molar heat of combustion of gaseous isooctane.

$$C_8H_{18}(g) + 12\frac{1}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(\ell)$$
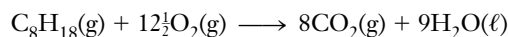
(b) How many grams of $C_8H_{18}(g)$ must be burned to obtain 362 kJ of heat energy?

14. Methanol, CH_3OH, is an efficient fuel with a high octane rating that can be produced from coal and hydrogen.
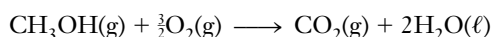
$$CH_3OH(g) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$$
$$\Delta H = -764 \text{ kJ/mol rxn}$$

(a) Find the heat evolved when 90.0 g $CH_3OH(g)$ burns in excess oxygen. (b) What mass of O_2 is consumed when 945 kJ of heat is given out?

15. How much heat is liberated when 0.0662 mole of sodium reacts with excess water according to the following equation?
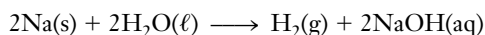
$$2Na(s) + 2H_2O(\ell) \longrightarrow H_2(g) + 2NaOH(aq)$$
$$\Delta H = -368 \text{ kJ/mol rxn}$$

16. What is ΔH for the reaction

$$PbO(s) + C(s) \longrightarrow Pb(s) + CO(g)$$
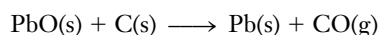
if 35.7 kJ must be supplied to convert 74.6 g lead(II) oxide to lead?

17. The standard molar enthalpy of formation, ΔH_f^0, listed in Appendix K is zero for almost all elements. A few entries are not zero; explain why, and give two examples.

18. Why is the standard molar enthalpy of formation, ΔH_f^0, for liquid water different than is ΔH_f^0 for water vapor, both at 25°C. Which formation reaction is more exothermic? Does your answer indicate that $H_2O(\ell)$ is at a higher or lower enthalpy than $H_2O(g)$?

19. Methylhydrazine is burned with dinitrogen tetroxide in the attitude-control engines of the space shuttles.

$$CH_6N_2(\ell) + \frac{5}{4}N_2O_4(\ell) \longrightarrow$$
$$CO_2(g) + 3H_2O(\ell) + \frac{9}{4}N_2(g)$$
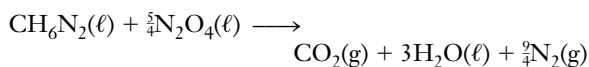
The two substances ignite instantly on contact, producing a flame temperature of 3000 K. The energy liberated per 0.100 g of CH_6N_2 at constant atmospheric pressure

after the products are cooled back to 25°C is 750 J. (a) Find ΔH for the reaction as written. (b) How many kilojoules are liberated when 44.0 g of N_2 is produced?
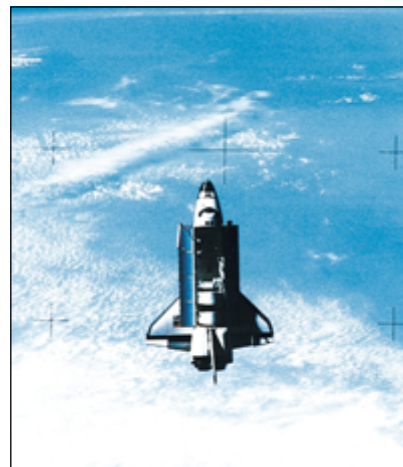
A space shuttle.

20. Which is more exothermic, the combustion of one mole of methane to form $CO_2(g)$ and liquid water or the combustion of one mole of methane to form $CO_2(g)$ and steam? Why? (No calculations are necessary.)

21. Which is more exothermic, the combustion of one mole of gaseous benzene, C_6H_6, or the combustion of one mole of liquid benzene? Why? (No calculations are necessary.)

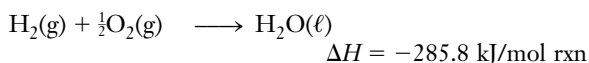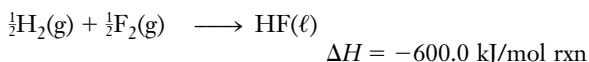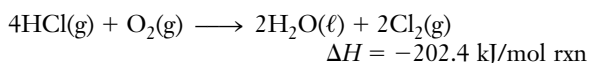## Thermochemical Equations, ΔH_f^0, and Hess's Law

22. Explain the meaning of each word in the term "thermodynamic standard state of a substance."

23. Explain the meaning of each word in the term "standard molar enthalpy of formation."

24. From the data in Appendix K, determine the form that represents the standard state for each of the following elements: (a) chlorine; (b) chromium; (c) nitrogen; (d) iodine; (e) sulfur.

25. From the data in Appendix K, determine the form that represents the standard state for each of the following elements: (a) oxygen; (b) carbon; (c) phosphorus; (d) rubidium; (e) calcium.

26. Write the balanced chemical equation whose ΔH_{rxn}^0 value is equal to ΔH_f^0 for each of the following substances: (a) calcium hydroxide, $Ca(OH)_2(s)$; (b) benzene, $C_6H_6(\ell)$; (c) sodium carbonate, $Na_2CO_3(s)$; (d) calcium fluoride, $CaF_2(s)$; (e) phosphine, $PH_3(g)$; (f) propane, $C_3H_8(g)$; (g) atomic sulfur, $S(g)$.

27. Write the balanced chemical equation whose ΔH_{rxn}^0 value is equal to ΔH_f^0 for each of the following substances: (a) hydrogen sulfide, $H_2S(g)$; (b) lead(II) chloride,

PbCl$_2$(s); (c) atomic oxygen, O(g); (d) benzoic acid, C$_6$H$_5$COOH(s); (e) hydrogen peroxide, H$_2$O$_2$(ℓ); (f) dinitrogen tetroxide, N$_2$O$_4$(g).

*28. We burn 14.4 g of lithium in excess oxygen at constant atmospheric pressure to form Li$_2$O. Then we bring the reaction mixture back to 25°C. In this process 605 kJ of heat is given off. What is the standard molar enthalpy of formation of Li$_2$O?
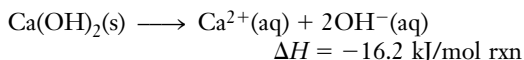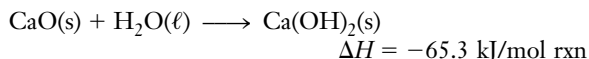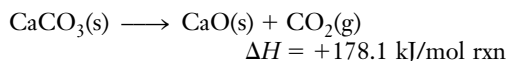
*29. We burn 14.4 g of magnesium in excess nitrogen at constant atmospheric pressure to form Mg$_3$N$_2$. Then we bring the reaction mixture back to 25°C. In this process 136.7 kJ of heat is given off. What is the standard molar enthalpy of formation of Mg$_3$N$_2$?

30. From the following enthalpies of reaction,

$$4HCl(g) + O_2(g) \longrightarrow 2H_2O(\ell) + 2Cl_2(g)$$
$$\Delta H = -202.4 \text{ kJ/mol rxn}$$

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}F_2(g) \longrightarrow HF(\ell)$$
$$\Delta H = -600.0 \text{ kJ/mol rxn}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$$
$$\Delta H = -285.8 \text{ kJ/mol rxn}$$

find ΔH_{rxn} for $2HCl(g) + F_2(g) \longrightarrow 2HF(\ell) + Cl_2(g)$.

31. From the following enthalpies of reaction,

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$
$$\Delta H = +178.1 \text{ kJ/mol rxn}$$

$$CaO(s) + H_2O(\ell) \longrightarrow Ca(OH)_2(s)$$
$$\Delta H = -65.3 \text{ kJ/mol rxn}$$

$$Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$
$$\Delta H = -16.2 \text{ kJ/mol rxn}$$

calculate ΔH_{rxn} for

$$Ca^{2+}(aq) + 2OH^-(aq) + CO_2(g) \longrightarrow$$
$$CaCO_3(s) + H_2O(\ell)$$

32. Given that

$$S(s) + O_2(g) \longrightarrow SO_2(g) \quad \Delta H = -296.8 \text{ kJ/mol}$$
$$S(s) + \tfrac{3}{2}O_2(g) \longrightarrow SO_3(g) \quad \Delta H = -395.6 \text{ kJ/mol}$$
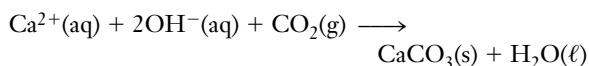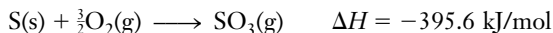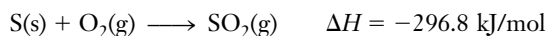
determine the enthalpy change for the decomposition reaction $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$.

33. Aluminum reacts vigorously with many oxidizing agents. For example,

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$
$$\Delta H = -3352 \text{ kJ/mol}$$

$$4Al(s) + 3MnO_2(s) \longrightarrow 3Mn(s) + 2Al_2O_3(s)$$
$$\Delta H = -1792 \text{ kJ/mol}$$
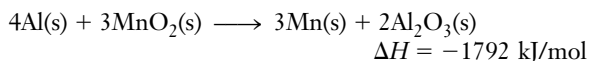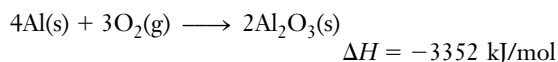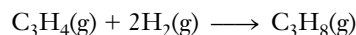
Use this information to determine the enthalpy of formation of MnO$_2$(s).

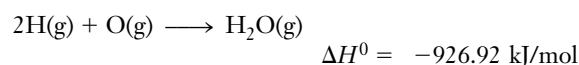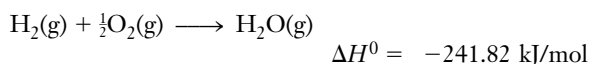34. Given that

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

$$C_3H_4(g) + 4O_2(g) \longrightarrow 3CO_2(g) + 2H_2O(\ell)$$
$$\Delta H = -1937 \text{ kJ/mol}$$

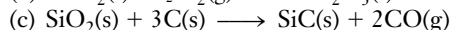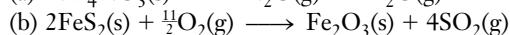$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(\ell)$$
$$\Delta H = -2220 \text{ kJ/mol}$$
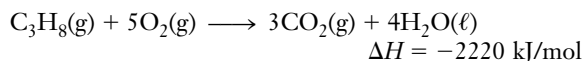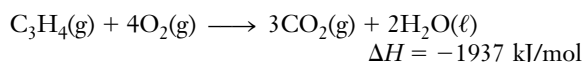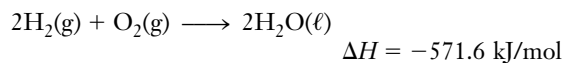
determine the heat of the hydrogenation reaction

$$C_3H_4(g) + 2H_2(g) \longrightarrow C_3H_8(g)$$
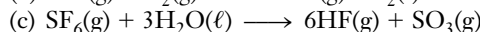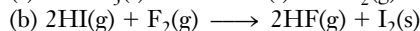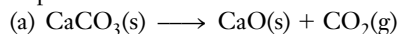
35. Determine the heat of formation of liquid hydrogen peroxide at 25°C from the following thermochemical equations.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$$
$$\Delta H^0 = -241.82 \text{ kJ/mol}$$

$$2H(g) + O(g) \longrightarrow H_2O(g)$$
$$\Delta H^0 = -926.92 \text{ kJ/mol}$$

$$2H(g) + 2O(g) \longrightarrow H_2O_2(g)$$
$$\Delta H^0 = -1070.60 \text{ kJ/mol}$$

$$2O(g) \longrightarrow O_2(g)$$
$$\Delta H^0 = -498.34 \text{ kJ/mol}$$

$$H_2O_2(\ell) \longrightarrow H_2O_2(g)$$
$$\Delta H^0 = 51.46 \text{ kJ/mol}$$
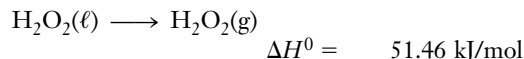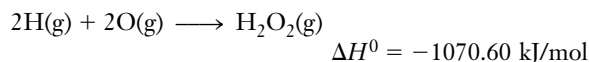
36. Use data in Appendix K to find the enthalpy of reaction for
(a) NH$_4$NO$_3$(s) $\longrightarrow$ N$_2$O(g) + 2H$_2$O(g)
(b) 2FeS$_2$(s) + $\tfrac{11}{2}$O$_2$(g) $\longrightarrow$ Fe$_2$O$_3$(s) + 4SO$_2$(g)
(c) SiO$_2$(s) + 3C(s) $\longrightarrow$ SiC(s) + 2CO(g)
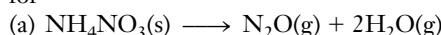
37. Repeat Exercise 36 for
(a) CaCO$_3$(s) $\longrightarrow$ CaO(s) + CO$_2$(g)
(b) 2HI(g) + F$_2$(g) $\longrightarrow$ 2HF(g) + I$_2$(s)
(c) SF$_6$(g) + 3H$_2$O(ℓ) $\longrightarrow$ 6HF(g) + SO$_3$(g)

38. The internal combustion engine uses heat produced during the burning of a fuel. Propane, C$_3$H$_8$(g), is sometimes used as the fuel. Gasoline is the most commonly used fuel. Assume that the gasoline is pure octane, C$_8$H$_{18}$(ℓ) and the fuel and oxygen are completely converted into CO$_2$(g) and H$_2$O(g). For each of these fuels, determine the heat released per gram of fuel burned.

39. Propane, C$_3$H$_8$(g), is used as the fuel for some modern internal combustion engines. Methane, CH$_4$(g), has been proposed by the movie industry as the post-Apocalypse fuel when gasoline and propane are supposedly no longer available. Assume that the fuel and oxygen are completely converted into CO$_2$(g) and H$_2$O(g). For each of these fuels determine the heat released per gram of fuel burned. Compare your answers to the answers for Exercise 38.

40. The thermite reaction, used for welding iron, is the reaction of Fe_3O_4 with Al.

$$8Al(s) + 3Fe_3O_4(s) \longrightarrow 4Al_2O_3(s) + 9Fe(s)$$
$$\Delta H^0 = -3350 \text{ kJ/mol rxn}$$
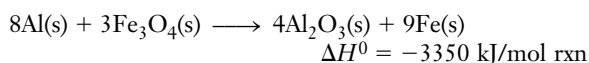
Because this large amount of heat cannot be rapidly dissipated to the surroundings, the reacting mass may reach temperatures near 3000°C. How much heat is released by the reaction of 23.0 g of Al with 57.6 g of Fe_3O_4?


The thermite reaction.

41. When a welder uses an acetylene torch, the combustion of acetylene liberates the intense heat needed for welding metals together. The equation for this combustion reaction is

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$$
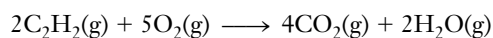
The heat of combustion of acetylene is -1255.5 kJ/mol of C_2H_2. How much heat is liberated when 3.462 kg of C_2H_2 is burned?

42. Silicon carbide, or carborundum, SiC, is one of the hardest substances known and is used as an abrasive. It has the structure of diamond with half of the carbons replaced by silicon. It is prepared industrially by reduction of sand (SiO_2) with carbon in an electric furnace.

$$SiO_2(s) + 3C(graphite) \longrightarrow SiC(s) + 2CO(g)$$
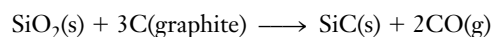
ΔH^0 for this reaction is 624.6 kJ, and the ΔH_f^0 for $SiO_2(s)$ and CO(g) are -910.9 kJ/mol and -110.5 kJ/mol, respectively. Calculate ΔH_f^0 for silicon carbide.

43. Natural gas is mainly methane, $CH_4(g)$. Assume that gasoline is octane, $C_8H_{18}(\ell)$, and that kerosene is $C_{10}H_{22}(\ell)$. (a) Write the balanced equations for the combustion of each of these three hydrocarbons in excess O_2. The products are $CO_2(g)$ and $H_2O(\ell)$. (b) Calculate ΔH_{rxn}^0 at 25°C for each combustion reaction. ΔH_f^0 for $C_{10}H_{22}$ is -300.9 kJ/mol. (c) When burned at standard conditions, which of these three fuels would produce the most heat per mole? (d) When burned at standard conditions, which of the three would produce the most heat per gram?

Bond Energies

44. (a) How is the heat released or absorbed in a *gas phase reaction* related to bond energies of products and reactants? (b) Hess's Law states that
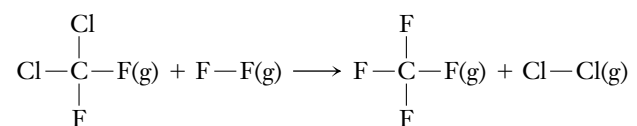
$$\Delta H_{rxn}^0 = \Sigma \, n \, \Delta H_{f \text{ products}}^0 - \Sigma \, n \, \Delta H_{f \text{ reactants}}^0$$

The relationship between ΔH_{rxn}^0 and bond energies for a *gas phase reaction* is

$$\Delta H_{rxn}^0 = $$
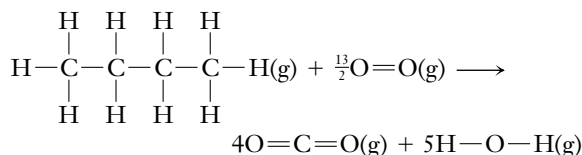$$\Sigma \text{ bond energies}_{reactants} - \Sigma \text{ bond energies}_{products}$$

It is *not* true, in general, that ΔH_f^0 for a substance is equal to the negative of the sum of the bond energies of the substance. Why?

45. (a) Suggest a reason for the fact that different amounts of energy are required for the successive removal of the three hydrogen atoms of an ammonia molecule, even though all N—H bonds in ammonia are equivalent. (b) Suggest why the N—H bonds in different compounds such as ammonia, NH_3; methylamine, CH_3NH_2; and ethylamine, $C_2H_5NH_2$, have slightly different bond energies.

46. Use tabulated bond energies to estimate the enthalpy of reaction for each of the following gas phase reactions.
(a) $H_2C=CH_2 + Br_2 \longrightarrow BrH_2C—CH_2Br$
(b) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

47. Use tabulated bond energies to estimate the enthalpy of reaction for each of the following gas phase reactions.
(a) $N_2 + 3H_2 \longrightarrow 2NH_3$
(b) $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$
(c) $CO + H_2O \longrightarrow CO_2 + H_2$

48. Use the bond energies listed in Table 15-2 to estimate the heat of reaction for

$$\underset{\overset{|}{F}}{\overset{\overset{Cl}{|}}{Cl-C-F}}(g) + F-F(g) \longrightarrow \underset{\overset{|}{F}}{\overset{\overset{F}{|}}{F-C-F}}(g) + Cl-Cl(g)$$

49. Estimate ΔH for the burning of one mole of butane, using the bond energies listed in Tables 15-2 and 15-3.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H(g) + \tfrac{13}{2}O=O(g) \longrightarrow$$
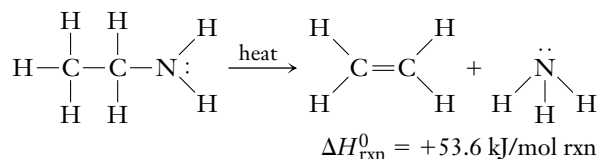
$$4O=C=O(g) + 5H-O-H(g)$$

50. (a) Use the bond energies listed in Table 15-2 to estimate the heats of formation of $HCl(g)$ and $HF(g)$. (b) Compare your answers to the standard heats of formation in Appendix K.

51. (a) Use the bond energies listed in Table 15-2 to estimate the heats of formation of $H_2O(g)$ and $O_3(g)$. (b) Compare your answers to the standard heats of formation in Appendix K.

52. Using data in Appendix K, calculate the average S—F bond energy in $SF_6(g)$.

53. Using data in Appendix K, calculate the average H—S bond energy in $H_2S(g)$.

54. Using data in Appendix K, calculate the average O—F bond energy in $OF_2(g)$.

*55. Methane undergoes several different exothermic reactions with gaseous chlorine. One of these forms chloroform, $CHCl_3(g)$.

$$CH_4(g) + 3Cl_2(g) \longrightarrow CHCl_3(g) + 3HCl(g)$$
$$\Delta H^0_{rxn} = -305.2 \text{ kJ/mol rxn}$$

Average bond energies per mole of bonds are: C—H = 413 kJ; Cl—Cl = 242 kJ; H—Cl = 432 kJ. Use these to calculate the average C—Cl bond energy in chloroform. Compare this with the value in Table 15-2.

*56. Ethylamine undergoes an endothermic gas phase dissociation to produce ethylene (or ethene) and ammonia.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{}}{\overset{\overset{H}{}}{N}}: \xrightarrow{heat} \overset{H}{\underset{H}{}}C=C\overset{H}{\underset{H}{}} + \overset{..}{N}\overset{|}{\underset{H}{\underset{H}{}}}$$

$$\Delta H^0_{rxn} = +53.6 \text{ kJ/mol rxn}$$

The following average bond energies per mole of bonds are given: C—H = 413 kJ; C—C = 346 kJ; C=C = 602 kJ; N—H = 391 kJ. Calculate the C—N bond energy in ethylamine. Compare this with the value in Table 15-2.

Calorimetry

57. What is a coffee-cup calorimeter? How do coffee-cup calorimeters give us useful information?

58. A calorimeter contained 75.0 g of water at 16.95°C. A 93.3-g sample of iron at 65.58°C was placed in it, giving a final temperature of 19.68°C for the system. Calculate the heat capacity of the calorimeter. Specific heats are 4.184 J/g·°C for H_2O and 0.444 J/g·°C for Fe.

59. A student wishes to determine the heat capacity of a coffee-cup calorimeter. After she mixes 100.0 g of water at 58.5°C with 100.0 g of water, already in the calorimeter, at 22.8°C, the final temperature of the water is 39.7°C. (a) Calculate the heat capacity of the calorimeter in J/°C. Use 4.18 J/g·°C as the specific heat of water. (b) Why is it more useful to express the value in J/°C rather than units of J/(g calorimeter·°C)?

60. A coffee-cup calorimeter is used to determine the specific heat of a metallic sample. The calorimeter is filled with 50.0 mL of water at 25.0°C (density = 0.997 g/mL). A 36.5-gram sample of the metallic material is taken from water boiling at 100.0°C and placed in the calorimeter. The equilibrium temperature of the water and sample is 32.5°C. The calorimeter constant is known to be 1.87 J/°C. Calculate the specific heat of the metallic material.

61. A 5.1-gram piece of gold jewelry is removed from water at 100.0°C and placed in a coffee-cup calorimeter containing 16.9 g of water at 22.5°C. The equilibrium temperature of the water and jewelry is 23.2°C. The calorimeter constant is known from calibration experiments to be 1.87 J/°C. What is the specific heat of this piece of jewelry? The specific heat of pure gold is 0.129 J/g · °C. Is the jewelry pure gold?

62. A coffee-cup calorimeter having a heat capacity of 472 J/°C is used to measure the heat evolved when the following aqueous solutions, both initially at 22.6°C, are mixed: 100. g of solution containing 6.62 g of lead(II) nitrate, $Pb(NO_3)_2$, and 100. g of solution containing 6.00 g of sodium iodide, NaI. The final temperature is 24.2°C. Assume that the specific heat of the mixture is the same as that for water, 4.18 J/g·°C. The reaction is

$$Pb(NO_3)_2(aq) + 2NaI(aq) \longrightarrow PbI_2(s) + 2NaNO_3(aq)$$

(a) Calculate the heat evolved in the reaction. (b) Calculate the ΔH for the reaction under the conditions of the experiment.

63. A coffee-cup calorimeter is used to determine the heat of reaction for the acid–base neutralization

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow$$
$$NaCH_3COO(aq) + H_2O(\ell)$$
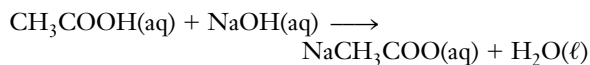
When we add 20.00 mL of 0.625 M NaOH at 21.400°C to 30.00 mL of 0.500 M CH_3COOH already in the calorimeter at the same temperature, the resulting temperature is observed to be 24.347°C. The heat capacity of the calorimeter has previously been determined to be 27.8 J/°C. Assume that the specific heat of the mixture is the same as that of water, 4.18 J/g·°C, and that the density of the mixture is 1.02 g/mL. (a) Calculate the amount of heat given off in the reaction. (b) Determine ΔH for the reaction under the conditions of the experiment.

64. In a bomb calorimeter compartment surrounded by 945 g of water, the combustion of 1.048 g of benzene, $C_6H_6(\ell)$, raised the temperature of the water from 23.640°C to 32.692°C. The heat capacity of the calorimeter is 891 J/°C. (a) Write the balanced equation for the

combustion reaction, assuming that $CO_2(g)$ and $H_2O(\ell)$ are the only products. (b) Use the calorimetric data to calculate ΔE for the combustion of benzene in kJ/g and in kJ/mol.

65. A 2.00-g sample of hydrazine, N_2H_4, is burned in a bomb calorimeter that contains 6.40×10^3 g of H_2O, and the temperature increases from 25.00°C to 26.17°C. The heat capacity of the calorimeter is 3.76 kJ/°C. Calculate ΔE for the combustion of N_2H_4 in kJ/g and in kJ/mol.

*66. A strip of magnesium metal having a mass of 1.22 g dissolves in 100. mL of 6.02 *M* HCl, which has a specific gravity of 1.10. The hydrochloric acid is initially at 23.0°C, and the resulting solution reaches a final temperature of 45.5°C. The heat capacity of the calorimeter in which the reaction occurs is 562 J/°C. Calculate ΔH for the reaction under the conditions of the experiment, assuming the specific heat of the final solution is the same as that for water, 4.18 J/g·°C.

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$
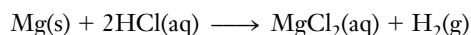
67. When 3.16 g of salicylic acid, $C_7H_6O_3$, is burned in a bomb calorimeter containing 5.00 kg of water originally at 23.00°C, 69.3 kJ of heat is evolved. The calorimeter constant is 3612 J/°C. Calculate the final temperature.

68. A 6.620-gram sample of decane, $C_{10}H_{22}(\ell)$, was burned in a bomb calorimeter whose heat capacity had been determined to be 2.45 kJ/°C. The temperature of 1250.0 grams of water rose from 24.6°C to 26.4°C. Calculate ΔE for the reaction in joules per gram of decane and in kilojoules per mole of decane. The specific heat of water is 4.184 J/g·°C.

69. A nutritionist determines the caloric value of a 10.00-gram sample of beef fat by burning it in a bomb calorimeter. The calorimeter held 2.500 kg of water, the heat capacity of the bomb is 1.360 kJ/°C, and the temperature of the calorimeter increased from 25.0°C to 56.9°C. (a) Calculate the number of joules released per gram of beef fat. (b) One nutritional Calorie is 1 kcal or 4184 joules. What is the dietary, caloric value of beef fat, in nutritional Calories per gram?

Internal Energy and Changes in Internal Energy

70. (a) What are the sign conventions for q, the amount of heat added to or removed from a system? (b) What are the sign conventions for w, the amount of work done on or by a system?

71. What happens to ΔE for a system during a process in which (a) $q < 0$ and $w < 0$, (b) $q = 0$ and $w > 0$, and (c) $q > 0$ and $w < 0$?

72. What happens to ΔE for a system during a process in which (a) $q > 0$ and $w > 0$, (b) $q = w = 0$, and (c) $q < 0$ and $w > 0$?

73. A system performs 720 L·atm of pressure–volume work

(1 L·atm = 101.325 J) on its surroundings and absorbs 5500. J of heat from its surroundings. What is the change in internal energy of the system?

74. A system receives 93 J of electrical work, performs 227 J of pressure–volume work, and releases 155 J of heat. What is the change in internal energy of the system?

75. For each of the following chemical and physical changes carried out at constant pressure, state whether work is done by the system on the surroundings or by the surroundings on the system, or whether the amount of work is negligible.
(a) $C_6H_6(\ell) \longrightarrow C_6H_6(g)$
(b) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$
(c) $SiO_2(s) + 3C(s) \longrightarrow SiC(s) + 2CO(g)$

76. Repeat Exercise 75 for
(a) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
(b) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
(c) $CO_2(g) + H_2O(\ell) + CaCO_3(s) \longrightarrow$
$$Ca^{2+}(aq) + 2HCO_3^-(aq)$$
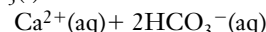
77. Assuming that the gases are ideal, calculate the amount of work done (in joules) in each of the following reactions. In each case, is the work done *on* or *by* the system?
(a) A reaction in the Mond process for purifying nickel that involves formation of the gas nickel(0) tetracarbonyl at 50–100°C. Assume one mole of nickel is used and a constant temperature of 75°C is maintained.

$$Ni(s) + 4CO(g) \longrightarrow Ni(CO)_4(g)$$
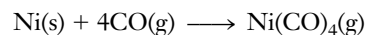
(b) The conversion of one mole of brown nitrogen dioxide into colorless dinitrogen tetroxide at 10.0°C.

$$2NO_2(g) \longrightarrow N_2O_4(g)$$
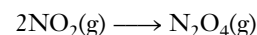
78. Assuming that the gases are ideal, calculate the amount of work done (in joules) in each of the following reactions. In each case, is the work done *on* or *by* the system?
(a) The oxidation of one mole of HCl(g) at 200°C.

$$4HCl(g) + O_2(g) \longrightarrow 2Cl_2(g) + 2H_2O(g)$$
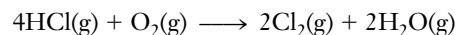
(b) The decomposition of one mole of nitric oxide (an air pollutant) at 300°C.

$$2NO(g) \longrightarrow N_2(g) + O_2(g)$$
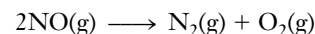
*79. When an ideal gas expands at *constant temperature*, there is no change in molecular kinetic energy (kinetic energy is proportional to temperature), and there is no change in potential energy due to intermolecular attractions (these are zero for an ideal gas). Thus, for the isothermal (constant temperature) expansion of an ideal gas, $\Delta E = 0$. Suppose we allow an ideal gas to expand isothermally from 2.00 L to 5.00 L in two steps: (a) against a constant external pressure of 3.00 atm until equilibrium is reached, then (b) against a constant external pressure of 2.00 atm until equilibrium is reached. Calculate q and w for this two-step expansion.

Entropy and Entropy Changes

80. A car uses gasoline as a fuel. Describe the burning of the fuel in terms of chemical and physical changes. Relate your answer to the Second Law of Thermodynamics.

81. State the Second Law of Thermodynamics. We cannot use ΔS_{univ} directly as a measure of the spontaneity of a reaction. Why?

82. State the Third Law of Thermodynamics. What does it mean?

83. Explain why ΔS may be referred to as a contributor to spontaneity.

84. For each of the following processes, tell whether the entropy of the system increases, decreases, or remains constant:
(a) Melting one mole of ice to water at 0°C
(b) Freezing one mole of water to ice at 0°C
(c) Freezing one mole of water to ice at −10°C
(d) Freezing one mole of water to ice at 0°C and then cooling it to −10°C

85. When solid sodium chloride is cooled from 25°C to 0°C, the entropy change is −4.4 J/mol·K. Is this an increase or decrease in randomness? Explain this entropy change in terms of what happens in the solid at the molecular level.

86. When a one-mole sample of argon gas at 0°C is compressed to one half its original volume, the entropy change is −5.76 J/mol·K. Is this an increase or a decrease in randomness? Explain this entropy change in terms of what happens in the gas at the molecular level.

87. Which of the following processes are accompanied by an increase in entropy of the system? (No calculation is necessary.) (a) A building is constructed from bricks, mortar, lumber, and nails. (b) A building collapses into bricks, mortar, lumber, and nails. (c) Iodine sublimes, $I_2(s) \rightarrow I_2(g)$. (d) White silver sulfate, Ag_2SO_4, precipitates from a solution containing silver ions and sulfate ions. (e) A marching band is gathered into formation. (f) A partition is removed to allow two gases to mix.

88. Which of the following processes are accompanied by an increase in entropy of the system? (No calculation is necessary.) (a) Thirty-five pennies are removed from a bag and placed heads-up on a table. (b) The pennies of part (a) are swept off the table and back into the bag. (c) Water freezes. (d) Carbon tetrachloride, CCl_4, evaporates. (e) The reaction $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ occurs. (f) The reaction $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ occurs.

89. For each of the following processes, tell whether the entropy of the *universe* increases, decreases, or remains constant. (a) melting one mole of ice to water at 0°C; (b) freezing one mole of water to ice at 0°C; (c) freezing one mole of water to ice at −10°C; (d) freezing one mole of water to ice at 0°C and then cooling it to −10°C.

*90. Consider the boiling of a pure liquid at constant pressure. Is each of the following greater than, less than, or equal to zero? (a) ΔS_{sys}; (b) ΔH_{sys}; (c) ΔT_{sys}.

91. Use S^0 data from Appendix K to calculate the value of ΔS^0_{298} for each of the following reactions. Compare the signs and magnitudes for these ΔS^0_{298} values and explain your observations.
(a) $2NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$
(b) $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$
(c) $2NH_4NO_3(s) \longrightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$

92. Use S^0 data from Appendix K to calculate the value of ΔS^0_{298} for each of the following reactions. Compare the signs and magnitudes for these ΔS^0_{298} values and explain your observations.
(a) $4HCl(g) + O_2(g) \longrightarrow 2Cl_2(g) + 2H_2O(g)$
(b) $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$
(c) $2NO(g) \longrightarrow N_2(g) + O_2(g)$

Gibbs Free Energy Changes and Spontaneity

93. (a) What are the two factors that favor spontaneity of a process? (b) What is Gibbs free energy? What is change in Gibbs free energy? (c) Most spontaneous reactions are exothermic, but some are not. Explain. (d) Explain how the signs and magnitudes of ΔH and ΔS are related to the spontaneity of a process and how they affect it.

94. Which of the following conditions would predict a process that is (a) always spontaneous, (b) always non-spontaneous, or (c) spontaneous or nonspontaneous depending on the temperature and magnitudes of ΔH and ΔS? (i) $\Delta H > 0$, $\Delta S > 0$; (ii) $\Delta H > 0$, $\Delta S < 0$; (iii) $\Delta H < 0$, $\Delta S > 0$; (iv) $\Delta H < 0$, $\Delta S < 0$.
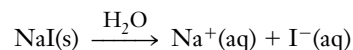
95. For the decomposition of $O_3(g)$ to $O_2(g)$

$$2O_3(g) \longrightarrow 3O_2(g)$$
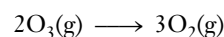
$\Delta H^0 = -285.4$ kJ/mol and $\Delta S^0 = 137.55$ J/mol·K at 25°C. Calculate ΔG^0 for the reaction. Is the reaction spontaneous? Is either or both of the driving forces (ΔH^0 and ΔS^0) for the reaction favorable?

96. Calculate ΔG^0 at 25°C for the reaction

$$2NO_2(g) \longrightarrow N_2O_4(g)$$
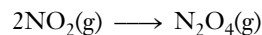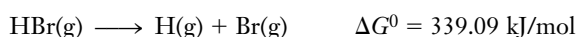
given $\Delta H^0 = -57.20$ kJ/mol and $\Delta S^0 = -175.83$ J/mol·K. Is this reaction spontaneous? What is the driving force for spontaneity?

97. The standard Gibbs free energy of formation is −286.06 kJ/mol for NaI(s), −261.90 kJ/mol for $Na^+(aq)$, and −51.57 kJ/mol for $I^-(aq)$ at 25°C. Calculate ΔG^0 for the reaction

$$NaI(s) \xrightarrow{\ H_2O\ } Na^+(aq) + I^-(aq)$$

*98. Use the following equations to find ΔG^0_f for HBr(g) at 25°C.

$Br_2(\ell) \longrightarrow Br_2(g)$ $\qquad\qquad$ $\Delta G^0 = 3.14$ kJ/mol

$HBr(g) \longrightarrow H(g) + Br(g)$ $\qquad$ $\Delta G^0 = 339.09$ kJ/mol

$Br_2(g) \longrightarrow 2Br(g)$ $\Delta G^0 = 161.7$ kJ/mol

$H_2(g) \longrightarrow 2H(g)$ $\Delta G^0 = 406.494$ kJ/mol
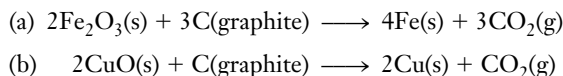
99. Use values of standard free energy of formation, ΔG_f^0, from Appendix K, to calculate the standard free energy change for each of the following reactions at 25°C and 1 atm.
(a) $3NO_2(g) + H_2O(\ell) \longrightarrow 2HNO_3(\ell) + NO(g)$
(b) $SnO_2(s) + 2CO(g) \longrightarrow 2CO_2(g) + Sn(s)$
(c) $2Na(s) + 2H_2O(\ell) \longrightarrow 2NaOH(aq) + H_2(g)$
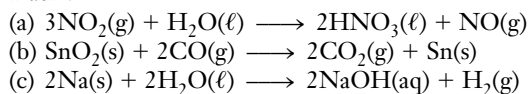
100. Make the same calculations as in Exercise 99, using values of standard enthalpy of formation and absolute entropy instead of values of ΔG_f^0.

101. Calculate ΔG^0 for the reduction of the oxides of iron and copper by carbon at 700 K represented by the equations

(a) $2Fe_2O_3(s) + 3C(\text{graphite}) \longrightarrow 4Fe(s) + 3CO_2(g)$

(b) $2CuO(s) + C(\text{graphite}) \longrightarrow 2Cu(s) + CO_2(g)$

Values of ΔG_f^0 at 700K are -92 kJ/mol for CuO(s), -632 kJ/mol for Fe_2O_3(s), and -395 kJ/mol for CO_2(g).
(c) Which oxide can be reduced using carbon in a wood fire (which has a temperature of about 700 K), assuming standard state conditions?

Temperature Range of Spontaneity

102. Are the following statements true or false? Justify your answers. (a) An exothermic reaction is spontaneous. (b) If ΔH and ΔS are both positive, then ΔG will decrease when the temperature increases. (c) A reaction for which ΔS_{sys} is positive is spontaneous.
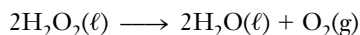
103. For the reaction

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
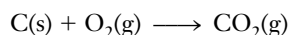
$\Delta H^0 = -393.51$ kJ/mol and $\Delta S^0 = 2.86$ J/mol·K at 25°C. (a) Does this reaction become more or less favorable as the temperature increases? (b) For the reaction

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$$
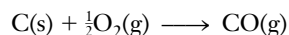
$\Delta H^0 = -110.52$ kJ/mol and $\Delta S^0 = 89.36$ J/mol·K at 25°C. Does this reaction become more or less favorable as the temperature increases? (c) Compare the temperature dependencies of these reactions.

104. (a) Calculate ΔH^0, ΔG^0, and ΔS^0 for the reaction

$$2H_2O_2(\ell) \longrightarrow 2H_2O(\ell) + O_2(g)$$
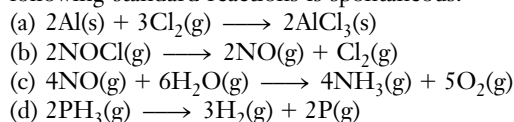
at 25°C. (b) Is there any temperature at which $H_2O_2(\ell)$ is stable at 1 atm?

105. When is it true that $\Delta S = \dfrac{\Delta H}{T}$?

106. Dissociation reactions are those in which molecules break apart. Why do high temperatures favor the spontaneity of most dissociation reactions?

107. Estimate the temperature range over which each of the following standard reactions is spontaneous.
(a) $2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$
(b) $2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$
(c) $4NO(g) + 6H_2O(g) \longrightarrow 4NH_3(g) + 5O_2(g)$
(d) $2PH_3(g) \longrightarrow 3H_2(g) + 2P(g)$

108. Estimate the temperature range over which each of the following standard reactions is spontaneous.
(a) The reaction by which sulfuric acid droplets from polluted air convert water-insoluble limestone or marble (calcium carbonate) to slightly soluble calcium sulfate, which is slowly washed away by rain:

$CaCO_3(s) + H_2SO_4(\ell) \longrightarrow$
$\qquad\qquad CaSO_4(s) + H_2O(\ell) + CO_2(g)$
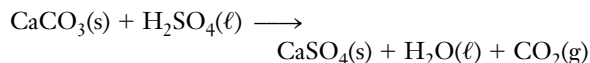
(b) The reaction by which Antoine Lavoisier achieved the first laboratory preparation of oxygen in the late eighteenth century: the thermal decomposition of the red-orange powder, mercury(II) oxide, to oxygen and the silvery liquid metal, mercury:

$$2HgO(s) \longrightarrow 2Hg(\ell) + O_2(g)$$
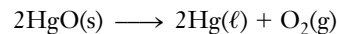
(c) The reaction of coke (carbon) with carbon dioxide to form the reducing agent, carbon monoxide, which is used to reduce some metal ores to metals:

$$CO_2(g) + C(s) \longrightarrow 2CO(g)$$
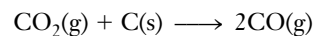
(d) The reverse of the reaction by which iron rusts:

$$2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g)$$
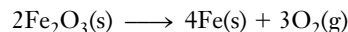
109. Estimate the normal boiling point of tin(IV) chloride, $SnCl_4$, at 1 atm pressure, using Appendix K.

110. (a) Estimate the normal boiling point of water, at 1 atm pressure, using Appendix K. (b) Compare the temperature obtained with the known boiling point of water. Can you explain the discrepancy?

111. Sublimation and subsequent deposition onto a cold surface are a common method of purification of I_2 and other solids that sublime readily. Estimate the sublimation temperature (solid to vapor) of the dark violet solid iodine, I_2, at 1 atm pressure, using the data of Appendix K.


Sublimation and deposition of I_2.

*112. (a) Is the reaction C(diamond) → C(graphite) sponta-neous at 25°C and 1 atm? (b) Now are you worried about your diamonds turning to graphite? Why or why not? (c) Is there a temperature at which diamond and graphite are in equilibrium? If so, what is this temperature? (d) How do you account for the formation of diamonds in nature? (*Hint:* Diamond has a higher density than graphite.)

Mixed Exercises

*113. An ice calorimeter, shown here, can be used to measure the amount of heat released or absorbed by a reaction that is carried out at a constant temperature of 0°C. If heat is transferred from the system to the bath, some of the ice melts. A given mass of liquid water has a smaller volume than the same mass of ice, so the total volume of the ice and water mixture decreases. Measuring the volume decrease using the scale at the left indicates the amount of heat released by the reacting system. As long as some ice remains in the bath, the temperature remains at 0°C. In Example 15-2 we saw that the reaction
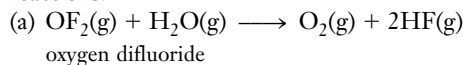
$$CuSO_4(aq) + 2NaOH(aq) \longrightarrow$$
$$Cu(OH)_2(s) + Na_2SO_4(aq)$$
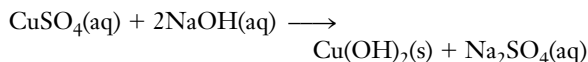
releases 846 J of heat at constant temperature and pressure when 50.0 mL of 0.400 M $CuSO_4$ solution and 50.0 mL of 0.600 M NaOH solution are allowed to react. (Because no gases are involved in the reaction, the volume change of the reaction mixture is negligible.) Calculate the change in volume of the ice and water mixture that would be observed if we carried out the same experiment in an ice calorimeter. The density of $H_2O(\ell)$ at 0°C is 0.99987 g/mL and that of ice is 0.917 g/mL. The heat of fusion of ice at 0°C is 334 J/g.
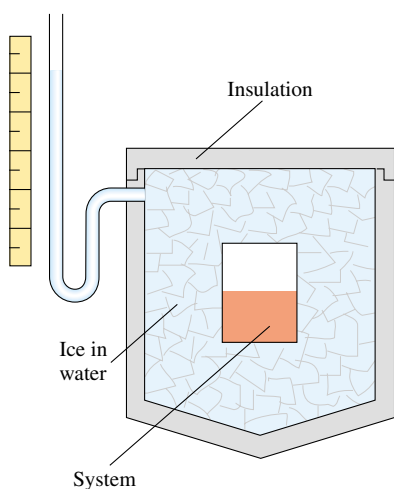
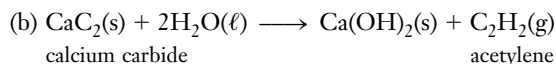**114.** It is difficult to prepare many compounds directly from their elements, so ΔH_f^0 values for these compounds cannot be measured directly. For many organic compounds,

it is easier to measure the standard enthalpy of combustion by reaction of the compound with excess $O_2(g)$ to form $CO_2(g)$ and $H_2O(\ell)$. From the following standard enthalpies of combustion at 25°C, determine ΔH_f^0 for the compound. (a) cyclohexane, $C_6H_{12}(\ell)$, a useful organic solvent: $\Delta H_{combustion}^0 = -3920$ kJ/mol; (b) phenol, $C_6H_5OH(s)$, used as a disinfectant and in the production of thermo-setting plastics: $\Delta H_{combustion}^0 = -3053$ kJ/mol.
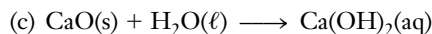
*115. Standard entropy changes cannot be measured directly in the laboratory. They are calculated from experimentally obtained values of ΔG^0 and ΔH^0. From the data given here, calculate ΔS^0 at 298 K for each of the following reactions.

(a) $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$
    oxygen difluoride

   $\Delta H^0 = -323.2$ kJ/mol $\Delta G^0 = -358.4$ kJ/mol

(b) $CaC_2(s) + 2H_2O(\ell) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$
    calcium carbide   acetylene

   $\Delta H^0 = -125.4$ kJ/mol $\Delta G^0 = -145.4$ kJ/mol

(c) $CaO(s) + H_2O(\ell) \longrightarrow Ca(OH)_2(aq)$

   $\Delta H^0 = 81.5$ kJ/mol $\Delta G^0 = -26.20$ kJ/mol

*116. Calculate q, w, and ΔE for the vaporization of 10.0 g of liquid ethanol (C_2H_5OH) at 1.00 atm at 78.0°C, to form gaseous ethanol at 1.00 atm at 78.0°C. Make the following simplifying assumptions: (a) the density of liquid ethanol at 78.0°C is 0.789 g/mL, and (b) gaseous ethanol is adequately described by the ideal gas equation. The heat of vaporization of ethanol is 855 J/g.

117. We add 0.100 g of CaO(s) to 125 g H_2O at 23.6°C in a coffee-cup calorimeter. The following reaction occurs. What will be the final temperature of the solution?

$$CaO(s) + H_2O(\ell) \longrightarrow Ca(OH)_2(aq)$$
$$\Delta H^0 = 81.5 \text{ kJ/mol rxn}$$
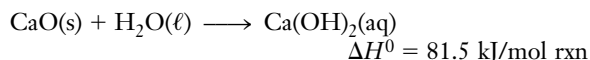
118. (a) The accurately known molar heat of combustion of naphthalene, $C_{10}H_8(s)$, $\Delta H = -5156.8$ kJ/mol $C_{10}H_8$, is used to calibrate calorimeters. The complete combustion of 0.01520 g of $C_{10}H_8$ at constant pressure raises the temperature of a calorimeter by 0.212°C. Find the heat capacity of the calorimeter. (b) The initial temperature of the calorimeter (part a) is 22.102°C; 0.1040 g of $C_8H_{18}(\ell)$, octane (molar heat of combustion $\Delta H = -5451.4$ kJ/mol C_8H_{18}), is completely burned in the calorimeter. Find the final temperature of the calorimeter.

CONCEPTUAL EXERCISES

119. When a gas expands suddenly, it may not have time to absorb a significant amount of heat: $q = 0$. Assume that 1.00 mol N_2 expands suddenly, doing 3000 J of work.

(a) What is ΔE for the process? (b) The heat capacity of N_2 is 20.9 J/mol·°C. How much does its temperature fall during this expansion? (This is the principle of most snow-making machines, which use compressed air mixed with water vapor.)

120. As a rubber band is stretched, it gets warmer; when released, it gets cooler. To obtain the more nearly linear arrangement of the rubber band's polymeric material from the more random relaxed rubber band requires that there be rotation about carbon–carbon single bonds. Based on these data, give the sign of ΔG, ΔH, and ΔS for the stretching of a rubber band and for the relaxing of a stretched rubber band. What drives the spontaneous process?

121. (a) The decomposition of mercury(II) oxide has been used as a method for producing oxygen, but this is not a recommended method. Why not? (b) Write the balanced equation for the decomposition of mercury(II) oxide. (c) Calculate the ΔH^0, ΔS^0, and ΔG^0 for the reaction. (d) Is the reaction spontaneous at room temperature?

*122. (a) A student heated a sample of a metal weighing 32.6 g to 99.83°C and put it into 100.0 g of water at 23.62°C in a calorimeter. The final temperature was 24.41°C. The student calculated the specific heat of the metal, but neglected to use the heat capacity of the calorimeter. The specific heat of water is 4.184 J/g·°C. What was his answer? The metal was known to be chromium, molybdenum, or tungsten. By comparing the value of the specific heat to those of the metals (Cr, 0.460; Mo, 0.250; W, 0.135 J/g·°C), the student identified the metal. What was the metal? (b) A student at the next laboratory bench did the same experiment, obtained the same data, and used the heat capacity of the calorimeter in his calculations. The heat capacity of the calorimeter was 410 J/°C. Was his identification of the metal different?

*123. A sugar cube dissolves in a cup of coffee in an endothermic process. (a) Is the entropy change of the system (sugar plus coffee) greater than, less than, or equal to zero? (b) Is the entropy change of the universe greater than, less than, or equal to zero? (c) Is the entropy change of the surroundings greater than, less than, or equal to zero?

BUILDING YOUR KNOWLEDGE

*124. Energy to power muscular work is produced from stored carbohydrate (glycogen) or fat (triglycerides). Metabolic consumption and production of energy are described with the nutritional "Calorie," which is equal to 1 kilocalorie. Average energy output per minute for various activities follows: sitting, 1.7 kcal; walking, level, 3.5 mph, 5.5 kcal; cycling, level, 13 mph, 10 kcal; swimming, 8.4 kcal; running, 10 mph, 19 kcal. Approximate energy values of some common foods are also given: large apple, 100 kcal; 8-oz cola drink, 105 kcal; malted milkshake, 8 oz milk, 500 kcal; $\frac{3}{4}$ cup pasta with tomato sauce and cheese, 195 kcal; hamburger on bun with sauce, 350 kcal; 10-oz sirloin steak, including fat, 1000 kcal. To maintain body weight, fuel intake should balance energy output. Prepare a table showing (a) each given food, (b) its fuel value, and (c) the minutes of each activity that would balance the kcal of each food.

125. From its heat of fusion, calculate the entropy change associated with the melting of one mole of ice at its melting point. From its heat of vaporization, calculate the entropy change associated with the boiling of one mole of water at its boiling point. Are your calculated values consistent with the simple model that we use to describe order in solids, liquids, and gases?

126. The energy content of dietary fat is 39 kJ/g, and for protein and carbohydrate it is 17 and 16 kJ/g, respectively. A 70.0-kg (155-lb) person utilizes 335 kJ/hr while resting and 1250 kJ/h while walking 6 km/h. How many hours would the person need to walk per day instead of resting if he or she consumed 100 g (about $\frac{1}{4}$ lb) of fat instead of 100 g of protein?

127. The enthalpy change for melting one mole of water at 273 K is $\Delta H^0_{273} = 6010$ J/mol, whereas that for vaporizing a mole of water at 373 K is $\Delta H^0_{373} = 40,660$ J/mol. Why is the second value so much larger?

128. A 436-g chunk of lead was removed from a beaker of boiling water, quickly dried, and dropped into a Styrofoam cup containing 50.0 g of water at 25.0°C. As the system reached equilibrium, the water temperature rose to 40.8°C. Calculate the heat capacity and the specific heat of the lead.

129. Methane, $CH_4(g)$, is the main constituent of natural gas. In excess oxygen, methane burns to $CO_2(g)$ and $H_2O(\ell)$, whereas in limited oxygen, the products are $CO(g)$ and $H_2O(\ell)$. Which would result in a higher temperature: a gas–air flame or a gas–oxygen flame? How can you tell?

A methane flame.

130. A 0.483-g sample of butter was burned in a bomb calorimeter whose heat capacity was 4572 J/°C, and the temperature was observed to rise from 24.76 to 27.93°C. Calculate the fuel value of butter in (a) kJ/g; (b) nutritional Calories/g (one nutritional Calorie is equal to one kilocalorie); (c) nutritional Calories/5-gram pat.