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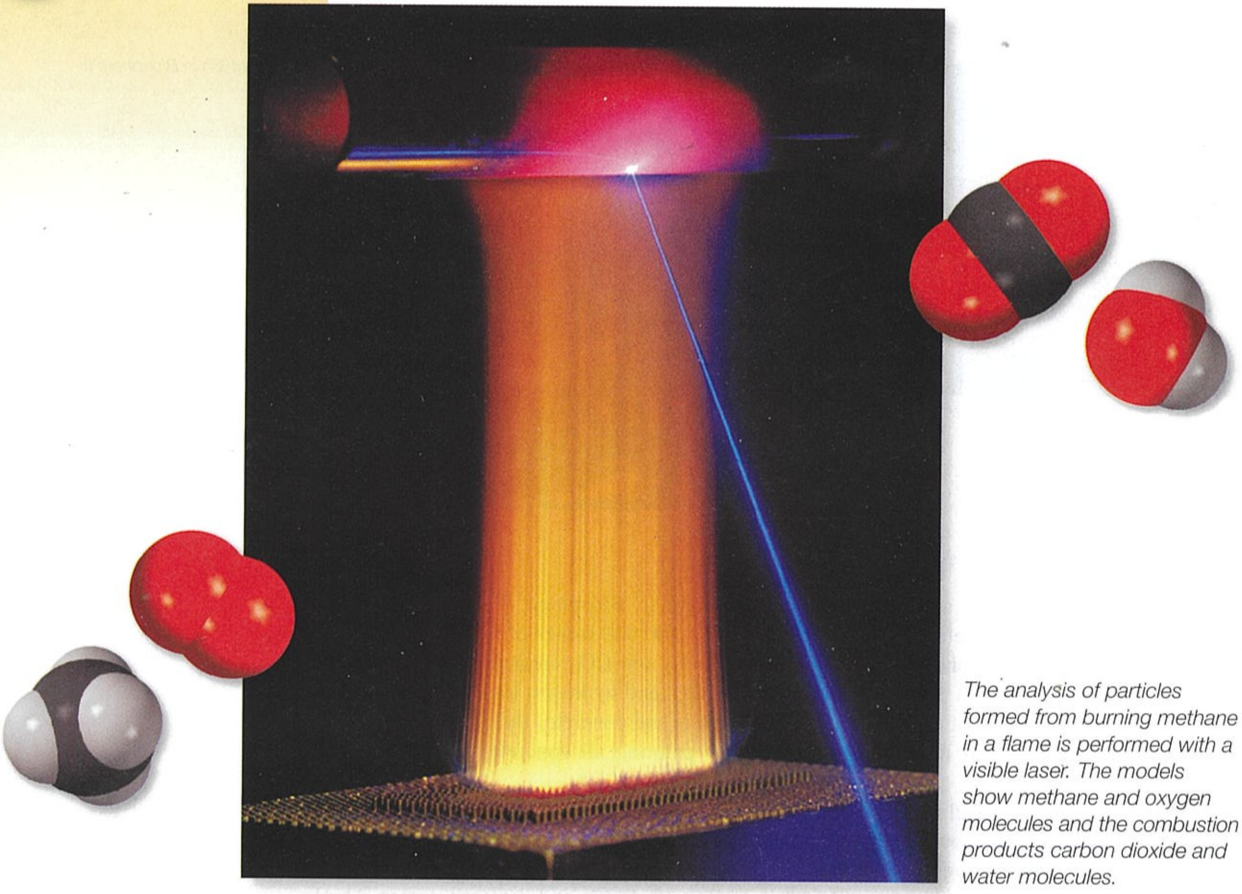


The analysis of particles formed from burning methane in a flame is performed with a visible laser. The models show methane and oxygen molecules and the combustion products carbon dioxide and water molecules.

Thermochemistry

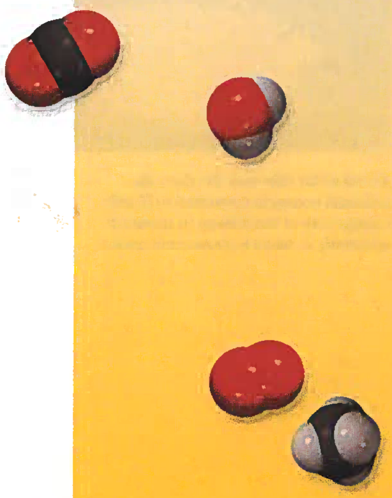
A LOOK AHEAD

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

Interactive Activity Summary

1. Interactivity: Conservation of Energy (6.3)
2. Animation: Heat Flow (6.4)

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



6.1 The Nature of Energy and Types of Energy

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

Kinetic energy was introduced in Chapter 5 (p. 197).

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

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

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

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

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

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

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

6.2 Energy Changes in Chemical Reactions

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

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

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

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

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

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

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

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

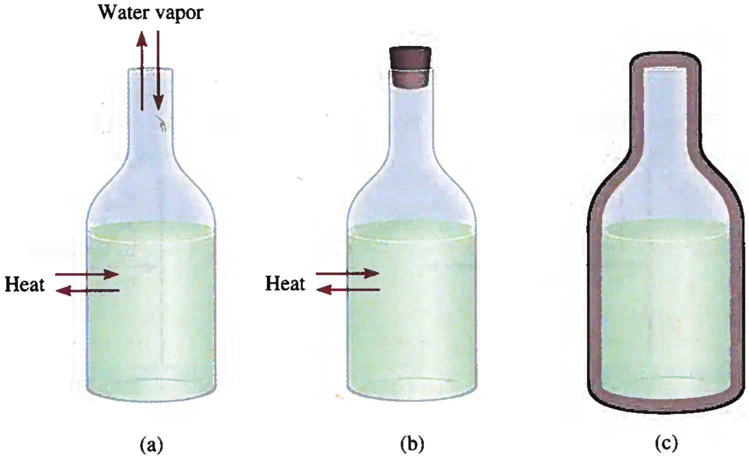
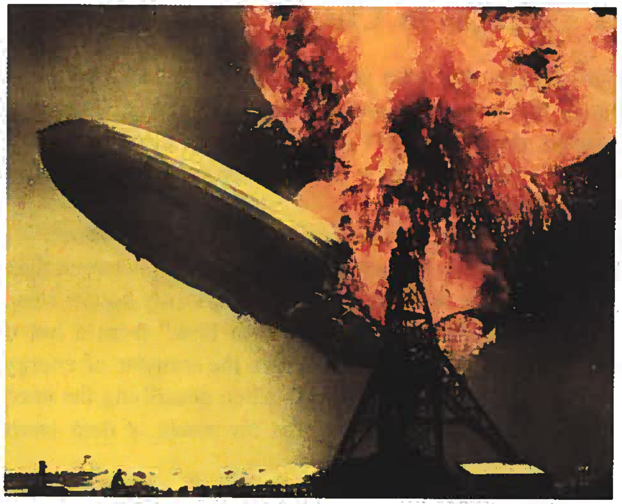


Figure 6.1 *Three systems represented by water in a flask: (a) an open system, which allows the exchange of both energy and mass with surroundings; (b) a closed system, which allows the exchange of energy but not mass; and (c) an isolated system, which allows neither energy nor mass to be exchanged (here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

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



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

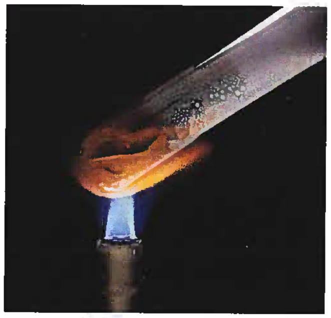
Exo- comes from the Greek word meaning "outside"; *endo-* means "within."

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

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

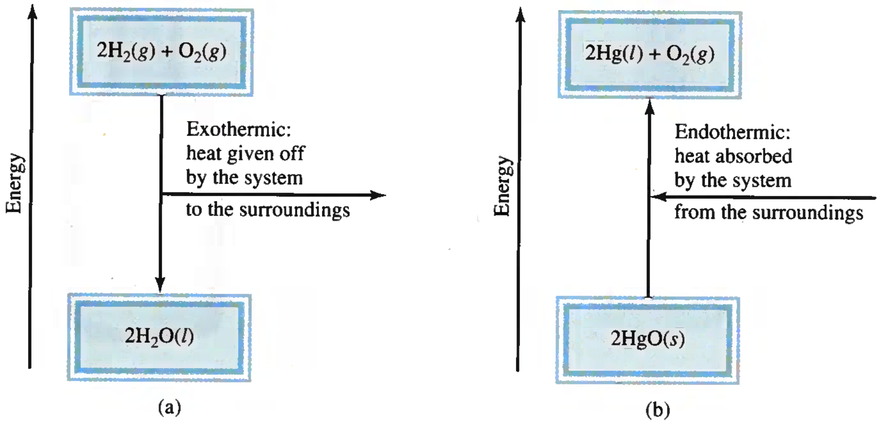
This reaction is an ***endothermic process,*** *in which heat has to be supplied to the system* (that is, to HgO) *by the surroundings* [Figure 6.3(b)].

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



On heating, HgO decomposes to give Hg and O_2.

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



6.3 Introduction to Thermodynamics

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

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

The state of a given amount of a gas is specified by its volume, pressure, and temperature. Consider a gas at 2 atm, 300 K, and 1 L (the initial state). Suppose a process is carried out at constant temperature such that the gas pressure decreases to 1 atm. According to Boyle's law, its volume must increase to 2 L. The final state then corresponds to 1 atm, 300 K, and 2 L. The change in volume (ΔV) is

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

$$\begin{aligned}\Delta V &= V_f - V_i \\ &= 2\text{ L} - 1\text{ L} \\ &= 1\text{ L}\end{aligned}$$

where V_i and V_f denote the initial and final volume, respectively. No matter how we arrive at the final state (for example, the pressure of the gas can be increased first and then decreased to 1 atm), the change in volume is always 1 L. Thus, the volume of a gas is a state function. In a similar manner, we can show that pressure and temperature are also state functions.

Energy is another state function. Using potential energy as an example, we find that the net increase in gravitational potential energy when we go from the same starting point to the top of a mountain is always the same, regardless of how we get there (Figure 6.4).

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

The First Law of Thermodynamics

The ***first law of thermodynamics,*** which is based on the law of conservation of energy, states that *energy can be converted from one form to another, but cannot be created or destroyed.*[†] How do we know this is so? It would be impossible to prove the validity of the first law of thermodynamics if we had to determine the total energy content

Interactivity:
Conservation of Energy
ARIS, Interactives

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

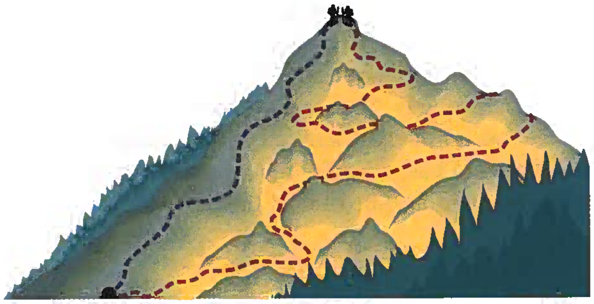


Figure 6.4 *The gain in gravitational potential energy that occurs when a person climbs from the base to the top of a mountain is independent of the path taken.*

of the universe. Even determining the total energy content of 1 g of iron, say, would be extremely difficult. Fortunately, we can test the validity of the first law by measuring only the *change* in the internal energy of a system between its *initial state* and its *final state* in a process. The change in internal energy ΔE is given by

$$\Delta E = E_f - E_i$$

where E_i and E_f are the internal energies of the system in the initial and final states, respectively.

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

Sulfur burning in air to form SO_2.

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

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

In this case, our system is composed of the reactant molecules S and O_2 and the product molecules SO_2. We do not know the internal energy content of either the reactant molecules or the product molecules, but we can accurately measure the *change* in energy content, ΔE, given by

$$\begin{aligned}\Delta E &= E(\text{product}) - E(\text{reactants})\\ &= \text{energy content of 1 mol } SO_2(g) - \text{energy content of } [1 \text{ mol } S(s) + 1 \text{ mol } O_2(g)]\end{aligned}$$

We find that this reaction gives off heat. Therefore, the energy of the product is less than that of the reactants, and ΔE is negative.

Interpreting the release of heat in this reaction to mean that some of the chemical energy contained in the molecules has been converted to thermal energy, we conclude that the transfer of energy from the system to the surroundings does not change the total energy of the universe. That is, the sum of the energy changes must be zero:

$$\Delta E_{sys} + \Delta E_{surr} = 0$$

or

$$\Delta E_{sys} = -\Delta E_{surr}$$

where the subscripts "sys" and "surr" denote system and surroundings, respectively. Thus, if one system undergoes an energy change ΔE_{sys}, the rest of the universe, or the surroundings, must undergo a change in energy that is equal in magnitude but opposite in sign ($-\Delta E_{surr}$); energy gained in one place must have been lost somewhere else. Furthermore, because energy can be changed from one form to another, the energy lost by one system can be gained by another system in a different form. For example, the energy lost by burning oil in a power plant may ultimately turn up in our homes as electrical energy, heat, light, and so on.

In chemistry, we are normally interested in the energy changes associated with the system (which may be a flask containing reactants and products), not with its surroundings. Therefore, a more useful form of the first law is

We use lowercase letters (such as *w* and *q*) to represent thermodynamic quantities that are not state functions.

$$\boxed{\Delta E = q + w} \qquad (6.1)$$

TABLE 6.1 Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	−
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	−

(We drop the subscript "sys" for simplicity.) Equation (6.1) says that the change in the internal energy ΔE of a system is the sum of the heat exchange q between the system and the surroundings and the work done w on (or by) the system. The sign conventions for q and w are as follows: q is positive for an endothermic process and negative for an exothermic process and w is positive for work done on the system by the surroundings and negative for work done by the system on the surroundings. We can think of the first law of thermodynamics as an energy balance sheet, much like a money balance sheet kept in a bank that does currency exchange. You can withdraw or deposit money in either of two different currencies (like energy change due to heat exchange and work done). However, the value of your bank account depends only on the net amount of money left in it after these transactions, not on which currency you used.

For convenience, we sometimes omit the word "internal" when discussing the energy of a system.

Equation (6.1) may seem abstract, but it is actually quite logical. If a system loses heat to the surroundings or does work on the surroundings, we would expect its internal energy to decrease because they are energy-depleting processes. For this reason, both q and w are negative. Conversely, if heat is added to the system or if work is done on the system, then the internal energy of the system would increase. In this case, both q and w are positive. Table 6.1 summarizes the sign conventions for q and w.

Work and Heat

We will now look at the nature of work and heat in more detail.

Work

We have seen that work can be defined as force F multiplied by distance d:

$$w = Fd \tag{6.2}$$

In thermodynamics, work has a broader meaning that includes mechanical work (for example, a crane lifting a steel beam), electrical work (a battery supplying electrons to light the bulb of a flashlight), and surface work (blowing up a soap bubble). In this section we will concentrate on mechanical work; in Chapter 19 we will discuss the nature of electrical work.

One way to illustrate mechanical work is to study the expansion or compression of a gas. Many chemical and biological processes involve gas volume changes. Breathing and exhaling air involves the expansion and contraction of the tiny sacs called alveoli in the lungs. Another example is the internal combustion engine of the automobile. The successive expansion and compression of the cylinders due to the combustion of the gasoline-air mixture provide power to the vehicle. Figure 6.5 shows a

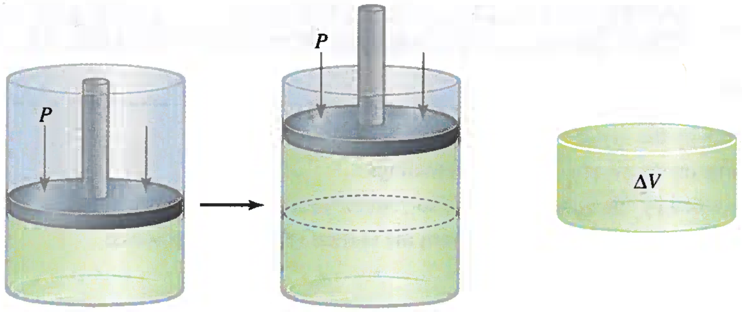


Figure 6.5 *The expansion of a gas against a constant external pressure (such as atmospheric pressure). The gas is in a cylinder fitted with a weightless movable piston. The work done is given by* $-P\Delta V$*. Because* $\Delta V > 0$*, the work done is a negative quantity.*

gas in a cylinder fitted with a weightless, frictionless movable piston at a certain temperature, pressure, and volume. As it expands, the gas pushes the piston upward against a constant opposing external atmospheric pressure P. The work done by the gas on the surroundings is

$$w = -P\Delta V \tag{6.3}$$

where ΔV, the change in volume, is given by $V_f - V_i$. The minus sign in Equation (6.3) takes care of the convention for w. For gas expansion, $\Delta V > 0$, so $-P\Delta V$ is a negative quantity. For gas compression (work done on the system), $\Delta V < 0$, and $-P\Delta V$ is a positive quantity.

Equation (6.3) derives from the fact that pressure × volume can be expressed as (force/area) × volume; that is,

$$P \times V = \underset{\text{pressure}}{\frac{F}{d^2}} \times \underset{\text{volume}}{d^3} = Fd = w$$

where F is the opposing force and d has the dimension of length, d^2 has the dimensions of area, and d^3 has the dimensions of volume. Thus, the product of pressure and volume is equal to force times distance, or work. You can see that for a given increase in volume (that is, for a certain value of ΔV), the work done depends on the magnitude of the external, opposing pressure P. If P is zero (that is, if the gas is expanding against a vacuum), the work done must also be zero. If P is some positive, nonzero value, then the work done is given by $-P\Delta V$.

According to Equation (6.3), the units for work done by or on a gas are liters atmospheres. To express the work done in the more familiar unit of joules, we use the conversion factor (see Appendix 2).

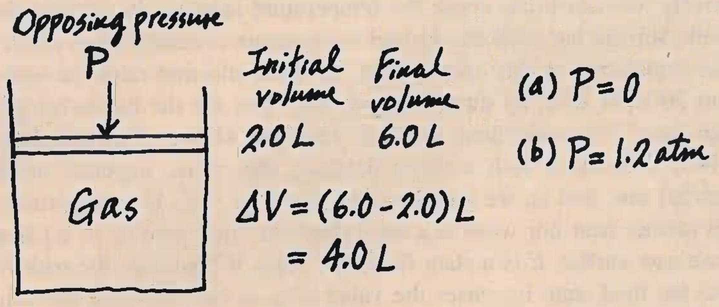
$$1\ \text{L} \cdot \text{atm} = 101.3\ \text{J}$$

Example 6.1

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work done by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 1.2 atm.

(Continued)

Strategy A simple sketch of the situation is helpful here:



The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume. What is the conversion factor between L · atm and J?

Solution

(a) Because the external pressure is zero, no work is done in the expansion.

$$\begin{aligned} w &= -P\Delta V \\ &= -(0)(6.0 - 2.0)\text{ L} \\ &= \boxed{0} \end{aligned}$$

(b) The external, opposing pressure is 1.2 atm, so

$$\begin{aligned} w &= -P\Delta V \\ &= -(1.2\text{ atm})(6.0 - 2.0)\text{ L} \\ &= -4.8\text{ L}\cdot\text{atm} \end{aligned}$$

To convert the answer to joules, we write

$$\begin{aligned} w &= -4.8\text{ L}\cdot\text{atm} \times \frac{101.3\text{ J}}{1\text{ L}\cdot\text{atm}} \\ &= \boxed{-4.9 \times 10^2\text{ J}} \end{aligned}$$

Check Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

Similar problems: 6.15, 6.16.

Practice Exercise A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.

Example 6.1 shows that work is not a state function. Although the initial and final states are the same in (a) and (b), the amount of work done is different because the external, opposing pressures are different. We *cannot* write $\Delta w = w_f - w_i$ for a change. Work done depends not only on the initial state and final state, but also on how the process is carried out, that is, on the path.

Because temperature is kept constant, you can use Boyle's law to show that the final pressure is the same in (a) and (b).

Heat

The other component of internal energy is q, heat. Like work, heat is not a state function. Suppose that we raise the temperature of 100.0 g of water initially at 20.0°C and 1 atm to 30.0°C and 1 atm. What is the heat transferred to the water for this process? We do not know the answer because the process is not specified. One way to raise the temperature is to heat the water using a Bunsen burner or electrically using an immersion heater. In either case, we can calculate the heat transferred to be 4184 J.[†]

Alternatively, we can bring about the temperature increase by stirring the water with a magnetic stirring bar until the desired temperature is reached as a result of friction. The heat transferred in this case is zero. Or we could first raise the temperature of water from 20°C to 25°C by direct heating, and then stir the bar to bring it up to 30°C. In each case, q is somewhere between zero and 4184 J. This simple example shows that heat associated with a given process, like work, depends on how the process is carried out; that is, we *cannot* write $\Delta q = q_f - q_i$. It is important to note that although neither heat nor work is a state function, their sum $(q + w)$ is equal to ΔE and, as we saw earlier, E is a state function. Thus, if changing the path from the initial state to the final state increases the value of q, it will decrease the value of w by the same amount and vice versa.

In summary, heat and work are not state functions because they are not properties of a system. They manifest themselves only during a process (during a change). Thus, their values depend on the path of the process and vary accordingly.

Example 6.2

The work done when a gas is compressed in a cylinder like that shown in Figure 6.5 is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process.

Strategy Compression is work done on the gas, so what is the sign for w? Heat is released by the gas to the surroundings. Is this an endothermic or exothermic process? What is the sign for q?

Solution To calculate the energy change of the gas, we need Equation (6.1). Work of compression is positive and because heat is released by the gas, q is negative. Therefore, we have

$$\begin{aligned}\Delta E &= q + w \\ &= -128\text{ J} + 462\text{ J} \\ &= \boxed{334\text{ J}}\end{aligned}$$

As a result, the energy of the gas increases by 334 J.

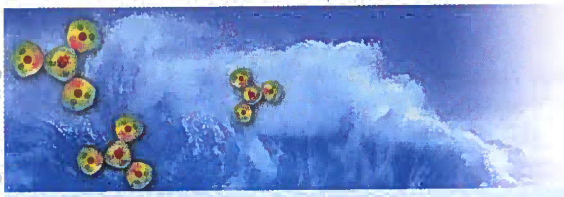
Similar problems: 6.17, 6.18.

Practice Exercise A gas expands and does P-V work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

6.4 Enthalpy of Chemical Reactions

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

[†] The heat transferred to water is $q = ms\Delta t$, where m is the mass of water in grams, s is the specific heat of water (4.184 J/g · °C), and Δt is the temperature change. Thus, $q = (100.0\text{ g})(4.184\text{ J/g}\cdot{}^\circ\text{C})(10^\circ\text{C}) = 4184\text{ J}$. Specific heat will be discussed in Section 6.5.



CHEMISTRY in Action

Making Snow and Inflating a Bicycle Tire

Many phenomena in everyday life can be explained by the first law of thermodynamics. Here we will discuss two examples of interest to lovers of the outdoors.

Making Snow

If you are an avid downhill skier, you have probably skied on artificial snow. How is this stuff made in quantities large enough to meet the needs of skiers on snowless days? The secret of snowmaking is in the equation $\Delta E = q + w$. A snowmaking machine contains a mixture of compressed air and water vapor at about 20 atm. Because of the large difference in pressure between the tank and the outside atmosphere, when the mixture is sprayed into the atmosphere it expands so rapidly that, as a good approximation, no heat exchange occurs between the system (air and water) and its surroundings; that is, $q = 0$. (In thermodynamics, such a process is called an *adiabatic process.*) Thus, we write

$$\Delta E = q + w = w$$

Because the system does work on the surroundings, w is a negative quantity, and there is a decrease in the system's energy.

Kinetic energy is part of the total energy of the system. In Section 5.7 we saw that the average kinetic energy of a gas is directly proportional to the absolute temperature [Equation (5.15)]. It follows, therefore, that the change in energy ΔE is given by

$$\Delta E = C\Delta T$$

where C is the proportionality constant. Because ΔE is negative, ΔT must also be negative, and it is this cooling effect (or the decrease in the kinetic energy of the water molecules) that is responsible for the formation of snow. Although we need only water to form snow, the presence of air, which also cools on expansion, helps to lower the temperature of the water vapor.

Inflating a Bicycle Tire

If you have ever pumped air into a bicycle tire, you probably noticed a warming effect at the valve stem. This phenomenon, too, can be explained by the first law of thermodynamics. The action of the pump compresses the air inside the pump and the tire. The process is rapid enough to be treated as approximately adiabatic, so that $q = 0$ and $\Delta E = w$. Because work is done on the gas in this case (it is being compressed), w is positive, and there is an increase in energy. Hence, the temperature of the system increases also, according to the equation

$$\Delta E = C\Delta T$$

A snowmaking machine in operation.

If a chemical reaction is run at constant volume, then $\Delta V = 0$ and no P-V work will result from this change. From Equation (6.1) it follows that

$$\begin{aligned}\Delta E &= q - P\Delta V \\ &= q_v \end{aligned} \qquad (6.4)$$

We add the subscript "v" to remind us that this is a constant-volume process. This equality may seem strange at first, for we showed earlier that q is not a state function.

The process is carried out under constant-volume conditions, however, so that the heat change can have only a specific value, which is equal to ΔE.

Enthalpy

Constant-volume conditions are often inconvenient and sometimes impossible to achieve. Most reactions occur under conditions of constant pressure (usually atmospheric pressure). If such a reaction results in a net increase in the number of moles of a gas, then the system does work on the surroundings (expansion). This follows from the fact that for the gas formed to enter the atmosphere, it must push the surrounding air back. Conversely, if more gas molecules are consumed than are produced, work is done on the system by the surroundings (compression). Finally, no work is done if there is no net change in the number of moles of gases from reactants to products.

In general, for a constant-pressure process we write

$$\Delta E = q + w$$
$$= q_p - P\Delta V$$

or

$$q_p = \Delta E + P\Delta V \qquad (6.5)$$

where the subscript "p" denotes constant-pressure condition.

We now introduce a new thermodynamic function of a system called ***enthalpy* (*H*)**, which is defined by the equation

$$\boxed{H = E + PV} \qquad (6.6)$$

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

For any process, the change in enthalpy according to Equation (6.6) is given by

$$\Delta H = \Delta E + \Delta(PV) \qquad (6.7)$$

If the pressure is held constant, then

$$\boxed{\Delta H = \Delta E + P\Delta V} \qquad (6.8)$$

Comparing Equation (6.8) with Equation (6.5), we see that for a constant-pressure process, $q_p = \Delta H$. Again, although q is not a state function, the heat change at constant pressure is equal to ΔH because the "path" is defined and therefore it can have only a specific value.

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

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

Enthalpy of Reactions

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

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

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

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

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

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

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

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

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

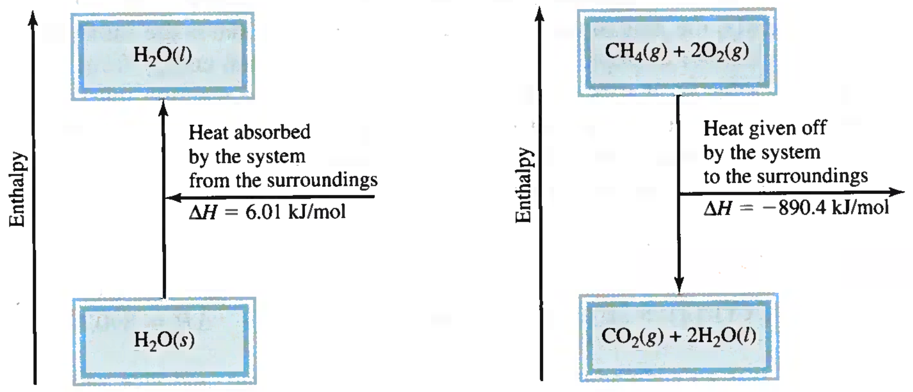
Now let us apply the idea of enthalpy changes to two common processes, the first involving a physical change, the second a chemical change.

Thermochemical Equations

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

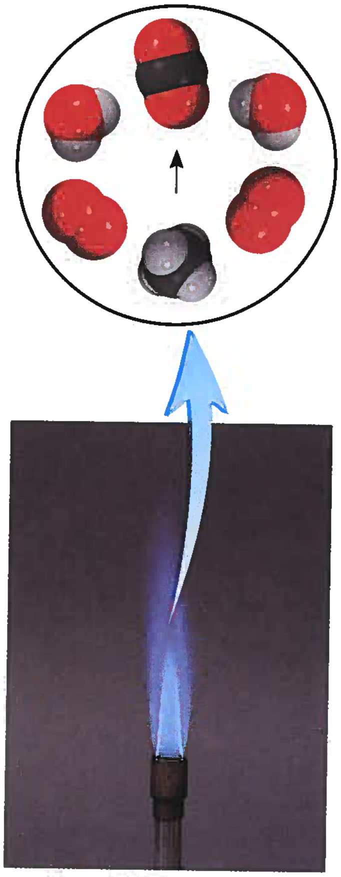
$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = 6.01 \text{ kJ/mol}$$

Animation:
Heat Flow
ARIS, Animations



(a) (b)

Figure 6.6 *(a) Melting 1 mole of ice at 0°C (an endothermic process) results in an enthalpy increase in the system of 6.01 kJ. (b) Burning 1 mole of methane in oxygen gas (an exothermic process) results in an enthalpy decrease in the system of 890.4 kJ.*



Methane gas burning from a Bunsen burner.

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

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

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

From experience we know that burning natural gas releases heat to the surroundings, so it is an exothermic process. Under constant-pressure condition this heat change is equal to enthalpy change and ΔH must have a negative sign [Figure 6.6(b)]. Again, the per mole of reaction unit for ΔH means that when 1 mole of CH_4 reacts with 2 moles of O_2 to yield 1 mole of CO_2 and 2 moles of liquid H_2O, 890.4 kJ of heat are released to the surroundings. It is important to keep in mind that each ΔH value relates to the reaction as written in the chemical equation.

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

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

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

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

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

Keep in mind that H is an extensive property.

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

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

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

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

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

Example 6.3

Given the thermochemical equation

$$SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow SO_3(g) \qquad \Delta H = -99.1 \text{ kJ/mol}$$

calculate the heat evolved when 74.6 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3.

Strategy The thermochemical equation shows that for every mole of SO_2 burned, 99.1 kJ of heat are given off (note the negative sign). Therefore, the conversion factor is

$$\frac{-99.1 \text{ kJ}}{1 \text{ mol } SO_2}$$

How many moles of SO_2 are in 74.6 g of SO_2? What is the conversion factor between grams and moles?

Solution We need to first calculate the number of moles of SO_2 in 74.6 g of the compound and then find the number of kilojoules produced from the exothermic reaction. The sequence of conversions is as follows:

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

Therefore, the heat produced is given by

$$74.6 \text{ g} \cancel{SO_2} \times \frac{1 \cancel{\text{mol } SO_2}}{64.07 \text{ g} \cancel{SO_2}} \times \frac{-99.1 \text{ kJ}}{1 \cancel{\text{mol } SO_2}} = -115 \text{ kJ}$$

Check Because 74.6 g is greater than the molar mass of SO_2, we expect the heat released to be larger than −99.1 kJ. The negative sign indicates that this is an exothermic reaction.

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

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

Similar problem: 6.26.

A Comparison of ΔH and ΔE

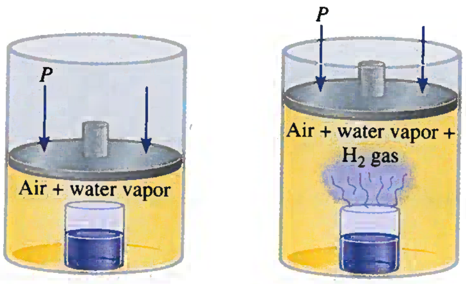
What is the relationship between ΔH and ΔE for a process? To find out, let us consider the reaction between sodium metal and water:

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g) \qquad \Delta H = -367.5 \text{ kJ/mol}$$

Sodium reacting with water to form hydrogen gas.

This thermochemical equation says that when two moles of sodium react with an excess of water, 367.5 kJ of heat are given off. Note that one of the products is hydrogen gas, which must push back air to enter the atmosphere. Consequently, some of the energy produced by the reaction is used to do work of pushing back a volume of air (ΔV) against atmospheric pressure (P) (Figure 6.7). To calculate the change in internal energy, we rearrange Equation (6.8) as follows:

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



(a) (b)

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

If we assume the temperature to be 25°C and ignore the small change in the volume of the solution, we can show that the volume of 1 mole of H_2 gas at 1.0 atm and 298 K is 24.5 L, so that $-P\Delta V = -24.5\ \text{L} \cdot \text{atm}$ or -2.5 kJ. Finally,

$$\begin{aligned}\Delta E &= -367.5\ \text{kJ/mol} - 2.5\ \text{kJ/mol} \\ &= -370.0\ \text{kJ/mol}\end{aligned}$$

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

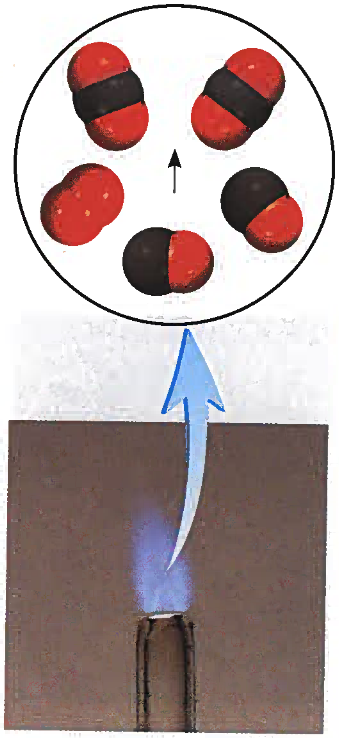
This calculation shows that ΔE and ΔH are approximately the same. The reason ΔH is smaller than ΔE in magnitude is that some of the internal energy released is used to do gas expansion work, so less heat is evolved. For reactions that do not involve gases, ΔV is usually very small and so ΔE is practically the same as ΔH.

Another way to calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature. In this case,

$$\begin{aligned}\Delta E &= \Delta H - \Delta(PV) \\ &= \Delta H - \Delta(nRT) \\ &= \Delta H - RT\Delta n \qquad (6.10)\end{aligned}$$

where Δn is defined as

$$\Delta n = \text{number of moles of product gases} - \text{number of moles of reactant gases}$$



Carbon monoxide burns in air to form carbon dioxide.

Example 6.4

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 atm and 25°C:

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -566.0\ \text{kJ/mol}$$

Strategy We are given the enthalpy change, ΔH, for the reaction and are asked to calculate the change in internal energy, ΔE. Therefore, we need Equation (6.10). What is the change in the number of moles of gases? ΔH is given in kilojoules, so what units should we use for R?

Solution From the chemical equation we see that 3 moles of gases are converted to 2 moles of gases so that

$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases} \\ &= 2 - 3 \\ &= -1\end{aligned}$$

(Continued)

Using 8.314 J/K · mol for R and T = 298 K in Equation (6.10), we write

$$\begin{aligned}\Delta E &= \Delta H - RT\Delta n \\ &= -566.0\text{ kJ/mol} - (8.314\text{ J/K}\cdot\text{mol})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)(298\text{ K})(-1) \\ &= -563.5\text{ kJ/mol}\end{aligned}$$

Check Knowing that the reacting gaseous system undergoes a compression (3 moles to 2 moles), is it reasonable to have $\Delta H > \Delta E$ in magnitude?

Practice Exercise What is ΔE for the formation of 1 mole of CO at 1 atm and 25°C?

$$\text{C(graphite)} + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g) \qquad \Delta H = -110.5\text{ kJ/mol}$$

Similar problem: 6.27.

6.5 Calorimetry

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

Specific Heat and Heat Capacity

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

$$C = ms \qquad (6.11)$$

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

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

Table 6.2 shows the specific heat of some common substances.

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

$$q = ms\Delta t \qquad (6.12)$$

$$q = C\Delta t \qquad (6.13)$$

where Δt is the temperature change:

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

TABLE 6.2 The Specific Heats of Some Common Substances

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

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

Example 6.5

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

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

Solution Using Equation (6.12), we write

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

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

Similar problem: 6.34.

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

Constant-Volume Calorimetry

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

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

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

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

$$q_{\text{rxn}} = -q_{\text{cal}} \qquad (6.15)$$

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

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

$$q_{\text{cal}} = C_{\text{cal}}\Delta t \qquad (6.16)$$

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

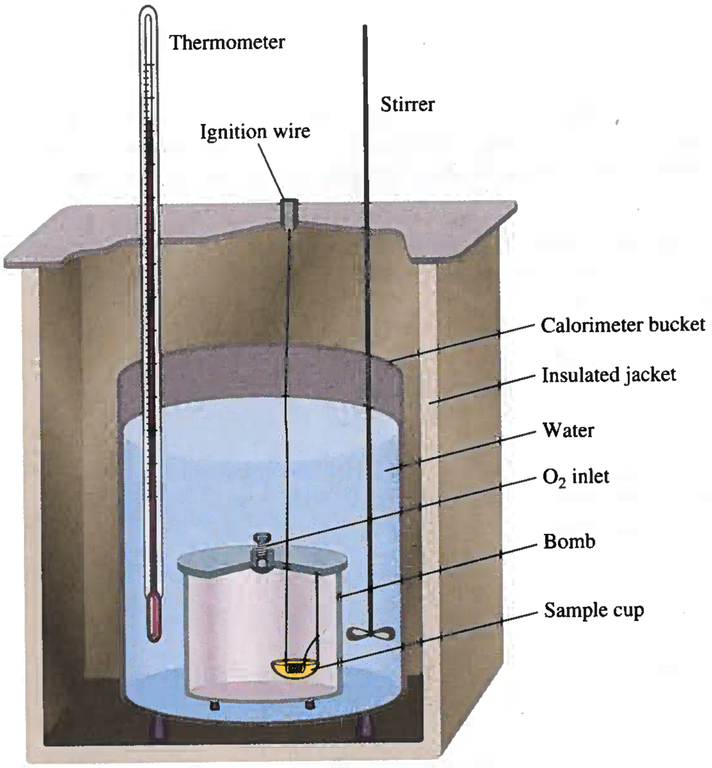


Figure 6.8 *A constant-volume bomb calorimeter. The calorimeter is filled with oxygen gas before it is placed in the bucket. The sample is ignited electrically, and the heat produced by the reaction can be accurately determined by measuring the temperature increase in the known amount of surrounding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

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

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

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

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

Example 6.6

A quantity of 1.435 g of naphthalene ($C_{10}H_8$), a pungent-smelling substance used in moth repellents, was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 20.28°C to 25.95°C. If the heat capacity of the

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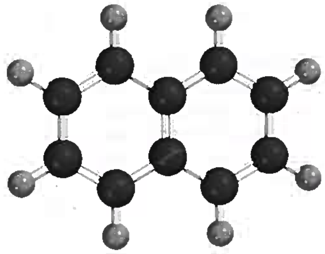


$C_{10}H_8$

bomb plus water was 10.17 kJ/°C, calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.

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

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

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

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

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

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

Similar problem: 6.37.

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

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

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

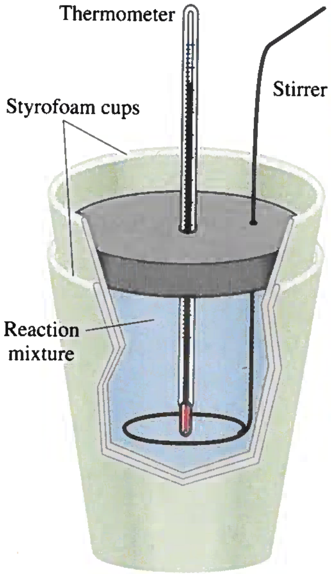


Figure 6.9 *A constant-pressure calorimeter made of two Styrofoam coffee cups. The outer cup helps to insulate the reacting mixture from the surroundings. Two solutions of known volume containing the reactants at the same temperature are carefully mixed in the calorimeter. The heat produced or absorbed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

Constant-Pressure Calorimetry

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

TABLE 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

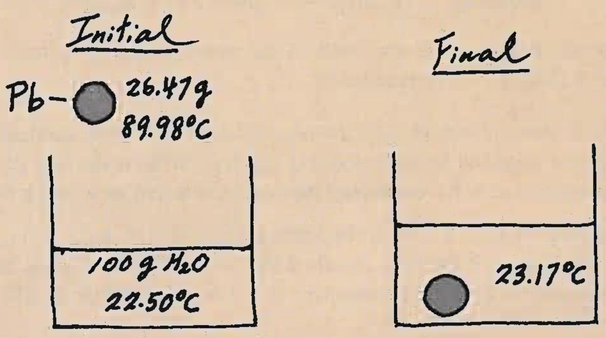
Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	−56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	44.0*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

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

Example 6.7

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

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



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

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

$$q_{Pb} + q_{H_2O} = 0$$

or

$$q_{Pb} = -q_{H_2O}$$

The heat gained by the water is given by

$$q_{H_2O} = ms\Delta t$$

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

$$\begin{aligned} q_{H_2O} &= (100.0\ g)(4.184\ J/g\cdot°C)(23.17°C - 22.50°C) \\ &= 280.3\ J \end{aligned}$$

(Continued)

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

$$q_{Pb} = ms\Delta t$$
$$-280.3 \text{ J} = (26.47 \text{ g})(s)(23.17°\text{C} - 89.98°\text{C})$$
$$s = \boxed{0.158 \text{ J/g} \cdot °\text{C}}$$

Similar problem: 6.82.

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

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

Example 6.8

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

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

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

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

Solution Assuming no heat is lost to the surroundings, $q_{sys} = q_{soln} + q_{rxn} = 0$, so $q_{rxn} = -q_{soln}$, where q_{soln} is the heat absorbed by the combined solution. Because the density of the solution is 1.00 g/mL, the mass of a 100-mL solution is 100 g. Thus,

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

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

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

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

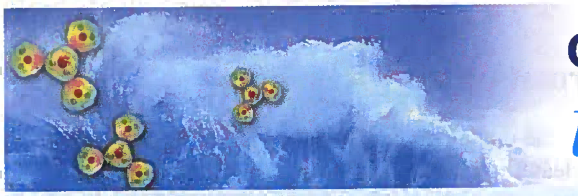
Therefore, the heat of neutralization when 1.00 mole of HCl reacts with 1.00 mole of NaOH is

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

Similar problem: 6.38.

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

(Continued)



CHEMISTRY in Action

Fuel Values of Foods and Other Substances

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

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

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

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

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

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

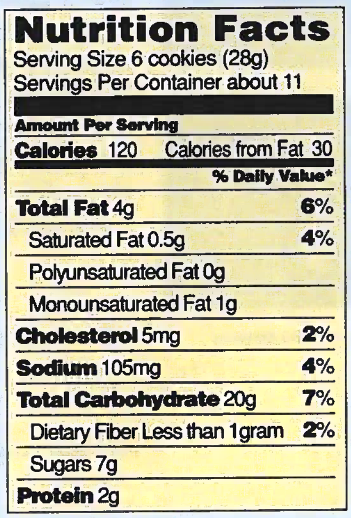
$$1 \text{ Cal} = 1000 \text{ cal} = 4184 \text{ J}$$

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

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

Fuel Values of Foods and Some Common Fuels

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



Nutrition Facts

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

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

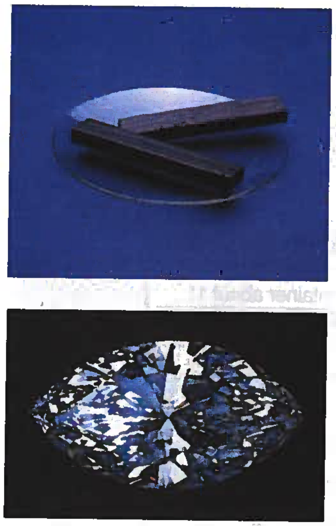
The labels on food packages reveal the calorie content of the food inside.

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

6.6 Standard Enthalpy of Formation and Reaction

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

The "sea level" reference point for all enthalpy expressions is called the ***standard enthalpy of formation*** **(ΔH°_f)**. Substances are said to be in the ***standard state*** at 1 atm,[†] hence the term "standard enthalpy." The superscript "°" represents standard-state conditions (1 atm), and the subscript "f" stands for formation. By convention, *the standard enthalpy of formation of any element in its most stable form is zero.* Take the element oxygen as an example. Molecular oxygen (O_2) is more stable than the other allotropic form of oxygen, ozone (O_3), at 1 atm and 25°C. Thus, we can write $\Delta H^\circ_f(O_2) = 0$, but $\Delta H^\circ_f(O_3) \neq 0$. Similarly, graphite is a more stable allotropic form of carbon than diamond at 1 atm and 25°C, so we have $\Delta H^\circ_f(\text{C, graphite}) = 0$ and $\Delta H^\circ_f(\text{C, diamond}) \neq 0$. Based on this reference for elements, we can now define the standard enthalpy of formation of a compound as *the heat change that results when 1 mole of the compound is formed from its elements at a pressure of 1 atm.* Table 6.4 lists the standard enthalpies of formation for a number of elements and compounds. (For a more complete list of ΔH°_f values, see Appendix 2.) Note that although the standard state does not specify a temperature, we will always use ΔH°_f values measured at 25°C for our discussion because most of the thermodynamic data are collected at this temperature.


Graphite (top) and diamond (bottom).

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

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

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

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

We can generalize Equation (6.17) as

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

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

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

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

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

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

The Direct Method

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

$$\text{C(graphite)} + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ_{rxn} = -393.5 \text{ kJ/mol}$$

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

$$\begin{aligned}\Delta H^\circ_{rxn} &= \Delta H_f^\circ(CO_2, g) - [\Delta H_f^\circ(\text{C, graphite}) + \Delta H_f^\circ(O_2, g)] \\ &= -393.5 \text{ kJ/mol}\end{aligned}$$

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

$$\Delta H^\circ_{rxn} = \Delta H_f^\circ(CO_2, g) = -393.5 \text{ kJ/mol}$$

or

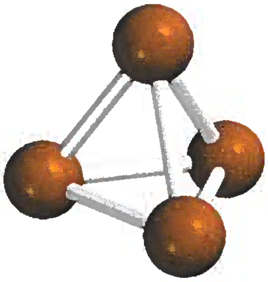
$$\Delta H_f^\circ(CO_2, g) = -393.5 \text{ kJ/mol}$$

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

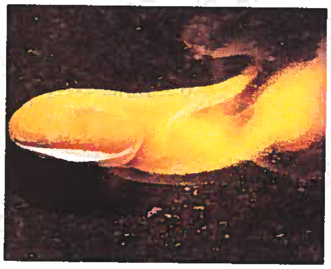
Other compounds that can be studied by the direct method are SF_6, P_4O_{10}, and CS_2. The equations representing their syntheses are

$$\text{S(rhombic)} + 3F_2(g) \longrightarrow SF_6(g)$$
$$P_4\text{(white)} + 5O_2(g) \longrightarrow P_4O_{10}(s)$$
$$\text{C(graphite)} + 2\text{S(rhombic)} \longrightarrow CS_2(l)$$

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



P_4



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

The Indirect Method

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

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

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

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

However, burning graphite also produces some carbon dioxide (CO_2), so we cannot measure the enthalpy change for CO directly as shown. Instead, we must employ an

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

indirect route, based on Hess's law. It is possible to carry out the following two separate reactions, which do go to completion:

$$\begin{array}{lrl} \text{(a)} & \text{C(graphite)} + O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ/mol} \\ \text{(b)} & CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ_{\text{rxn}} = -283.0 \text{ kJ/mol} \end{array}$$

First, we reverse Equation (b) to get

$$\begin{array}{lrl} \text{(c)} & CO_2(g) \longrightarrow CO(g) + \tfrac{1}{2}O_2(g) & \Delta H^\circ_{\text{rxn}} = +283.0 \text{ kJ/mol} \end{array}$$

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

$$\begin{array}{lrl} \text{(a)} & \text{C(graphite)} + O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ/mol} \\ \text{(c)} & CO_2(g) \longrightarrow CO(g) + \tfrac{1}{2}O_2(g) & \Delta H^\circ_{\text{rxn}} = +283.0 \text{ kJ/mol} \\ \hline \text{(d)} & \text{C(graphite)} + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) & \Delta H^\circ_{\text{rxn}} = -110.5 \text{ kJ/mol} \end{array}$$

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

The general rule in applying Hess's law is to arrange a series of chemical equations (corresponding to a series of steps) in such a way that, when added together, all species will cancel except for the reactants and products that appear in the overall reaction. This means that we want the elements on the left and the compound of interest on the right of the arrow. Further, we often need to multiply some or all of the equations representing the individual steps by the appropriate coefficients.

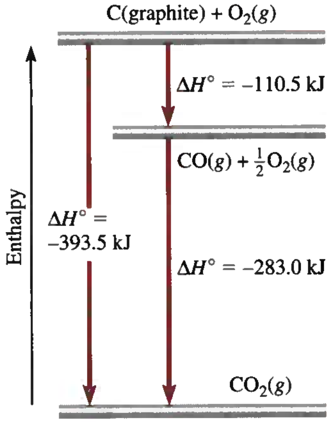


Figure 6.10 *The enthalpy change for the formation of 1 mole of CO_2 from graphite and O_2 can be broken down into two steps according to Hess's law.*

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

Example 6.9

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

$$2\text{C(graphite)} + H_2(g) \longrightarrow C_2H_2(g)$$

The equations for each step and the corresponding enthalpy changes are

$$\begin{array}{lrl} \text{(a)} & \text{C(graphite)} + O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ/mol} \\ \text{(b)} & H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) & \Delta H^\circ_{\text{rxn}} = -285.8 \text{ kJ/mol} \\ \text{(c)} & 2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) & \Delta H^\circ_{\text{rxn}} = -2598.8 \text{ kJ/mol} \end{array}$$

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

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

$$\begin{array}{lrl} \text{(d)} & 2\text{C(graphite)} + 2O_2(g) \longrightarrow 2CO_2(g) & \Delta H^\circ_{\text{rxn}} = 2(-393.5 \text{ kJ/mol}) \\ & & \phantom{\Delta H^\circ_{\text{rxn}}} = -787.0 \text{ kJ/mol} \end{array}$$

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

$$\begin{array}{lrl} \text{(e)} & 2CO_2(g) + H_2O(l) \longrightarrow C_2H_2(g) + \tfrac{5}{2}O_2(g) & \Delta H^\circ_{\text{rxn}} = \tfrac{1}{2}(2598.8 \text{ kJ/mol}) \\ & & \phantom{\Delta H^\circ_{\text{rxn}}} = 1299.4 \text{ kJ/mol} \end{array}$$

(Continued)

C_2H_2

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

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

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

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

Similar problems: 6.62, 6.63.

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

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

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

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

Example 6.10

The thermite reaction involves aluminum and iron(III) oxide

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

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

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

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

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

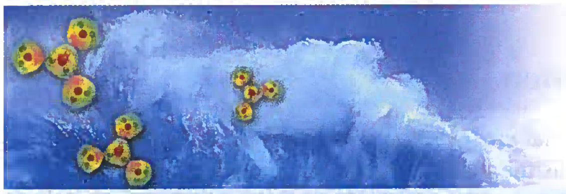
This is the amount of heat released for two moles of Al reacted. We use the following ratio

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

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

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

(Continued)



CHEMISTRY *in Action*

How a Bombardier Beetle Defends Itself

Survival techniques of insects and small animals in a fiercely competitive environment take many forms. For example, chameleons have developed the ability to change color to match their surroundings and the butterfly *Limenitis* has evolved into a form that mimics the poisonous and unpleasant-tasting monarch butterfly (*Danaus*). A less passive defense mechanism is employed by bombardier beetles (*Brachinus*), which repel predators with a "chemical spray."

The bombardier beetle has a pair of glands at the tip of its abdomen. Each gland consists of two compartments. The inner compartment contains an aqueous solution of hydroquinone and hydrogen peroxide, and the outer compartment holds a mixture of enzymes. (Enzymes are biological molecules that can speed up a reaction.) When threatened, the beetle squeezes some fluid from the inner compartment into the outer compartment, where, in the presence of the enzymes, an exothermic reaction takes place:

$$\text{(a)}\quad \underset{\text{hydroquinone}}{C_6H_4(OH)_2(aq)} + H_2O_2(aq) \longrightarrow \underset{\text{quinone}}{C_6H_4O_2(aq)} + 2H_2O(l)$$

To estimate the heat of reaction, let us consider the following steps:

$$\text{(b)}\quad C_6H_4(OH)_2(aq) \longrightarrow C_6H_4O_2(aq) + H_2(g) \qquad \Delta H^\circ = 177\ \text{kJ/mol}$$

$$\text{(c)}\quad H_2O_2(aq) \longrightarrow H_2O(l) + \tfrac{1}{2}O_2(g) \qquad \Delta H^\circ = -94.6\ \text{kJ/mol}$$

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

Recalling Hess's law, we find that the heat of reaction for (a) is simply the *sum* of those for (b), (c), and (d).

A bombardier beetle discharging a chemical spray.

Therefore, we write

$$\begin{aligned}\Delta H^\circ_a &= \Delta H^\circ_b + \Delta H^\circ_c + \Delta H^\circ_d \\ &= (177 - 94.6 - 286)\ \text{kJ/mol} \\ &= -204\ \text{kJ/mol}\end{aligned}$$

The large amount of heat generated is sufficient to bring the mixture to its boiling point. By rotating the tip of its abdomen, the beetle can quickly discharge the vapor in the form of a fine mist toward an unsuspecting predator. In addition to the thermal effect, the quinones also act as a repellent to other insects and animals. One bombardier beetle carries enough reagents to produce 20 to 30 discharges in quick succession, each with an audible detonation.

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

Similar problems: 6.54, 6.57.

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

In general, the more negative the standard enthalpy of formation of a compound the more stable is the compound. Thus, in the thermite reaction the less stable Fe_2O_3 is converted to the more stable Al_2O_3 and we expect the reaction to release a large amount of heat.

6.7 Heat of Solution and Dilution

Although we have focused so far on the thermal energy effects resulting from chemical reactions, many physical processes, such as the melting of ice or the condensation of a vapor, also involve the absorption or release of heat. Enthalpy changes occur as well when a solute dissolves in a solvent or when a solution is diluted. Let us look at these two related physical processes, involving heat of solution and heat of dilution.

Heat of Solution

In the vast majority of cases, dissolving a solute in a solvent produces measurable heat change. At constant pressure, the heat change is equal to the enthalpy change. The ***heat of solution,*** or ***enthalpy of solution,*** $\boldsymbol{\Delta H_{soln}}$, is *the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.* The quantity ΔH_{soln} represents the difference between the enthalpy of the final solution and the enthalpies of its original components (that is, solute and solvent) before they are mixed. Thus,

$$\Delta H_{\text{soln}} = H_{\text{soln}} - H_{\text{components}} \tag{6.19}$$

Neither H_{soln} nor $H_{\text{components}}$ can be measured, but their difference, ΔH_{soln}, can be readily determined in a constant-pressure calorimeter. Like other enthalpy changes, ΔH_{soln} is positive for endothermic (heat-absorbing) processes and negative for exothermic (heat-generating) processes.

Consider the heat of solution of a process in which an ionic compound is the solute and water is the solvent. For example, what happens when solid NaCl dissolves in water? In solid NaCl, the Na^+ and Cl^- ions are held together by strong positive-negative (electrostatic) forces, but when a small crystal of NaCl dissolves in water, the three-dimensional network of ions breaks into its individual units. (The structure of solid NaCl is shown in Figure 2.13.) The separated Na^+ and Cl^- ions are stabilized in solution by their interaction with water molecules (see Figure 4.2). These ions are said to be *hydrated.* In this case water plays a role similar to that of a good electrical insulator. Water molecules shield the ions (Na^+ and Cl^-) from each other and effectively reduce the electrostatic attraction that held them together in the solid state. The heat of solution is defined by the following process:

$$\text{NaCl}(s) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(aq) + \text{Cl}^-(aq) \qquad \Delta H_{\text{soln}} = ?$$

Dissolving an ionic compound such as NaCl in water involves complex interactions among the solute and solvent species. However, for the sake of analysis we can imagine that the solution process takes place in two separate steps, illustrated in Figure 6.11. First, the Na^+ and Cl^- ions in the solid crystal are separated from each other and converted to the gaseous state:

$$\text{energy} + \text{NaCl}(s) \longrightarrow \text{Na}^+(g) + \text{Cl}^-(g)$$

The word "lattice" describes arrangement in space of isolated points (occupied by ions) in a regular pattern. Lattice energy is a positive quantity.

The energy required to completely separate one mole of a solid ionic compound into gaseous ions is called ***lattice energy*** ***(U).*** The lattice energy of NaCl is 788 kJ/mol. In other words, we would need to supply 788 kJ of energy to break 1 mole of solid NaCl into 1 mole of Na^+ ions and 1 mole of Cl^- ions.

Next, the "gaseous" Na^+ and Cl^- ions enter the water and become hydrated:

$$\text{Na}^+(g) + \text{Cl}^-(g) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{energy}$$

The enthalpy change associated with the hydration process is called the ***heat of hydration,*** $\boldsymbol{\Delta H_{hydr}}$ (heat of hydration is a negative quantity for cations and anions).

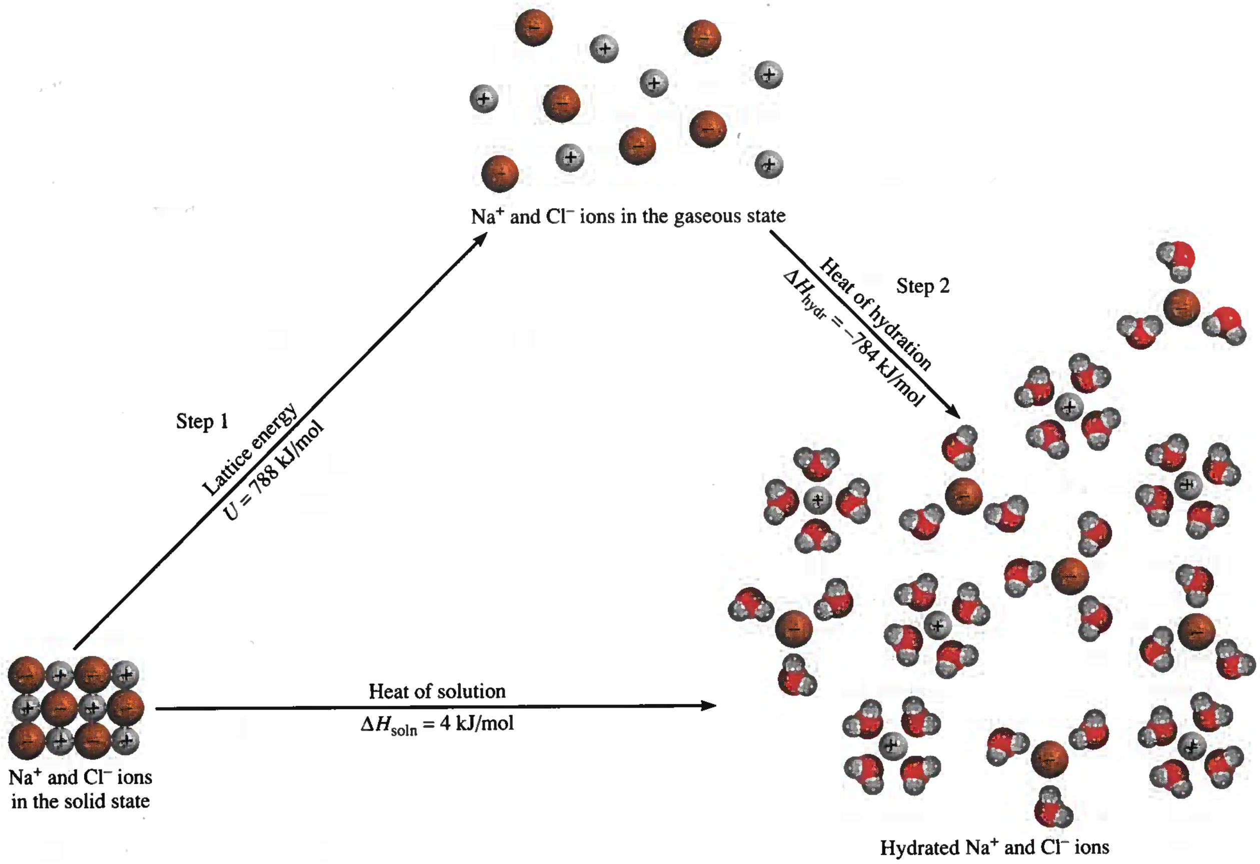


Figure 6.11 *The solution process for NaCl. The process can be considered to occur in two separate steps: (1) separation of ions from the crystal state to the gaseous state and (2) hydration of the gaseous ions. The heat of solution is equal to the energy changes for these two steps,* $\Delta H_{soln}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

Applying Hess's law, it is possible to consider ΔH_{soln} as the sum of two related quantities, lattice energy (U) and heat of hydration (ΔH_{hydr}), as shown in Figure 6.11:

$$\Delta H_{soln} = U + \Delta H_{hydr} \tag{6.20}$$

Therefore,

$$\begin{array}{rlrl} NaCl(s) & \longrightarrow Na^+(g) + Cl^-(g) & U &= 788 \text{ kJ/mol} \\ Na^+(g) + Cl^-(g) & \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq) & \Delta H_{hydr} &= -784 \text{ kJ/mol} \\ \hline NaCl(s) & \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq) & \Delta H_{soln} &= 4 \text{ kJ/mol} \end{array}$$

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

TABLE 6.5

Heats of Solution of Some Ionic Compounds

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

Heat of Dilution

When a previously prepared solution is *diluted,* that is, when more solvent is added to lower the overall concentration of the solute, additional heat is usually given off or absorbed. The ***heat of dilution*** is *the heat change associated with the dilution process.*

If a certain solution process is endothermic and the solution is subsequently diluted, *more* heat will be absorbed by the same solution from the surroundings. The converse holds true for an exothermic solution process—more heat will be liberated if additional solvent is added to dilute the solution. Therefore, always be cautious when working on a dilution procedure in the laboratory. Because of its highly exothermic heat of dilution, concentrated sulfuric acid (H_2SO_4) poses a particularly hazardous problem if its concentration must be reduced by mixing it with additional water. Concentrated H_2SO_4 is composed of 98 percent acid and 2 percent water by mass. Diluting it with water releases considerable amount of heat to the surroundings. This process is so exothermic that you must *never* attempt to dilute the concentrated acid by adding water to it. The heat generated could cause the acid solution to boil and splatter. The recommended procedure is to add the concentrated acid slowly to the water (while constantly stirring).

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

Summary of Facts and Concepts

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

Key Words

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Questions and Problems

Definitions

Review Questions

6.1 Define these terms: system, surroundings, open system, closed system, isolated system, thermal energy, chemical energy, potential energy, kinetic energy, law of conservation of energy.

6.2 What is heat? How does heat differ from thermal energy? Under what condition is heat transferred from one system to another?

6.3 What are the units for energy commonly employed in chemistry?

6.4 A truck initially traveling at 60 km per hour is brought to a complete stop at a traffic light. Does this change violate the law of conservation of energy? Explain.

6.5 These are various forms of energy: chemical, heat, light, mechanical, and electrical. Suggest ways of interconverting these forms of energy.

6.6 Describe the interconversions of forms of energy occurring in these processes: (a) You throw a softball up into the air and catch it. (b) You switch on a flashlight. (c) You ride the ski lift to the top of the hill and then ski down. (d) You strike a match and let it burn down.

Energy Changes in Chemical Reactions

Review Questions

6.7 Define these terms: thermochemistry, exothermic process, endothermic process.

6.8 Stoichiometry is based on the law of conservation of mass. On what law is thermochemistry based?

6.9 Describe two exothermic processes and two endothermic processes.

6.10 Decomposition reactions are usually endothermic, whereas combination reactions are usually exothermic. Give a qualitative explanation for these trends.

First Law of Thermodynamics

Review Questions

6.11 On what law is the first law of thermodynamics based? Explain the sign conventions in the equation $\Delta E = q + w$.

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

6.13 The internal energy of an ideal gas depends only on its temperature. Do a first-law analysis of this process. A sample of an ideal gas is allowed to expand at constant temperature against atmospheric pressure. (a) Does the gas do work on its surroundings? (b) Is there heat exchange between the system and the surroundings? If so, in which direction? (c) What is ΔE for the gas for this process?

6.14 Consider these changes.

(a) $Hg(l) \longrightarrow Hg(g)$

(b) $3O_2(g) \longrightarrow 2O_3(g)$

(c) $CuSO_4 \cdot 5H_2O(s) \longrightarrow CuSO_4(s) + 5H_2O(g)$

(d) $H_2(g) + F_2(g) \longrightarrow 2HF(g)$

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

Problems

6.15 A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. Calculate the work done in joules if the gas expands (a) against a vacuum, (b) against a constant pressure of 0.80 atm, and (c) against a constant pressure of 3.7 atm.

6.16 A gas expands in volume from 26.7 mL to 89.3 mL at constant temperature. Calculate the work done (in joules) if the gas expands (a) against a vacuum, (b) against a constant pressure of 1.5 atm, and (c) against a constant pressure of 2.8 atm.

6.17 A gas expands and does *P-V* work on the surroundings equal to 325 J. At the same time, it absorbs 127 J of heat from the surroundings. Calculate the change in energy of the gas.

6.18 The work done to compress a gas is 74 J. As a result, 26 J of heat is given off to the surroundings. Calculate the change in energy of the gas.

6.19 Calculate the work done when 50.0 g of tin dissolves in excess acid at 1.00 atm and 25°C:

$$Sn(s) + 2H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$$

Assume ideal gas behavior.

6.20 Calculate the work done in joules when 1.0 mole of water vaporizes at 1.0 atm and 100°C. Assume that the volume of liquid water is negligible compared with that of steam at 100°C, and ideal gas behavior.

Enthalpy of Chemical Reactions

Review Questions

6.21 Define these terms: enthalpy, enthalpy of reaction. Under what condition is the heat of a reaction equal to the enthalpy change of the same reaction?

6.22 In writing thermochemical equations, why is it important to indicate the physical state (that is, gaseous, liquid, solid, or aqueous) of each substance?

6.23 Explain the meaning of this thermochemical equation:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \qquad \Delta H = -904 \text{ kJ/mol}$$

6.24 Consider this reaction:

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 4H_2O(l) + 2CO_2(g) \qquad \Delta H = -1452.8 \text{ kJ/mol}$$

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

Problems

6.25 The first step in the industrial recovery of zinc from the zinc sulfide ore is roasting, that is, the conversion of ZnS to ZnO by heating:

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g) \qquad \Delta H = -879 \text{ kJ/mol}$$

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

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

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = -114.6 \text{ kJ/mol}$$

6.27 Consider the reaction

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = 483.6 \text{ kJ/mol}$$

If 2.0 moles of $H_2O(g)$ are converted to $H_2(g)$ and $O_2(g)$ against a pressure of 1.0 atm at 125°C, what is ΔE for this reaction?

6.28 Consider the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -184.6 \text{ kJ/mol}$$

If 3 moles of H_2 react with 3 moles of Cl_2 to form HCl, calculate the work done (in joules) against a pressure of 1.0 atm at 25°C. What is ΔE for this reaction? Assume the reaction goes to completion.

Calorimetry

Review Questions

6.29 What is the difference between specific heat and heat capacity? What are the units for these two quantities? Which is the intensive property and which is the extensive property?

6.30 Consider two metals A and B, each having a mass of 100 g and an initial temperature of 20°C. The specific heat of A is larger than that of B. Under the same heating conditions, which metal would take longer to reach a temperature of 21°C?

6.31 Define calorimetry and describe two commonly used calorimeters. In a calorimetric measurement, why is it important that we know the heat capacity of the calorimeter? How is this value determined?

6.32 Consider the following data:

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

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

(a) Heat will flow from Al to Cu because Al has a larger specific heat.

(b) Heat will flow from Cu to Al because Cu has a larger mass.

(c) Heat will flow from Cu to Al because Cu has a larger heat capacity.

(d) Heat will flow from Cu to Al because Cu is at a higher temperature.

(e) No heat will flow in either direction.

Problems

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

6.34 A 6.22-kg piece of copper metal is heated from 20.5°C to 324.3°C. Calculate the heat absorbed (in kJ) by the metal.

6.35 Calculate the amount of heat liberated (in kJ) from 366 g of mercury when it cools from 77.0°C to 12.0°C.

6.36 A sheet of gold weighing 10.0 g and at a temperature of 18.0°C is placed flat on a sheet of iron weighing 20.0 g and at a temperature of 55.6°C. What is the final temperature of the combined metals? Assume that no heat is lost to the surroundings. (*Hint:* The heat gained by the gold must be equal to the heat lost by the iron. The specific heats of the metals are given in Table 6.2.)

6.37 A 0.1375-g sample of solid magnesium is burned in a constant-volume bomb calorimeter that has a heat capacity of 3024 J/°C. The temperature increases by 1.126°C. Calculate the heat given off by the burning Mg, in kJ/g and in kJ/mol.

6.38 A quantity of 2.00×10^2 mL of 0.862 *M* HCl is mixed with 2.00×10^2 mL of 0.431 *M* $Ba(OH)_2$ in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and $Ba(OH)_2$ solutions is the same at 20.48°C. For the process

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

the heat of neutralization is −56.2 kJ/mol. What is the final temperature of the mixed solution?

Standard Enthalpy of Formation and Reaction

Review Questions

6.39 What is meant by the standard-state condition?

6.40 How are the standard enthalpies of an element and of a compound determined?

6.41 What is meant by the standard enthalpy of a reaction?

6.42 Write the equation for calculating the enthalpy of a reaction. Define all the terms.

6.43 State Hess's law. Explain, with one example, the usefulness of Hess's law in thermochemistry.

6.44 Describe how chemists use Hess's law to determine the ΔH_f° of a compound by measuring its heat (enthalpy) of combustion.

Problems

6.45 Which of the following standard enthalpy of formation values is not zero at 25°C? $Na(s)$, $Ne(g)$, $CH_4(g)$, $S_8(s)$, $Hg(l)$, $H(g)$.

6.46 The ΔH_f° values of the two allotropes of oxygen, O_2 and O_3, are 0 and 142.2 kJ/mol, respectively, at 25°C. Which is the more stable form at this temperature?

6.47 Which is the more negative quantity at 25°C: ΔH_f° for $H_2O(l)$ or ΔH_f° for $H_2O(g)$?

6.48 Predict the value of ΔH_f° (greater than, less than, or equal to zero) for these elements at 25°C: (a) $Br_2(g)$; $Br_2(l)$, (b) $I_2(g)$; $I_2(s)$.

6.49 In general, compounds with negative ΔH_f° values are more stable than those with positive ΔH_f° values. $H_2O_2(l)$ has a negative ΔH_f° (see Table 6.4). Why, then, does $H_2O_2(l)$ have a tendency to decompose to $H_2O(l)$ and $O_2(g)$?

6.50 Suggest ways (with appropriate equations) that would enable you to measure the ΔH_f° values of $Ag_2O(s)$ and $CaCl_2(s)$ from their elements. No calculations are necessary.

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

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

(Look up the standard enthalpy of formation of the reactant and products in Table 6.4.)

6.52 The standard enthalpies of formation of ions in aqueous solutions are obtained by arbitrarily assigning a value of zero to H^+ ions; that is, $\Delta H_f^\circ[H^+(aq)] = 0$.

(a) For the following reaction

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq) \qquad \Delta H^\circ = -74.9 \text{ kJ/mol}$$

calculate ΔH_f° for the Cl^- ions.

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

6.53 Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 3:

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

(b) $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$

6.54 Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 3:

(a) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$

(b) $2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(l) + 2SO_2(g)$

6.55 Methanol, ethanol, and *n*-propanol are three common alcohols. When 1.00 g of each of these alcohols is burned in air, heat is liberated as shown by the following data: (a) methanol (CH_3OH), −22.6 kJ; (b) ethanol (C_2H_5OH), −29.7 kJ; (c) *n*-propanol (C_3H_7OH), −33.4 kJ. Calculate the heats of combustion of these alcohols in kJ/mol.

6.56 The standard enthalpy change for the following reaction is 436.4 kJ/mol:

$$H_2(g) \longrightarrow H(g) + H(g)$$

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

6.57 From the standard enthalpies of formation, calculate ΔH_{rxn}° for the reaction

$$C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

For $C_6H_{12}(l)$, $\Delta H_f^\circ = -151.9$ kJ/mol.

6.58 Pentaborane-9, B_5H_9, is a colorless, highly reactive liquid that will burst into flame when exposed to oxygen. The reaction is

$$2B_5H_9(l) + 12O_2(g) \longrightarrow 5B_2O_3(s) + 9H_2O(l)$$

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

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

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H_{rxn}^\circ = -92.6 \text{ kJ/mol}$$

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

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

6.61 From these data,

$$\mathrm{S(rhombic)} + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -296.06\ \mathrm{kJ/mol}$$

$$\mathrm{S(monoclinic)} + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -296.36\ \mathrm{kJ/mol}$$

calculate the enthalpy change for the transformation

$$\mathrm{S(rhombic)} \longrightarrow \mathrm{S(monoclinic)}$$

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

6.62 From the following data,

$$\mathrm{C(graphite)} + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -393.5\ \mathrm{kJ/mol}$$

$$\mathrm{H_2}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{H_2O}(l) \qquad \Delta H^\circ_{\mathrm{rxn}} = -285.8\ \mathrm{kJ/mol}$$

$$2\mathrm{C_2H_6}(g) + 7\mathrm{O_2}(g) \longrightarrow 4\mathrm{CO_2}(g) + 6\mathrm{H_2O}(l) \qquad \Delta H^\circ_{\mathrm{rxn}} = -3119.6\ \mathrm{kJ/mol}$$

calculate the enthalpy change for the reaction

$$2\mathrm{C(graphite)} + 3\mathrm{H_2}(g) \longrightarrow \mathrm{C_2H_6}(g)$$

6.63 From the following heats of combustion,

$$\mathrm{CH_3OH}(l) + \tfrac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\mathrm{H_2O}(l) \qquad \Delta H^\circ_{\mathrm{rxn}} = -726.4\ \mathrm{kJ/mol}$$

$$\mathrm{C(graphite)} + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -393.5\ \mathrm{kJ/mol}$$

$$\mathrm{H_2}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{H_2O}(l) \qquad \Delta H^\circ_{\mathrm{rxn}} = -285.8\ \mathrm{kJ/mol}$$

calculate the enthalpy of formation of methanol ($\mathrm{CH_3OH}$) from its elements:

$$\mathrm{C(graphite)} + 2\mathrm{H_2}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CH_3OH}(l)$$

6.64 Calculate the standard enthalpy change for the reaction

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

given that

$$2\mathrm{Al}(s) + \tfrac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Al_2O_3}(s) \qquad \Delta H^\circ_{\mathrm{rxn}} = -1669.8\ \mathrm{kJ/mol}$$

$$2\mathrm{Fe}(s) + \tfrac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s) \qquad \Delta H^\circ_{\mathrm{rxn}} = -822.2\ \mathrm{kJ/mol}$$

Heat of Solution and Dilution

Review Questions

6.65 Define the following terms: enthalpy of solution, hydration, heat of hydration, lattice energy, heat of dilution.

6.66 Why is the lattice of a solid always a positive quantity? Why is the hydration of ions always a negative quantity?

6.67 Consider two ionic compounds A and B. A has a larger lattice energy than B. Which of the two compounds is more stable?

6.68 $\mathrm{Mg^{2+}}$ is a smaller cation than $\mathrm{Na^+}$ and also carries more positive charge. Which of the two species has a larger hydration energy (in kJ/mol)? Explain.

6.69 Consider the dissolution of an ionic compound such as potassium fluoride in water. Break the process into the following steps: separation of the cations and anions in the vapor phase and the hydration of the ions in the aqueous medium. Discuss the energy changes associated with each step. How does the heat of solution of KF depend on the relative magnitudes of these two quantities? On what law is the relationship based?

6.70 Why is it dangerous to add water to a concentrated acid such as sulfuric acid in a dilution process?

Additional Problems

6.71 The convention of arbitrarily assigning a zero enthalpy value for the most stable form of each element in the standard state at 25°C is a convenient way of dealing with enthalpies of reactions. Explain why this convention cannot be applied to nuclear reactions.

6.72 Consider the following two reactions:

$$\mathrm{A} \longrightarrow 2\mathrm{B} \qquad \Delta H^\circ_{\mathrm{rxn}} = \Delta H_1$$

$$\mathrm{A} \longrightarrow \mathrm{C} \qquad \Delta H^\circ_{\mathrm{rxn}} = \Delta H_2$$

Determine the enthalpy change for the process

$$2\mathrm{B} \longrightarrow \mathrm{C}$$

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

$$\mathrm{AgNO_3}(s) \longrightarrow \mathrm{AgNO_2}(s) + \tfrac{1}{2}\mathrm{O_2}(g)$$

The standard enthalpy of formation of $\mathrm{AgNO_3}(s)$ is −123.02 kJ/mol. Calculate the standard enthalpy of formation of $\mathrm{AgNO_2}(s)$.

6.74 Hydrazine, $\mathrm{N_2H_4}$, decomposes according to the following reaction:

$$3\mathrm{N_2H_4}(l) \longrightarrow 4\mathrm{NH_3}(g) + \mathrm{N_2}(g)$$

(a) Given that the standard enthalpy of formation of hydrazine is 50.42 kJ/mol, calculate ΔH° for its decomposition. (b) Both hydrazine and ammonia burn in oxygen to produce $\mathrm{H_2O}(l)$ and $\mathrm{N_2}(g)$. Write balanced equations for each of these processes and calculate ΔH° for each of them. On a mass basis (per kg), would hydrazine or ammonia be the better fuel?

6.75 Consider the reaction

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -92.6\ \mathrm{kJ/mol}$$

If 2.0 moles of $\mathrm{N_2}$ react with 6.0 moles of $\mathrm{H_2}$ to form $\mathrm{NH_3}$, calculate the work done (in joules) against a pressure of 1.0 atm at 25°C. What is ΔE for this reaction? Assume the reaction goes to completion.

6.76 Calculate the heat released when 2.00 L of $Cl_2(g)$ with a density of 1.88 g/L react with an excess of sodium metal at 25°C and 1 atm to form sodium chloride.

6.77 Photosynthesis produces glucose, $C_6H_{12}O_6$, and oxygen from carbon dioxide and water:

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

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

6.78 A 2.10-mole sample of crystalline acetic acid, initially at 17.0°C, is allowed to melt at 17.0°C and is then heated to 118.1°C (its normal boiling point) at 1.00 atm. The sample is allowed to vaporize at 118.1°C and is then rapidly quenched to 17.0°C, so that it recrystallizes. Calculate ΔH° for the total process as described.

6.79 Calculate the work done in joules by the reaction

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

when 0.34 g of Na reacts with water to form hydrogen gas at 0°C and 1.0 atm.

6.80 You are given the following data:

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H^\circ = 436.4 \text{ kJ/mol}$$
$$Br_2(g) \longrightarrow 2Br(g) \qquad \Delta H^\circ = 192.5 \text{ kJ/mol}$$
$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g) \qquad \Delta H^\circ = -72.4 \text{ kJ/mol}$$

Calculate ΔH° for the reaction

$$H(g) + Br(g) \longrightarrow HBr(g)$$

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

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l) \qquad \Delta H^\circ_{rxn} = -1452.8 \text{ kJ/mol}$$

6.82 A 44.0-g sample of an unknown metal at 99.0°C was placed in a constant-pressure calorimeter containing 80.0 g of water at 24.0°C. The final temperature of the system was found to be 28.4°C. Calculate the specific heat of the metal. (The heat capacity of the calorimeter is 12.4 J/°C.)

6.83 A 1.00-mole sample of ammonia at 14.0 atm and 25°C in a cylinder fitted with a movable piston expands against a constant external pressure of 1.00 atm. At equilibrium, the pressure and volume of the gas are 1.00 atm and 23.5 L, respectively. (a) Calculate the final temperature of the sample. (b) Calculate q, w, and ΔE for the process. The specific heat of ammonia is 0.0258 J/g · °C.

6.84 Producer gas (carbon monoxide) is prepared by passing air over red-hot coke:

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

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

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

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

6.85 Compare the heat produced by the complete combustion of 1 mole of methane (CH_4) with a mole of water gas (0.50 mole H_2 and 0.50 mole CO) under the same conditions. On the basis of your answer, would you prefer methane over water gas as a fuel? Can you suggest two other reasons why methane is preferable to water gas as a fuel?

6.86 The so-called hydrogen economy is based on hydrogen produced from water using solar energy. The gas is then burned as a fuel:

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

A primary advantage of hydrogen as a fuel is that it is nonpolluting. A major disadvantage is that it is a gas and therefore is harder to store than liquids or solids. Calculate the volume of hydrogen gas at 25°C and 1.00 atm required to produce an amount of energy equivalent to that produced by the combustion of a gallon of octane (C_8H_{18}). The density of octane is 2.66 kg/gal, and its standard enthalpy of formation is −249.9 kJ/mol.

6.87 Ethanol (C_2H_5OH) and gasoline (assumed to be all octane, C_8H_{18}) are both used as automobile fuel. If gasoline is selling for \$2.50/gal, what would the price of ethanol have to be in order to provide the same amount of heat per dollar? The density and ΔH°_f of octane are 0.7025 g/mL and −249.9 kJ/mol and of ethanol are 0.7894 g/mL and −277.0 kJ/mol, respectively. 1 gal = 3.785 L.

6.88 The combustion of what volume of ethane (C_2H_6), measured at 23.0°C and 752 mmHg, would be required to heat 855 g of water from 25.0°C to 98.0°C?

6.89 If energy is conserved, how can there be an energy crisis?

6.90 The heat of vaporization of a liquid (ΔH_{vap}) is the energy required to vaporize 1.00 g of the liquid at its boiling point. In one experiment, 60.0 g of liquid nitrogen (boiling point −196°C) are poured into a Styrofoam cup containing 2.00×10^2 g of water at 55.3°C. Calculate the molar heat of vaporization of liquid nitrogen if the final temperature of the water is 41.0°C.

6.91 Explain the cooling effect experienced when ethanol is rubbed on your skin, given that

$$C_2H_5OH(l) \longrightarrow C_2H_5OH(g) \qquad \Delta H^\circ = 42.2 \text{ kJ/mol}$$

6.92 For which of the following reactions does $\Delta H^\circ_{rxn} = \Delta H^\circ_f$?

(a) $H_2(g) + S(\text{rhombic}) \longrightarrow H_2S(g)$

(b) $C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g)$

(c) $H_2(g) + CuO(s) \longrightarrow H_2O(l) + Cu(s)$

(d) $O(g) + O_2(g) \longrightarrow O_3(g)$

6.93 Calculate the work done (in joules) when 1.0 mole of water is frozen at 0°C and 1.0 atm. The volumes of one mole of water and ice at 0°C are 0.0180 L and 0.0196 L, respectively.

6.94 A quantity of 0.020 mole of a gas initially at 0.050 L and 20°C undergoes a constant-temperature expansion until its volume is 0.50 L. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 0.20 atm. (c) If the gas in (b) is allowed to expand unchecked until its pressure is equal to the external pressure, what would its final volume be before it stopped expanding, and what would be the work done?

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

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ = -393.5 \text{ kJ/mol}$$

$$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ = -395.4 \text{ kJ/mol}$$

6.96 (a) For most efficient use, refrigerator freezer compartments should be fully packed with food. What is the thermochemical basis for this recommendation? (b) Starting at the same temperature, tea and coffee remain hot longer in a thermal flask than chicken noodle soup. Explain.

6.97 Calculate the standard enthalpy change for the fermentation process. (See Problem 3.72.)

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

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

When the outside plastic envelope is removed, O_2 molecules penetrate the paper, causing the reaction to begin. A typical packet contains 250 g of iron to warm your hands or feet for up to 4 hours. How much heat (in kJ) is produced by this reaction? (*Hint:* See Appendix 3 for ΔH°_f values.)

6.99 A person ate 0.50 pound of cheese (an energy intake of 4000 kJ). Suppose that none of the energy was stored in his body. What mass (in grams) of water would he need to perspire in order to maintain his original temperature? (It takes 44.0 kJ to vaporize 1 mole of water.)

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

6.101 A 19.2-g quantity of dry ice (solid carbon dioxide) is allowed to sublime (evaporate) in an apparatus like the one shown in Figure 6.5. Calculate the expansion work done against a constant external pressure of 0.995 atm and at a constant temperature of 22°C. Assume that the initial volume of dry ice is negligible and that CO_2 behaves like an ideal gas.

6.102 The enthalpy of combustion of benzoic acid (C_6H_5COOH) is commonly used as the standard for calibrating constant-volume bomb calorimeters; its value has been accurately determined to be −3226.7 kJ/mol. When 1.9862 g of benzoic acid are burned in a calorimeter, the temperature rises from 21.84°C to 25.67°C. What is the heat capacity of the bomb? (Assume that the quantity of water surrounding the bomb is exactly 2000 g.)

6.103 The combustion of a 25.0-g gaseous mixture of H_2 and CH_4 releases 2354 kJ of heat. Calculate the amounts of the gases in grams.

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

$$2CaO(s) + 2SO_2(g) + O_2(g) \longrightarrow 2CaSO_4(s)$$

Calculate the enthalpy change for this process if 6.6×10^5 g of SO_2 are removed by this process every day.

6.105 Glauber's salt, sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), undergoes a phase transition (that is, melting or freezing) at a convenient temperature of about 32°C:

$$Na_2SO_4 \cdot 10H_2O(s) \longrightarrow Na_2SO_4 \cdot 10H_2O(l) \quad \Delta H^\circ = 74.4 \text{ kJ/mol}$$

As a result, this compound is used to regulate the temperature in homes. It is placed in plastic bags in the ceiling of a room. During the day, the endothermic melting process absorbs heat from the surroundings, cooling the room. At night, it gives off heat as it freezes. Calculate the mass of Glauber's salt in kilograms needed to lower the temperature of air in a room by 8.2°C at 1.0 atm. The dimensions of the room are 2.80 m × 10.6 m × 17.2 m, the specific heat of air is 1.2 J/g · °C, and the molar mass of air may be taken as 29.0 g/mol.

6.106 A balloon 16 m in diameter is inflated with helium at 18°C. (a) Calculate the mass of He in the balloon, assuming ideal behavior. (b) Calculate the work done (in joules) during the inflation process if the atmospheric pressure is 98.7 kPa.

6.107 An excess of zinc metal is added to 50.0 mL of a 0.100 *M* $AgNO_3$ solution in a constant-pressure calorimeter like the one pictured in Figure 6.9. As a result of the reaction

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

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

6.108 (a) A person drinks four glasses of cold water (3.0°C) every day. The volume of each glass is 2.5×10^2 mL. How much heat (in kJ) does the body have to supply to raise the temperature of the water to 37°C, the body temperature? (b) How much heat would your body lose if you were to ingest 8.0×10^2 g of snow at 0°C to quench thirst? (The amount of heat necessary to melt snow is 6.01 kJ/mol.)

6.109 A driver's manual states that the stopping distance quadruples as the speed doubles; that is, if it takes 30 ft to stop a car moving at 25 mph then it would take 120 ft to stop a car moving at 50 mph. Justify this statement by using mechanics and the first law of thermodynamics. [Assume that when a car is stopped, its kinetic energy ($\frac{1}{2}mu^2$) is totally converted to heat.]

6.110 At 25°C, the standard enthalpy of formation of $HF(aq)$ is given by −320.1 kJ/mol; of $OH^-(aq)$, it is −229.6 kJ/mol; of $F^-(aq)$, it is −329.1 kJ/mol; and of $H_2O(l)$, it is −285.8 kJ/mol.

(a) Calculate the standard enthalpy of neutralization of $HF(aq)$:

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

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

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

calculate the standard enthalpy change for the reaction

$$HF(aq) \longrightarrow H^+(aq) + F^-(aq)$$

6.111 Why are cold, damp air and hot, humid air more uncomfortable than dry air at the same temperatures? (The specific heats of water vapor and air are approximately 1.9 J/g · °C and 1.0 J/g · °C, respectively.)

6.112 From the enthalpy of formation for CO_2 and the following information, calculate the standard enthalpy of formation for carbon monoxide (CO).

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -283.0 \text{ kJ/mol}$$

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

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

6.113 A 46-kg person drinks 500 g of milk, which has a "caloric" value of approximately 3.0 kJ/g. If only 17 percent of the energy in milk is converted to mechanical work, how high (in meters) can the person climb based on this energy intake? [*Hint:* The work done in ascending is given by *mgh*, where *m* is the mass (in kilograms), *g* the gravitational acceleration (9.8 m/s^2), and *h* the height (in meters).]

6.114 The height of Niagara Falls on the American side is 51 m. (a) Calculate the potential energy of 1.0 g of water at the top of the falls relative to the ground level. (b) What is the speed of the falling water if all of the potential energy is converted to kinetic energy? (c) What would be the increase in temperature of the water if all the kinetic energy were converted to heat? (See Problem 6.113 for suggestions.)

6.115 In the nineteenth century two scientists named Dulong and Petit noticed that for a solid element, the product of its molar mass and its specific heat is approximately 25 J/°C. This observation, now called Dulong and Petit's law, was used to estimate the specific heat of metals. Verify the law for the metals listed in Table 6.2. The law does not apply to one of the metals. Which one is it? Why?

6.116 Determine the standard enthalpy of formation of ethanol (C_2H_5OH) from its standard enthalpy of combustion (−1367.4 kJ/mol).

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

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

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

6.118 Ice at 0°C is placed in a Styrofoam cup containing 361 g of a soft drink at 23°C. The specific heat of the drink is about the same as that of water. Some ice remains after the ice and soft drink reach an equilibrium temperature of 0°C. Determine the mass of ice that has melted. Ignore the heat capacity of the cup. (*Hint:* It takes 334 J to melt 1 g of ice at 0°C.)

6.119 A gas company in Massachusetts charges \$1.30 for 15 ft^3 of natural gas (CH_4) measured at 20°C and 1.0 atm. Calculate the cost of heating 200 mL of water (enough to make a cup of coffee or tea) from 20°C to 100°C. Assume that only 50 percent of the heat generated by the combustion is used to heat the water; the rest of the heat is lost to the surroundings.

6.120 Calculate the internal energy of a Goodyear blimp filled with helium gas at 1.2×10^5 Pa. The volume of the blimp is 5.5×10^3 m^3. If all the energy were used to heat 10.0 tons of copper at 21°C, calculate the final temperature of the metal. (*Hint:* See Section 5.7 for help in calculating the internal energy of a gas. 1 ton = 9.072×10^5 g.)

6.121 Decomposition reactions are usually endothermic, whereas combination reactions are usually exothermic. Give a qualitative explanation for these trends.

6.122 Acetylene (C_2H_2) can be made by reacting calcium carbide (CaC_2) with water. (a) Write an equation for the reaction. (b) What is the maximum amount of heat (in joules) that can be obtained from the combustion of acetylene, starting with 74.6 g of CaC_2?

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

6.124 When 1.034 g of naphthalene ($C_{10}H_8$) are burned in a constant-volume bomb calorimeter at 298 K, 41.56 kJ of heat are evolved. Calculate ΔE and ΔH for the reaction on a molar basis.

6.125 From a thermochemical point of view, explain why a carbon dioxide fire extinguisher or water should not be used on a magnesium fire.

Special Problems

6.126 Calculate the ΔE for the following reaction at 298 K

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

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

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H^\circ = 177.8 \text{ kJ/mol}$$

Slaked lime is produced by treating quicklime with water:

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) \qquad \Delta H^\circ = -65.2 \text{ kJ/mol}$$

The exothermic reaction of quicklime with water and the rather small specific heats of both quicklime ($0.946 \text{ J/g} \cdot {}^\circ\text{C}$) and slaked lime ($1.20 \text{ J/g} \cdot {}^\circ\text{C}$) make it hazardous to store and transport lime in vessels made of wood. Wooden sailing ships carrying lime would occasionally catch fire when water leaked into the hold. (a) If a 500-g sample of water reacts with an equimolar amount of CaO (both at an initial temperature of 25°C), what is the final temperature of the product, $Ca(OH)_2$? Assume that the product absorbs all of the heat released in the reaction. (b) Given that the standard enthalpies of formation of CaO and H_2O are −635.6 kJ/mol and −285.8 kJ/mol, respectively, calculate the standard enthalpy of formation of $Ca(OH)_2$.

6.128 A 4.117-g impure sample of glucose ($C_6H_{12}O_6$) was burned in a constant-volume calorimeter having a heat capacity of 19.65 kJ/°C. If the rise in temperature is 3.134°C, calculate the percent by mass of the glucose in the sample. Assume that the impurities are unaffected by the combustion process. See Appendix 3 for thermodynamic data.

6.129 Construct a table with the headings q, w, ΔE, and ΔH. For each of the following processes, deduce whether each of the quantities listed is positive (+), negative (−), or zero (0). (a) Freezing of benzene. (b) Compression of an ideal gas at constant temperature. (c) Reaction of sodium with water. (d) Boiling liquid ammonia, (e) Heating a gas at constant volume. (f) Melting of ice.

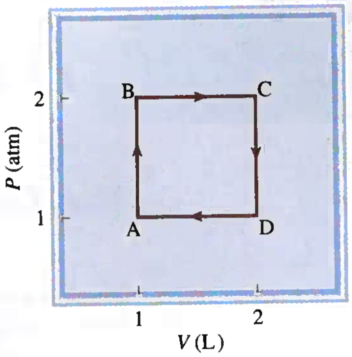
6.130 The combustion of 0.4196 g of a hydrocarbon releases 17.55 kJ of heat. The masses of the products are CO_2 = 1.419 g and H_2O = 0.290 g. (a) What is the empirical formula of the compound? (b) If the approximate molar mass of the compound is 76 g, calculate its standard enthalpy of formation.

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

6.132 From the following data, calculate the heat of solution for KI:

	NaCl	NaI	KCl	KI
Lattice energy (kJ/mol)	788	686	699	632
Heat of solution (kJ/mol)	4.0	−5.1	17.2	?

6.133 Starting at A, an ideal gas undergoes a cyclic process involving expansion and compression at constant temperature, as shown here. Calculate the total work done. Does your result support the notion that work is not a state function?



Answers to Practice Exercises

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

CHEMICAL Mystery

The Exploding Tire†

It was supposed to be a routine job: Fix the flat tire on Harvey Smith's car. The owner of Tom's Garage, Tom Lee, gave the tire to Jerry to work on, while he went outside to pump gas. A few minutes later, Tom heard a loud bang. He rushed inside to find the tire blown to pieces, a wall collapsed, equipment damaged, and Jerry lying on the floor, unconscious and bleeding. Luckily Jerry's injury was not serious. As he lay in the hospital recovering, the mystery of the exploding tire unfolded.

The tire had gone flat when Harvey drove over a nail. Being a cautious driver, Harvey carried a can of instant tire repair in the car, so he was able to reinflate the tire and drive safely home. The can of tire repair Harvey used contained latex (natural rubber) dissolved in a liquid propellant, which is a mixture of propane (C_3H_8) and butane (C_4H_{10}). Propane and butane are gases under atmospheric conditions but exist as liquids under compression in the can. When the valve on the top of the can is pressed, it opens, releasing the pressure inside. The mixture boils, forming a latex foam which is propelled by the gases into the tire to seal the puncture while the gas reinflates the tire.

The pressure in a flat tire is approximately one atmosphere, or roughly 15 pounds per square inch (psi). Using the aerosol tire repair, Harvey reinflated his damaged tire to a pressure of 35 psi. This is called the gauge pressure, which is the pressure of the tire *above* the atmospheric pressure. Thus, the total pressure in the tire was actually (15 + 35) psi, or 50 psi. One problem with using natural gases like propane and butane as propellants is that they are highly flammable. In fact, these gases can react explosively when mixed with air at a concentration of 2 percent to 9 percent by volume. Jerry was aware of the hazards of repairing Harvey's tire and look precautions to avoid an accident. First he let out the excess gas in the tire. Next he reinflated the tire to 35 psi with air. And he repeated the procedure once. Clearly, this is a dilution process intended to gradually decrease the concentrations of propane and butane. The fact that the tire exploded means that Jerry had not diluted the gases enough. But what was the source of ignition?

When Jerry found the nail hole in the tire, he used a tire reamer, a metal file-like instrument, to clean dirt and loose rubber from the hole before applying a rubber plug and liquid sealant. The last thing Jerry remembered was pulling the reamer out of the hole. The next thing he knew he was lying in the hospital, hurting all over. To solve this mystery, make use of the following clues.

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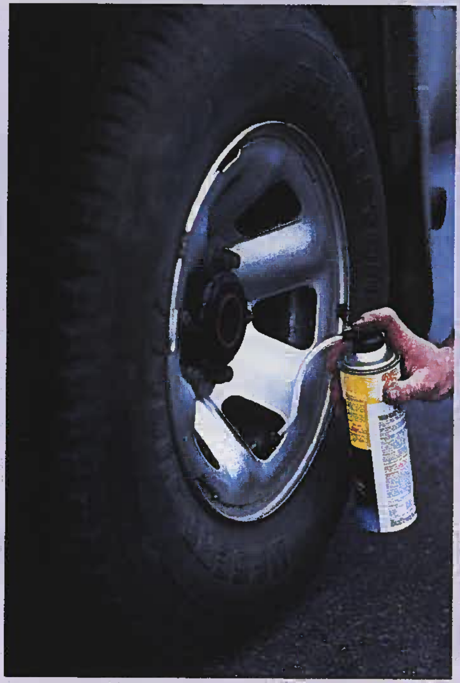
† Adapted with permission from "The Exploding Tire," by Jay A. Young, CHEM MATTERS, April, 1988, p. 12. Copyright 1995 American Chemical Society.

Chemical Clues

1. Write balanced equations for the combustion of propane and butane. The products are carbon dioxide and water.
2. When Harvey inflated his flat tire to 35 psi, the composition by volume of the propane and butane gases is given by (35 psi/50 psi) × 100%, or 70 percent. When Jerry deflated the tire the first time, the pressure fell to 15 psi but the composition remained at 70 percent. Based on these facts, calculate the percent composition of propane and butane at the end of two deflation-inflation steps. Does it fall within the explosive range?
3. Given that Harvey's flat tire is a steel-belted tire, explain how the ignition of the gas mixture might have been triggered. (A steel-belted tire has two belts of steel wire for outer reinforcement and two belts of polyester cord for inner reinforcement.)



Instant flat tire repair.