6

Thermochemistry: Energy Flow and Chemical Change

Heat Released and Absorbed As you digest food, heat is released, and some of it is absorbed by ice you hold in your hand. In this chapter, we explore energy flow during chemical or physical change.

Key Principles

to focus on while studying this chapter

- Chemical or physical change is *always* accompanied by a change in the energy content of the matter. ***(Introduction)***
- To study a *change in energy* (ΔE), scientists conceptually divide the universe into the *system* (the part being studied) and the *surroundings* (everything else). All energy changes occur as *heat* (q) and/or *work* (w), transferred either from the surroundings to the system or from the system to the surroundings ($\Delta E = q + w$). Thus, the total energy of the universe is constant *(law of conservation of energy, or first law of thermodynamics).* ***(Section 6.1)***
- Because E is a *state function*—a property that depends *only* on the current state of the system—ΔE depends only on the difference between the initial and final values of E. Therefore, the magnitude of ΔE is the same no matter how a given change in energy occurs. ***(Section 6.1)***
- *Enthalpy* (H) is also a state function and is related to E. The *change in enthalpy* (ΔH) equals the heat transferred at constant pressure, q_P. Most laboratory, environmental, and biological changes occur at constant P, so ΔH is more relevant than ΔE and easier to measure. ***(Section 6.2)***
- The *change in the enthalpy of a reaction* (ΔH_{rxn}) is negative (<0) if the reaction releases heat *(exothermic)* and positive (>0) if it absorbs heat *(endothermic).* ***(Section 6.2)***
- The more heat a substance absorbs, the higher its temperature becomes, but each material has its own *capacity* for absorbing heat. Knowing this capacity and measuring the change in temperature in a *calorimeter,* we can find ΔH_{rxn}. ***(Section 6.3)***
- The quantity of heat released or absorbed in a reaction is related *stoichiometrically* to the amounts (mol) of reactants and products. ***(Section 6.4)***
- Because H is a state function, we can find ΔH of any reaction by imagining the reaction occurring as the sum of other reactions whose enthalpies of reaction we know or can measure *(Hess's law).* ***(Section 6.5)***
- Chemists have specified a set of conditions, called *standard states,* to determine and compare enthalpies (and other thermodynamic variables) of different reactions. Each substance has a *standard enthalpy of formation* (ΔH_f°), the enthalpy of reaction when 1 mol of the substance is formed from its elements under these conditions. The ΔH_f° values for each substance in a reaction are used to calculate the *standard enthalpy of reaction* (ΔH_{rxn}°). ***(Section 6.6)***

Outline

All matter contains energy, so *whenever matter undergoes a change, the quantity of energy that the matter contains also changes*. If a burning candle melts a piece of ice, both chemical and physical changes occur. In the chemical change, the higher energy reactants (wax and O_2) form lower energy products (CO_2 and H_2O), and the difference in energy is *released* as heat and light. Then, during the physical change, some of that heat is *absorbed* when lower energy ice becomes higher energy water. In a thunderstorm, the changes in energy are reversed: lower energy N_2 and O_2 *absorb* energy from lightning to form higher energy NO, and higher energy water vapor *releases* energy as it condenses to lower energy liquid water that falls as rain.

This interplay of matter and energy has an enormous impact on society. On an everyday level, many familiar materials release, absorb, or alter the flow of energy. Fuels such as oil and wood release energy to warm our homes or power our vehicles. Fertilizers help crops convert solar energy into the energy in food. Metal wires speed the flow of electrical energy, and polymer fibers in winter clothing limit the flow of thermal energy away from our bodies.

Thermodynamics is the study of energy and its transformations, and two chapters in this text address this central topic. Our focus here is on **thermochemistry,** the branch of thermodynamics that deals with heat in chemical and physical change.

CONCEPTS & SKILLS TO REVIEW
before studying this chapter

- energy and its interconversion (Section 1.1)
- distinction between heat and temperature (Section 1.4)
- nature of chemical bonding (Section 2.7)
- calculations of reaction stoichiometry (Section 3.4)
- properties of the gaseous state (Section 5.1)
- relation between kinetic energy and temperature (Section 5.5)

6.1 • FORMS OF ENERGY AND THEIR INTERCONVERSION

In Chapter 1, we saw that all energy is either potential or kinetic, and that these forms are interconvertible. An object has potential energy by virtue of its position and kinetic energy by virtue of its motion. Let's re-examine these ideas by considering a weight raised above the ground. As your muscles or a motor raise the weight, its potential energy increases; this energy is converted to kinetic energy as the weight falls (see Figure 1.3). When it hits the ground, some of that kinetic energy appears as *work* done when the weight moves the soil and pebbles slightly, and some appears as *heat* when it warms them slightly. Thus, in this situation, *potential energy is converted to kinetic energy, which appears as work and heat.*

Several other forms of energy—solar, electrical, nuclear, and chemical—are examples of potential and kinetic energy on the atomic scale. No matter what the form of energy or the situation, *when energy is transferred from one object to another, it appears as work and/or heat.* In this section, we examine this idea in terms of the release or absorption of energy during a chemical or physical change.

Defining the System and Its Surroundings

In order to observe and measure a change in energy, we must first define the **system**—the part of the universe we are focusing on. The moment we define the system, everything else is defined as the **surroundings.**

For example, for a flask containing a solution, if we define the system as the contents of the flask, then the flask itself, other nearby equipment, and perhaps the rest of the laboratory are the surroundings. In principle, the rest of the universe is the surroundings, but in practice, we consider only the parts that are relevant to the system: it's not likely that a thunderstorm in central Asia or a methane blizzard on Neptune will affect the contents of the flask, but the temperature and pressure of the lab might.

THINK OF IT THIS WAY
Wherever You Look, There Is a System

If we define a weight falling to the ground as the system, then the soil and pebbles that are moved and warmed when it lands are the surroundings. An astronomer may define a galaxy as the system and nearby galaxies as the surroundings. An ecologist in Africa can define a zebra herd as the system and the animals, plants, and water supplies that the herd has contact with as the surroundings. A microbiologist may define a bacterial cell as the system and the extracellular solution as the surroundings. Thus, in general, the nature of the experiment and the focus of the experimenter define system and surroundings.

Energy Transfer to and from a System

Each particle in a system has potential energy and kinetic energy, and the sum of all these energies is the **internal energy, *E*,** of the system (some texts use the symbol U). When the reactants in a chemical system change to products, the system's internal energy has changed. This change, ΔE, is the difference between the internal energy *after* the change (E_{final}) and *before* the change (E_{initial}):

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}} \qquad \textbf{(6.1)}$$

where Δ (Greek *delta*) means "change (or difference) in" and refers to the *final state* ***minus*** *the initial state.* Thus, ΔE is the final quantity of energy of the system *minus* the initial quantity.

Because the universe consists of only system and surroundings, *a change in the energy of the system must be accompanied by an* ***equal*** *and* ***opposite*** *change in the energy of the surroundings.* In an *energy diagram,* the final and initial states are horizontal lines along a vertical energy axis, with ΔE the difference in the heights of the lines. A system can change its internal energy in one of two ways:

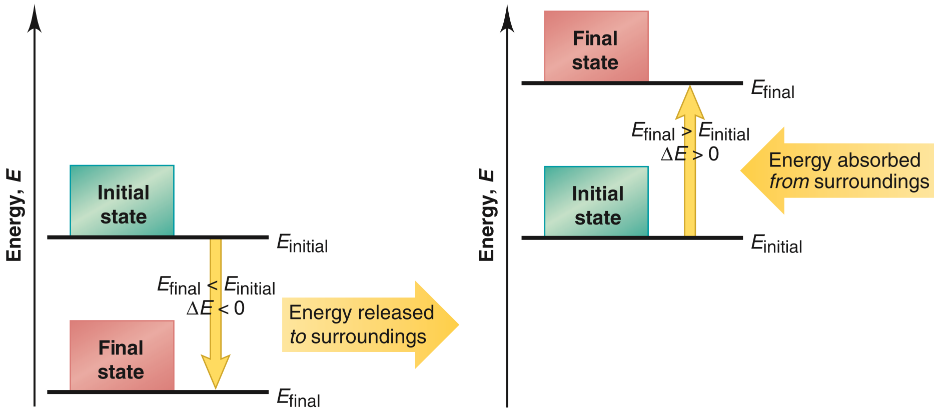
- By releasing some energy in a transfer *to* the surroundings (Figure 6.1A):

$$E_{\text{final}} < E_{\text{initial}} \qquad \text{so} \qquad \Delta E < 0$$

- By absorbing some energy in a transfer *from* the surroundings (Figure 6.1B):

$$E_{\text{final}} > E_{\text{initial}} \qquad \text{so} \qquad \Delta E > 0$$

Thus, ΔE is a *transfer* of energy from system to surroundings, or vice versa.



A **Energy of system decreases.**

B **Energy of system increases.**

Figure 6.1 Energy diagrams for the transfer of internal energy (E) between a system and its surroundings. **A,** When the system releases energy, ΔE ($E_{\text{final}} - E_{\text{initial}}$) is negative. **B,** When the system absorbs energy, ΔE ($E_{\text{final}} - E_{\text{initial}}$) is positive. (The vertical yellow arrow always has its tail at the initial state.)

Heat and Work: Two Forms of Energy Transfer

Energy transferred from system to surroundings or vice versa appears in two forms:

1. *Heat.* **Heat** or *thermal energy* (symbolized by q) is the energy transferred as a result of a difference in temperature between the system and the surroundings. For example, energy in the form of heat is transferred from hot soup (system) to the bowl, air, and table (surroundings) because they are at a lower temperature.

2. *Work.* All other forms of energy transfer involve some type of **work (w),** the energy transferred when an object is moved by a force. When you (system) kick a football, energy is transferred as work because the force of the kick moves the ball and air around it (surroundings). When you pump up a ball, energy is transferred as work because the added air (system) exerts a force on the inner wall of the ball (surroundings) and moves it outward.

The total change in a system's internal energy is the sum of the energy transferred as heat and/or work:

$$\Delta E = q + w \qquad \textbf{(6.2)}$$

The values of q and w (and, therefore, of ΔE) can have either a positive or negative sign. *We define the sign of the energy change from the* ***system's*** *perspective:*

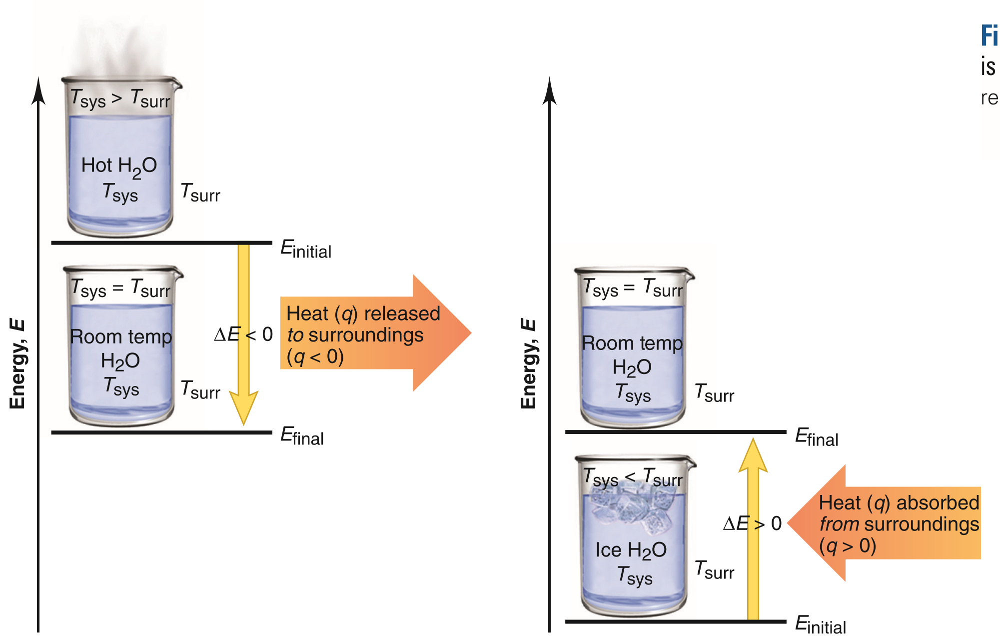
- Energy transferred *into* the system is *positive* because the *system ends up with more* energy.
- Energy transferred *out from* the system is *negative,* because the *system ends up with less* energy.

Innumerable combinations of heat and/or work can change a system's internal energy. In the rest of this subsection, we'll examine the four simplest cases—two that involve only heat and two that involve only work.

Energy Transferred as Heat Only For a system that transfers energy only as heat (q) and does no work ($w = 0$), we have, from Equation 6.2, $\Delta E = q + 0 = q$. There are two ways this transfer can happen:

1. *Heat flowing* ***out*** *from a system.* Suppose hot water is the system, and the beaker holding it and the rest of the lab are the surroundings. The water transfers energy as heat outward until the temperature of the water and the surroundings are equal. Since heat flows *out* from the system, the final energy of the system is less than the initial energy. Heat is released, so *q is negative,* and therefore *ΔE is negative* (Figure 6.2A).

2. *Heat flowing* ***into*** *a system.* If the system consists of ice water, the surroundings transfer energy as heat *into* the system, once again until the ice melts and the temperature of the water and the surroundings become equal. In this case, heat flows *in,* so the final energy of the system is higher than its initial energy. Heat is absorbed, so *q is positive,* and therefore *ΔE is positive* (Figure 6.2B).



A **Energy released as heat.**

B **Energy absorbed as heat.**

Figure 6.2 The two cases where energy is transferred as heat only. **A,** The system releases heat. **B,** The system absorbs heat.

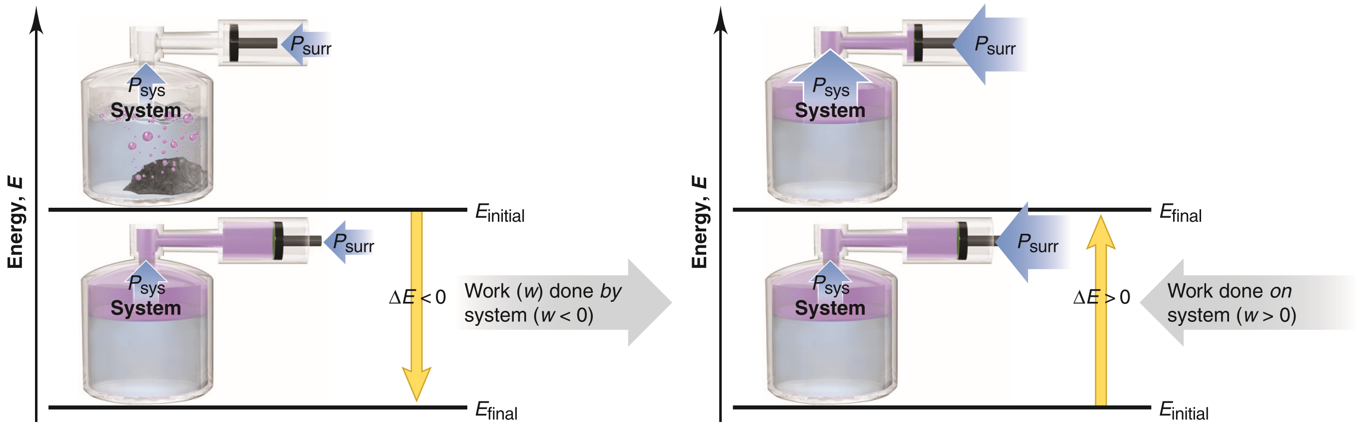
THINK OF IT THIS WAY

Thermodynamics in the Kitchen

A new view of two familiar kitchen appliances can clarify the sign of q. The air in a refrigerator (surroundings) has a lower temperature than a newly added piece of food (system), so the food releases energy as heat to the refrigerator air, $q < 0$. The air in a hot oven (surroundings) has a higher temperature than a newly added piece of food (system), so the food absorbs energy as heat from the oven air, $q > 0$.

Energy Transferred as Work Only For a system that transfers energy only as work, $q = 0$; therefore, $\Delta E = 0 + w = w$. There are two ways this transfer can happen:

1. *Work done* ***by*** *a system* (Figure 6.3A, *next page*). Consider the reaction between zinc and hydrochloric acid as it takes place in a nearly evacuated, insulated container attached to a piston-cylinder assembly. We define the system as the reaction mixture, and the surroundings as the container, piston-cylinder, outside air, and so forth. In the initial state, the internal energy is the energy of the reactants (metallic zinc and



A **Energy released as work.**

B **Energy absorbed as work.**

Figure 6.3 The two cases where energy is transferred as work only. **A,** The system does work *on* the surroundings. **B,** The system has work done on it *by* the surroundings.

aqueous H^+ and Cl^- ions), and in the final state, it is the energy of the products (H_2 gas and aqueous Zn^{2+} and Cl^- ions). As the gas forms, it pushes back the piston. Thus, energy is transferred as work done *by* the system *on* the surroundings. Since the system releases energy as work, *w is negative;* the final energy of the system is less than the initial energy, so *ΔE is negative*. (The work done here is not very useful because it just pushes back the piston and outside air. But, if the reaction mixture is gasoline and oxygen and the surroundings are an automobile engine, much of the internal energy is transferred as the work done to move the car.)

2. *Work done* ***on*** *a system* (Figure 6.3B). Suppose that, after the reaction of zinc and hydrochloric acid is over, we make another change (which makes the new $E_{initial}$ the same as the previous E_{final}): we increase the pressure of the surroundings (wider P_{surr} arrow) so that the piston moves in. Energy is transferred as work done *by* the surroundings *on* the system, so *w is positive.* The final energy of the system is greater than the initial energy, so *ΔE is positive.*

Table 6.1 summarizes the sign conventions for *q* and *w* and their effect on the sign of Δ*E*.

Table 6.1 The Sign Conventions* for *q, w,* and Δ*E*

q	**+**	***w***	**=**	**Δ*E***
+ (heat *absorbed*)		+ (work done *on*)		+ (energy *absorbed*)
+ (heat *absorbed*)		− (work done *by*)		Depends on the ***sizes*** of *q* and *w*
− (heat *released*)		+ (work done *on*)		Depends on the ***sizes*** of *q* and *w*
− (heat *released*)		− (work done *by*)		− (energy *released*)

*From the perspective of the system.

The Law of Energy Conservation

As you've seen, when a system absorbs energy, the surroundings release it, and when a system releases energy, the surroundings absorb it. Energy transferred between system and surroundings can be in the form of heat and/or various types of work—mechanical, electrical, radiant, chemical, and so forth.

Indeed, energy is often converted from one form to another during transfers. For example, when gasoline burns in a car engine, the reaction releases energy that is transferred as heat and work. The heat warms the car parts, passenger compartment, and surrounding air. The work is done when mechanical energy turns the car's wheels and belts. That energy is converted into the electrical energy of the sound system, the radiant energy of the headlights, the chemical energy of the battery, and so forth. The sum of all these forms equals the change in energy between reactants and products as the gasoline is burned.

Complex biological processes follow the same general pattern. During photosynthesis, green plants use solar energy to convert the lower energy bonds in CO_2 and H_2O into the higher energy bonds in starch and O_2; when you digest starch, this energy is converted into the muscular (mechanical) energy needed to run a marathon.

Thus, energy changes form but does not simply appear or disappear—energy cannot be created or destroyed. Put another way, *energy is conserved: the total energy of the system plus the surroundings remains constant*. The **law of conservation of energy,** also known as the **first law of thermodynamics,** restates this basic observation: *the total energy of the universe is constant.* It is expressed mathematically as

$$\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0 \qquad (6.3)$$

This law applies, as far as we know, to all systems, from a burning match to continental drift, from the pumping of your heart to the formation of the Solar System.

Units of Energy

The SI unit of energy is the **joule (J),** a derived unit composed of three base units:

$$1\text{ J} = 1\text{ kg}\cdot\text{m}^2/\text{s}^2$$

Both heat and work are expressed in joules. Let's see why the joule is the unit for work. The work (w) done on a mass is the force (F) times the distance (d) that the mass moves: $w = F \times d$. A *force* changes the velocity of a mass over time; that is, a force *accelerates* a mass. Velocity has units of meters per second (m/s), so acceleration (a) has units of meters per second per second (m/s^2). Force, therefore, has units of mass (m, in kilograms) times acceleration:

$$F = m \times a \quad \text{has units of} \quad \text{kg}\cdot\text{m/s}^2$$

Therefore, $$w = F \times d \quad \text{has units of} \quad (\text{kg}\cdot\text{m/s}^2) \times \text{m} = \text{kg}\cdot\text{m}^2/\text{s}^2 = \text{J}$$

The **calorie (cal)** is an older unit defined originally as the quantity of energy needed to raise the temperature of 1 g of water by 1°C (from 14.5°C to 15.5°C). The calorie is now defined in terms of the joule:

$$1\text{ cal} \equiv 4.184\text{ J} \qquad \text{or} \qquad 1\text{ J} = \frac{1}{4.184}\text{ cal} = 0.2390\text{ cal}$$

Since the quantities of energy involved in chemical reactions are usually quite large, chemists use the kilojoule (kJ), or, in earlier sources, the kilocalorie (kcal):

$$1\text{ kJ} = 1000\text{ J} = 0.2390\text{ kcal} = 239.0\text{ cal}$$

The nutritional Calorie (note the capital C), the unit that shows the energy available from food, is actually a kilocalorie.

The *British thermal unit (Btu),* a unit that you may have seen used for the energy output of appliances, is the quantity of energy required to raise the temperature of 1 lb of water by 1°F; *1 Btu is equivalent to 1055 J*. In general, the SI unit (J or kJ) is used in this text.

Sample Problem 6.1 Determining the Change in Internal Energy of a System

Problem When gasoline burns in a car engine, the heat released causes the products CO_2 and H_2O to expand, which pushes the pistons outward. Excess heat is removed by the car's radiator. If the expanding gases do 451 J of work on the pistons and the system releases 325 J to the surroundings as heat, calculate the change in energy (ΔE) in J, kJ, and kcal.

Plan We must define system and surroundings to choose signs for q and w, and then we calculate ΔE with Equation 6.2. The system is the reactants and products, and the surroundings are the pistons, the radiator, and the rest of the car. Heat is released by the system, so q is negative. Work is done by the system to push the pistons outward, so w is also negative. We obtain the answer in J and then convert it to kJ and kcal.

Solution Calculating ΔE (from Equation 6.2) in J:

$$q = -325\ \text{J}$$
$$w = -451\ \text{J}$$
$$\Delta E = q + w = -325\ \text{J} + (-451\ \text{J}) = -776\ \text{J}$$

Converting from J to kJ:

$$\Delta E = -776\ \text{J} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = -0.776\ \text{kJ}$$

Converting from kJ to kcal:

$$\Delta E = -0.776\ \text{kJ} \times \frac{1\ \text{kcal}}{4.184\ \text{kJ}} = -0.185\ \text{kcal}$$

Check The answer is reasonable: combustion of gasoline releases energy from the system, so $E_{\text{final}} < E_{\text{initial}}$ and ΔE should be negative. Rounding shows that, since 4 kJ $\approx$ 1 kcal, nearly 0.8 kJ should be nearly 0.2 kcal.

FOLLOW-UP PROBLEM 6.1 In a reaction, gaseous reactants form a liquid product. The heat absorbed by the surroundings is 26.0 kcal, and the work done on the system is 15.0 Btu. Calculate ΔE (in kJ).

State Functions and the Path Independence of the Energy Change

The internal energy (E) of a system is called a **state function,** a property dependent only on the *current* state of the system (its composition, volume, pressure, and temperature), *not* on the path the system takes to reach that state.

THINK OF IT THIS WAY

Your Personal Financial State Function

The *balance* in your checkbook is a state function of your personal financial system. You can open a new checking account with a birthday gift of \$50, or you can open one with a deposit of a \$100 paycheck and then write two \$25 checks. The two paths to the balance are different, but the balance (current state) is the same.

Thus, as in the financial analogy, the energy change of a system can occur by countless combinations of heat (q) and/or work (w). However, because E is a state function, the overall ΔE is the same no matter what the specific combination may be. That is, ΔE *does* ***not*** *depend on how the change takes place, but only on the* ***difference*** *between the final and initial states.*

As an example, let's define a system in its initial state as 1 mol of octane (a component of gasoline) together with enough O_2 to burn it completely. In its final state, the system is the CO_2 and H_2O that form:

$$\underset{\text{initial state } (E_{\text{initial}})}{C_8H_{18}(l) + \tfrac{25}{2}O_2(g)} \longrightarrow \underset{\text{final state } (E_{\text{final}})}{8CO_2(g) + 9H_2O(g)}$$

Energy is transferred *out* from the system as heat and/or work, so ΔE is negative. Figure 6.4 shows just two of the many ways the change can occur. If we burn the octane in an open container *(left)*, ΔE is transferred almost completely as heat (with

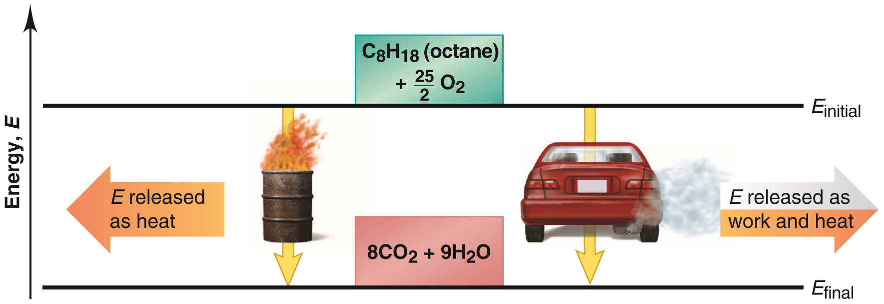


Figure 6.4 Two different paths for the energy change of a system. Even though q and w for the two paths are different, ΔE is the same.

a small quantity of work done to push back the atmosphere). If we burn it in a car engine *(right)*, a much larger portion (~30%) of ΔE is transferred as work that moves the car, with the rest released as heat that warms the car, exhaust gases, and surrounding air. If we burn the octane in a lawn mower or a motorcycle, ΔE appears as other combinations of work and heat. Thus, q and w are *not* state functions because their values *do* depend on the path the system takes, but ΔE (the *sum* of q and w) *does not.*

Pressure (P), volume (V), and temperature (T) are some other state functions. Path independence means that *changes in state functions—ΔE, ΔP, ΔV, and ΔT—depend only on the initial and final states.*

Summary of Section 6.1

- Internal energy (E) is transferred as heat (q) when system and surroundings are at different temperatures or as work (w) when an object is moved by a force.
- Heat absorbed by a system ($q > 0$) or work done on a system ($w > 0$) increases the system's E; heat released by a system ($q < 0$) or work done by a system ($w < 0$) decreases its E. The change in the internal energy is the sum of the heat and work: $\Delta E = q + w$. Heat and work are measured in joules (J).
- Energy is always conserved: it can change from one form to another and move into or out of the system, but the total quantity of energy in the universe (system *plus* surroundings) is constant.
- The internal energy of a system is a state function and, thus, is independent of how the system attained that energy; therefore, the same overall ΔE can occur through any combination of q and w.

6.2 • ENTHALPY: CHEMICAL CHANGE AT CONSTANT PRESSURE

Most physical and chemical changes occur at nearly constant atmospheric pressure—a reaction in an open flask, the freezing of a lake, a biochemical process in an organism. In this section, we discuss *enthalpy,* a thermodynamic variable that relates directly to energy changes at constant pressure.

The Meaning of Enthalpy

To determine ΔE, we must measure both heat and work. The two most important types of chemical work are electrical work, done by moving charged particles (Chapter 21), and **pressure-volume work (*PV* work),** the mechanical work done when the volume of the system changes in the presence of an external pressure (P). The quantity of PV work equals P times the change in volume (ΔV, or $V_{\text{final}} - V_{\text{initial}}$). In an open flask (or in a cylinder with a weightless, frictionless piston) (Figure 6.5), a system of an expanding gas does PV work *on* the surroundings, so it has a negative sign:

$$w = -P\Delta V \tag{6.4}$$

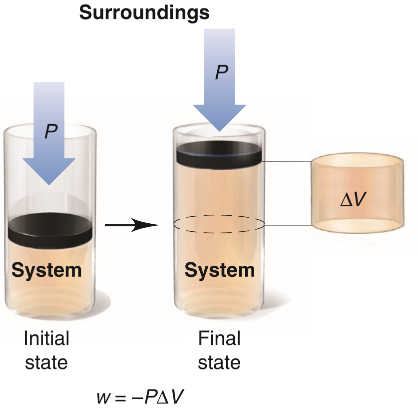


Figure 6.5 **Pressure-volume work.** An expanding gas pushing back the atmosphere does PV work ($w = -P\Delta V$).

For reactions *at constant pressure,* a thermodynamic variable called **enthalpy (*H*)** eliminates the need to measure PV work. The enthalpy of a system is defined as the internal energy *plus* the product of the pressure and volume:

$$H = E + PV$$

The **change in enthalpy (ΔH)** is the change in internal energy *plus* the product of the pressure, which is constant, and the change in volume (ΔV):

$$\Delta H = \Delta E + P\Delta V \tag{6.5}$$

Combining Equations 6.2 ($\Delta E = q + w$) and 6.4 ($w = -P\Delta V$) gives

$$\Delta E = q + w = q + (-P\Delta V) = q - P\Delta V$$

At constant pressure, we denote q as q_P, giving $\Delta E = q_P - P\Delta V$, which we can use to solve for q_P:

$$q_P = \Delta E + P\Delta V$$

Notice that the right sides of this equation and of Equation 6.5 are the same:

$$q_P = \Delta E + P\Delta V = \Delta H \tag{6.6}$$

Thus, *the change in enthalpy equals the heat absorbed or released at **constant** pressure*. For most changes at constant pressure, ΔH is more relevant than ΔE *and* easier to obtain: *to find* ΔH, *measure* q_P. We discuss the laboratory method in Section 6.3.

Exothermic and Endothermic Processes

Because H is a combination of the three state functions E, P, and V, it is also a state function. Therefore, ΔH equals H_{final} ***minus*** H_{initial}. For a reaction, H_{final} is H_{products} and H_{initial} is $H_{\text{reactants}}$, so the enthalpy change of a reaction is

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = H_{\text{products}} - H_{\text{reactants}}$$

Since H_{products} can be either more or less than $H_{\text{reactants}}$, the *sign* of ΔH indicates whether heat is absorbed or released during the reaction. We determine the sign of ΔH *by imagining the heat as "reactant" or "product."* The two possibilities are

1. *Exothermic process: heat as product*. An **exothermic** ("heat out") **process** *releases* heat and results in a *decrease* in the enthalpy of the system:

$$\text{Exothermic:} \qquad H_{\text{products}} < H_{\text{reactants}} \qquad \text{so} \qquad \Delta H < 0$$

For example, when methane burns in air, heat flows *out of* the system into the surroundings, so we show it as a product:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \textit{heat}$$

The reactants (1 mol of CH_4 and 2 mol of O_2) release heat during the reaction, so they originally had more enthalpy than the products (1 mol of CO_2 and 2 mol of H_2O):

$$H_{\text{reactants}} > H_{\text{products}} \qquad \text{so} \qquad \Delta H\ (H_{\text{products}} - H_{\text{reactants}}) < 0$$

This exothermic change is shown in the **enthalpy diagram** in Figure 6.6A.

2. *Endothermic process: heat as reactant*. An **endothermic** ("heat in") **process** *absorbs* heat and results in an *increase* in the enthalpy of the system:

$$\text{Endothermic:} \qquad H_{\text{products}} > H_{\text{reactants}} \qquad \text{so} \qquad \Delta H > 0$$

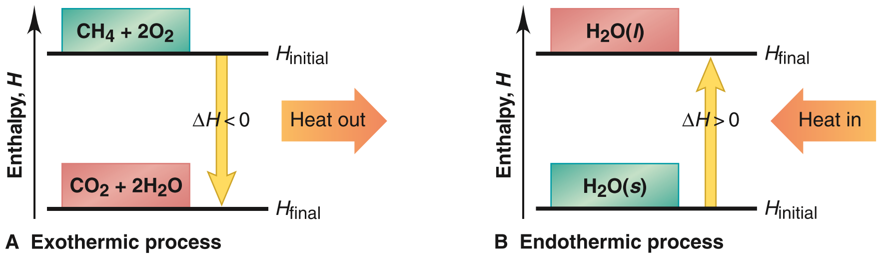
When ice melts, for instance, heat flows *into* the ice from the surroundings, so we show the heat as a reactant:

$$\textit{heat} + H_2O(s) \longrightarrow H_2O(l)$$

Because heat is absorbed, the enthalpy of the product (water) must be higher than that of the reactant (ice):

$$H_{\text{water}} > H_{\text{ice}} \qquad \text{so} \qquad \Delta H\ (H_{\text{water}} - H_{\text{ice}}) > 0$$

This endothermic change is shown in Figure 6.6B. (In general, the value of an enthalpy change assumes reactants and products are at the same temperature.)



A Exothermic process **B** Endothermic process

Figure 6.6 Enthalpy diagrams for exothermic and endothermic processes. **A,** The combustion of methane is exothermic: $\Delta H < 0$. **B,** The melting of ice is endothermic: $\Delta H > 0$.

Sample Problem 6.2 Drawing Enthalpy Diagrams and Determining the Sign of ΔH

Problem In each of the following cases, determine the sign of ΔH, state whether the reaction is exothermic or endothermic, and draw an enthalpy diagram:

(a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 285.8\ \text{kJ}$

(b) $40.7\ \text{kJ} + H_2O(l) \longrightarrow H_2O(g)$

Plan From each equation, we note whether heat is a "product" (exothermic; $\Delta H < 0$) or a "reactant" (endothermic; $\Delta H > 0$). For exothermic reactions, reactants are above products on the enthalpy diagram; for endothermic reactions, reactants are below products. The ΔH arrow *always* points from reactants to products.

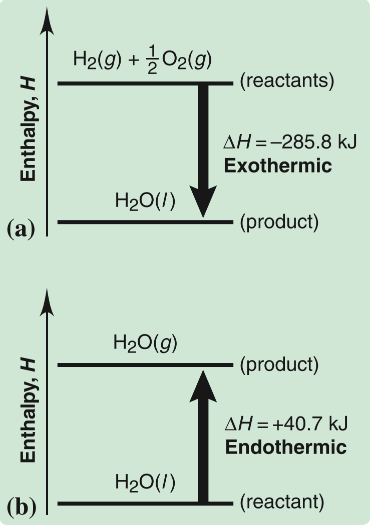
Solution **(a)** Heat is a product (on the right), so $\Delta H < 0$ and the reaction is exothermic. The enthalpy diagram appears in the margin *(top)*.
(b) Heat is a reactant (on the left), so $\Delta H > 0$ and the reaction is endothermic. The enthalpy diagram appears in the margin *(bottom)*.

Check Substances that are on the same side of the equation as the heat have less enthalpy than substances on the other side, so make sure those substances are placed on the lower line of the diagram.

FOLLOW-UP PROBLEM 6.2 When nitroglycerine decomposes, the reaction creates a violent explosion and releases 5.72×10^3 kJ of heat per mole:

$$C_3H_5(NO_3)_3(l) \longrightarrow 3CO_2(g) + \tfrac{5}{2}H_2O(g) + \tfrac{1}{4}O_2(g) + \tfrac{3}{2}N_2(g)$$

Is the decomposition of nitroglycerine exothermic or endothermic? Draw an enthalpy diagram for the process.



Summary of Section 6.2

- Enthalpy (H) is a state function, so any change in enthalpy (ΔH) is independent of how the change occurred. At constant P, the value of ΔH equals $\Delta E + PV$ work, which occurs when the volume of the system changes in the presence of an external pressure.
- ΔH equals q_P, the heat released or absorbed during a chemical or physical change that takes place at constant pressure.
- A change that releases heat is exothermic ($\Delta H < 0$); a change that absorbs heat is endothermic ($\Delta H > 0$).

6.3 • CALORIMETRY: MEASURING THE HEAT OF A CHEMICAL OR PHYSICAL CHANGE

Data about energy content and usage are everywhere, from the caloric value of a slice of bread to the gas mileage of a new car. In this section, we consider the basic ideas that allow these values to be determined.

Specific Heat Capacity

To find the energy change during a process, we measure the quantity of heat released or absorbed by relating it to the change in temperature. You know from everyday experience that the more you heat an object, the higher its temperature, and the more you cool it, the lower its temperature; in other words, the quantity of heat (q) absorbed or released by an object is proportional to its temperature change:

$$q \propto \Delta T \qquad \text{or} \qquad q = \text{constant} \times \Delta T \qquad \text{or} \qquad \frac{q}{\Delta T} = \text{constant}$$

Every object has its own **heat capacity,** the quantity of heat required to change its temperature by 1 K. Heat capacity is the proportionality constant in the preceding equation:

$$\text{Heat capacity} = \frac{q}{\Delta T} \quad [\text{in units of J/K}]$$

A related property is **specific heat capacity (*c*),** the quantity of heat required to change the temperature of 1 *gram* of the object by 1 K:

$$\text{Specific heat capacity } (c) = \frac{q}{\text{mass} \times \Delta T} \quad [\text{in units of J/g·K}]$$

If we know c of the object being heated (or cooled), we can measure the mass and the temperature change and calculate the heat absorbed (or released):

$$q = c \times \text{mass} \times \Delta T \tag{6.7}$$

Table 6.2 Specific Heat Capacities (*c*) of Some Elements, Compounds, and Materials

	c (J/g·K)*
Elements	
Aluminum, Al	0.900
Graphite, C	0.711
Iron, Fe	0.450
Copper, Cu	0.387
Gold, Au	0.129
Compounds	
Water, $H_2O(l)$	4.184
Ethyl alcohol, $C_2H_5OH(l)$	2.46
Ethylene glycol, $(CH_2OH)_2(l)$	2.42
Carbon tetrachloride, $CCl_4(l)$	0.862
Solid Materials	
Wood	1.76
Cement	0.88
Glass	0.84
Granite	0.79
Steel	0.45

*At 298 K (25°C).

Equation 6.7 says that when the object gets hotter, that is, when ΔT ($T_{\text{final}} - T_{\text{initial}}$) is positive, $q > 0$ (the object absorbs heat). And when the object gets cooler, that is, when ΔT is negative, $q < 0$ (the object releases heat). Table 6.2 lists the specific heat capacities of some representative substances and materials. Notice that metals have relatively low values of *c* and water has a very high value: for instance, it takes over 30 times as much energy to increase the temperature of a gram of water by 1 K as it does a gram of gold!

Closely related to the specific heat capacity (but reserved for *substances*) is the **molar heat capacity** (***C;*** note the capital letter), the quantity of heat required to change the temperature of 1 *mole* of a substance by 1 K:

$$\text{Molar heat capacity } (C) = \frac{q}{\text{amount (mol)} \times \Delta T} \quad [\text{in units of J/mol·K}]$$

To find *C* of liquid H_2O, we multiply *c* of liquid H_2O (4.184 J/g·K) by the molar mass of H_2O (18.02 g/mol):

$$C \text{ of } H_2O(l) = 4.184 \frac{\text{J}}{\text{g·K}} \times \frac{18.02 \text{ g}}{1 \text{ mol}} = 75.40 \frac{\text{J}}{\text{mol·K}}$$

Sample Problem 6.3 Finding the Quantity of Heat from a Temperature Change

Problem A layer of copper welded to the bottom of a skillet weighs 125 g. How much heat is needed to raise the temperature of the copper layer from 25°C to 300.°C? The specific heat capacity (*c*) of Cu is given in Table 6.2.

Plan We know the mass (125 g) and *c* (0.387 J/g·K) of Cu and can find ΔT in °C, which equals ΔT in K. We then use Equation 6.7 to calculate the heat.

Solution Calculating ΔT and then *q*:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 300.°\text{C} - 25°\text{C} = 275°\text{C} = 275 \text{ K}$$

$$q = c \times \text{mass (g)} \times \Delta T = 0.387 \text{ J/g·K} \times 125 \text{ g} \times 275 \text{ K} = \boxed{1.33{\times}10^4 \text{ J}}$$

Check Heat is absorbed by the copper layer (system), so *q* is positive. Rounding shows the arithmetic is reasonable: $q \approx 0.4 \text{ J/g·K} \times 100 \text{ g} \times 300 \text{ K} = 1.2{\times}10^4 \text{ J}$.

FOLLOW-UP PROBLEM 6.3 Find the heat released (in kJ) when 5.50 L of ethylene glycol (d = 1.11 g/mL; see Table 6.2) in a car radiator cools from 37.0°C to 25.0°C.

The Two Common Types of Calorimetry

A **calorimeter** is used to measure the heat released (or absorbed) by a physical or chemical process. This apparatus is the "surroundings" that changes temperature when heat is transferred to or from the system. Let's look at two types of calorimeter—one designed to measure the heat at constant pressure and the other at constant volume.

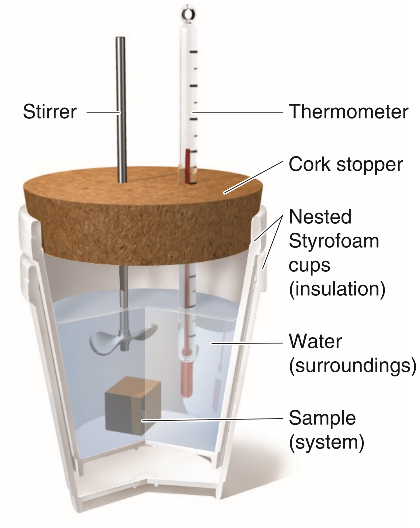


Figure 6.7 Coffee-cup calorimeter. This device measures the heat transferred at constant pressure (q_P).

Constant-Pressure Calorimetry For processes that take place at constant pressure, the heat transferred (q_P) can be measured in a simple *coffee-cup calorimeter* (Figure 6.7). This device is used to find the specific heat capacity of a solid that does not react with or dissolve in water. The solid (system) is weighed, heated to some known temperature, and added to a known mass and temperature of water (surroundings) in the calorimeter. After being stirred, the final water temperature, which is also the final temperature of the solid, is measured. Assuming no heat escapes the calorimeter, the heat released by the system ($-q_{\text{sys}}$, or $-q_{\text{solid}}$) is equal in magnitude but opposite in sign to the heat absorbed by the surroundings ($+q_{\text{surr}}$, or $+q_{H_2O}$):

$$-q_{\text{solid}} = q_{H_2O}$$

Substituting from Equation 6.7 on each side of this equation gives

$$-(c_{\text{solid}} \times \text{mass}_{\text{solid}} \times \Delta T_{\text{solid}}) = c_{H_2O} \times \text{mass}_{H_2O} \times \Delta T_{H_2O}$$

All the quantities are known or measured except c_{solid}:

$$c_{\text{solid}} = -\frac{c_{H_2O} \times \text{mass}_{H_2O} \times \Delta T_{H_2O}}{\text{mass}_{\text{solid}} \times \Delta T_{\text{solid}}}$$

Sample Problem 6.4 Determining the Specific Heat Capacity of a Solid

Problem You heat 22.05 g of a solid in a test tube to 100.00°C and add it to 50.00 g of water in a coffee-cup calorimeter. The water temperature changes from 25.10°C to 28.49°C. Find the specific heat capacity of the solid.

Plan We are given the masses of the solid (22.05 g) and of H_2O (50.00 g), and we can find the temperature changes of the water and of the solid by subtracting the given values, always using $T_{\text{final}} - T_{\text{initial}}$. Using Equation 6.7, we set the heat released by the solid ($-q_{\text{solid}}$) equal to the heat absorbed by the water (q_{water}). The specific heat of water is known, and we solve for c_{solid}.

Solution Finding ΔT_{solid} and ΔT_{water}:

$$\Delta T_{\text{water}} = T_{\text{final}} - T_{\text{initial}} = (28.49°\text{C} - 25.10°\text{C}) = 3.39°\text{C} = 3.39\text{ K}$$

$$\Delta T_{\text{solid}} = T_{\text{final}} - T_{\text{initial}} = (28.49°\text{C} - 100.00°\text{C}) = -71.51°\text{C} = -71.51\text{ K}$$

Solving for c_{solid}:

$$c_{\text{solid}} = -\frac{c_{H_2O} \times \text{mass}_{H_2O} \times \Delta T_{H_2O}}{\text{mass}_{\text{solid}} \times \Delta T_{\text{solid}}} = -\frac{4.184\text{ J/g·K} \times 50.00\text{ g} \times 3.39\text{ K}}{22.05\text{ g} \times (-71.51\text{ K})} = \boxed{0.450\text{ J/g·K}}$$

Check Rounding gives -4 J/g·K × 50 g × 3 K/[20 g × (−70°C)] = 0.4 J/g·K, so the answer seems correct.

FOLLOW-UP PROBLEM 6.4 A 12.18-g sample of a shiny, orange-brown metal is heated to 65.00°C in a controlled water bath. The metal is then added to 25.00 g of water in a coffee-cup calorimeter, and the water temperature changes from 25.55°C to 27.25°C. What is the unknown metal (see Table 6.2)?

In the next sample problem, the calorimeter is used to study the change in heat during an aqueous acid-base reaction. Recall that, if a reaction takes place at constant pressure, the heat of the reaction (q_{rxn}) is equal to its enthalpy change (ΔH).

Sample Problem 6.5 Determining the Enthalpy Change of an Aqueous Reaction

Problem You place 50.0 mL of 0.500 M NaOH in a coffee-cup calorimeter at 25.00°C and add 25.0 mL of 0.500 M HCl, also at 25.00°C. After stirring, the final temperature is 27.21°C. [Assume that the total volume is the sum of the individual volumes and that the final solution has the same density (1.00 g/mL) and specific heat capacity (Table 6.2) as water.]
(a) Calculate q_{soln} (in J).
(b) Calculate the change in enthalpy, ΔH, of the reaction (in kJ/mol of H_2O formed).

(a) Calculate q_{soln}

Plan The solution mixture is the surroundings, and as the reaction takes place, heat flows into it. To find q_{soln}, we use Equation 6.7, so we need the mass of solution, the change in temperature, and the specific heat capacity. We know the solutions' volumes (25.0 mL and 50.0 mL), so we find their masses with the given density (1.00 g/mL). Then, to find q_{soln}, we multiply the total mass by the given c (4.184 J/g·K) and the change in T, which we find from $T_{\text{final}} - T_{\text{initial}}$.

Solution Finding $\text{mass}_{\text{soln}}$ and ΔT_{soln}:

$$\text{Total mass (g) of solution} = (25.0\text{ mL} + 50.0\text{ mL}) \times 1.00\text{ g/mL} = 75.0\text{ g}$$

$$\Delta T = 27.21°\text{C} - 25.00°\text{C} = 2.21°\text{C} = 2.21\text{ K}$$

Finding q_{soln}:

$$q_{\text{soln}} = c_{\text{soln}} \times \text{mass}_{\text{soln}} \times \Delta T_{\text{soln}} = (4.184\text{ J/g·K})(75.0\text{ g})(2.21\text{ K}) = \boxed{693\text{ J}}$$

Check Rounding to check q_{soln} gives 4 J/g·K × 75 g × 2 K = 600 J, which is close to the answer.

(b) Calculate the change in enthalpy (ΔH)

Plan To find ΔH, we write the balanced equation for the acid-base reaction and use the volumes and the concentrations (0.500 M) to find amount (mol) of each reactant (H^+ and OH^-). Since the amounts of two reactants are given, we determine which is limiting, that is, which gives less product (H_2O). The heat of the surroundings is q_{soln}, and it is the negative of the heat of the reaction (q_{rxn}), which equals ΔH. And dividing q_{rxn} by the amount (mol) of water formed gives ΔH in kJ/mol of water formed.

Solution Writing the balanced equation:

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

Finding amounts (mol) of reactants:

$$\text{Amount (mol) of HCl} = 0.500 \text{ mol HCl/L} \times 0.0250 \text{ L} = 0.0125 \text{ mol HCl}$$
$$\text{Amount (mol) of NaOH} = 0.500 \text{ mol NaOH/L} \times 0.0500 \text{ L} = 0.0250 \text{ mol NaOH}$$

Finding the amount (mol) of product: All the coefficients in the equation are 1, which means that the amount (mol) of reactant yields that amount of product. Therefore, HCl is limiting because it yields less product: 0.0125 mol of H_2O.

Finding ΔH: Heat absorbed by the solution was released by the reaction; that is,

$$q_{\text{soln}} = -q_{\text{rxn}} = 693 \text{ J} \quad \text{so} \quad q_{\text{rxn}} = -693 \text{ J}$$

$$\Delta H \text{ (kJ/mol)} = \frac{q_{\text{rxn}}}{\text{mol H}_2\text{O}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \frac{-693 \text{ J}}{0.0125 \text{ mol H}_2\text{O}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -55.4 \text{ kJ/mol H}_2\text{O}$$

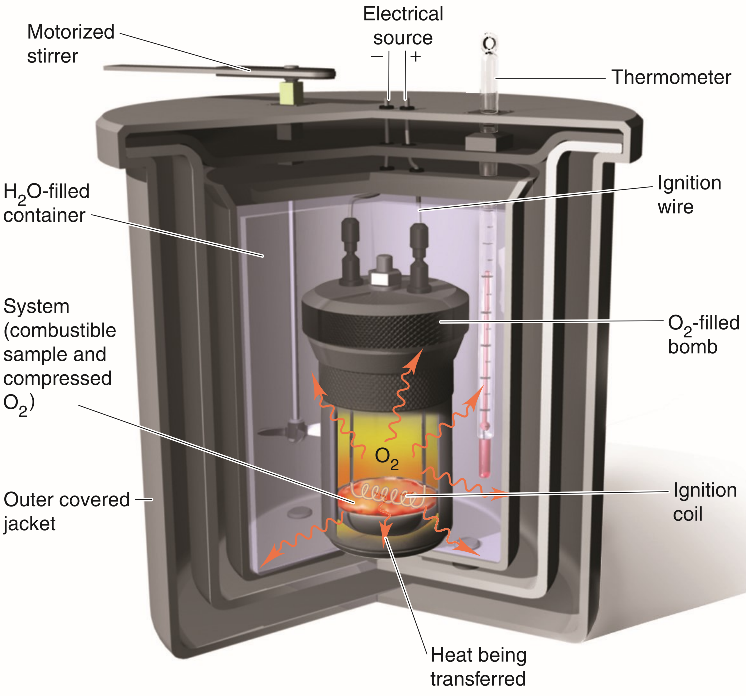
Check We check for the limiting reactant: The volume of H^+ is half the volume of OH^-, but they have the same concentration and a 1/1 stoichiometric ratio. Therefore, the amount (mol) of H^+ determines the amount of product. Rounding and taking the negative of q_{soln} to find ΔH gives -600 J/0.012 mol $= -5\times10^4$ J/mol, or -50 kJ/mol, so the answer seems correct.

FOLLOW-UP PROBLEM 6.5 After 50.0 mL of 0.500 *M* $Ba(OH)_2$ and the same volume and concentration of HCl react in a coffee-cup calorimeter, you find q_{soln} to be 1.386 kJ. Calculate ΔH of the reaction in kJ/mol of H_2O formed.

Constant-Volume Calorimetry Constant-volume calorimetry is often carried out in a *bomb calorimeter,* a device commonly used to measure the heat of combustion reactions, such as for fuels and foods. In the coffee-cup calorimeter, we assume all the heat is absorbed by the water, but in reality, some must be absorbed by the stirrer, thermometer, and so forth. With the much more precise bomb calorimeter, the *heat capacity of the entire calorimeter* is known (or can be determined).

Figure 6.8 depicts the preweighed combustible sample in a metal-walled chamber (the bomb), which is filled with oxygen gas and immersed in an insulated water bath fitted with motorized stirrer and thermometer. A heating coil connected to an electrical source ignites the sample, and the heat released raises the temperature of the bomb,

Figure 6.8 A bomb calorimeter. This device measures the heat released at constant volume (q_V). It is often used to study combustion reactions.



water, and other calorimeter parts. Because we know the mass of the sample and the heat capacity of the entire calorimeter, we can use the measured ΔT to calculate the heat released.

Sample Problem 6.6 Calculating the Heat of a Combustion Reaction

Problem A manufacturer claims that its new dietetic dessert has "fewer than 10 Calories per serving." To test the claim, a chemist at the Department of Consumer Affairs places one serving in a bomb calorimeter and burns it in O_2. The initial temperature is 21.862°C and the temperature rises to 26.799°C. If the heat capacity of the calorimeter is 8.151 kJ/K, is the manufacturer's claim correct?

Plan When the dessert (system) burns, the heat released is absorbed by the calorimeter:

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

The claim is correct if the heat of the system is less than 10 Calories. To find the heat, we multiply the given heat capacity of the calorimeter (8.151 kJ/K) by ΔT and then convert to Calories.

Solution Finding ΔT:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 26.799°\text{C} - 21.862°\text{C} = 4.937°\text{C} = 4.937\text{ K}$$

Calculating the heat absorbed by the calorimeter:

$$q_{\text{calorimeter}} = \text{heat capacity} \times \Delta T = 8.151\text{ kJ/K} \times 4.937\text{ K} = 40.24\text{ kJ}$$

Recall that 1 Calorie = 1 kcal = 4.184 kJ. Therefore, 10 Calories = 41.84 kJ, so the claim is correct.

Check A quick math check shows that the answer is reasonable: 8 kJ/K × 5 K = 40 kJ.

Comment The volume of the metal-walled bomb is fixed, so $\Delta V = 0$, and $P\Delta V = 0$. Thus, the energy change measured is the heat at constant volume (q_V), which equals ΔE, not ΔH:

$$\Delta E = q + w = q_V + 0 = q_V$$

However, in most cases, ΔH is usually very close to ΔE. For example, ΔH is only 0.5% larger than ΔE for the combustion of H_2 and only 0.2% smaller for the combustion of octane.

FOLLOW-UP PROBLEM 6.6 A chemist burns 0.8650 g of graphite (a form of carbon) in a new bomb calorimeter, and CO_2 forms. If 393.5 kJ of heat is released per mole of graphite and ΔT is 2.613 K, what is the heat capacity of the bomb calorimeter?

Summary of Section 6.3

- We calculate ΔH of a process by measuring the energy transferred as heat at constant pressure (q_P). To do this, we determine ΔT and multiply it by the mass of the substance and by its specific heat capacity (c), which is the quantity of energy needed to raise the temperature of 1 g of the substance by 1 K.
- Calorimeters measure the heat released (or absorbed) during a process either at constant pressure (coffee cup; $q_P = \Delta H$) or at constant volume (bomb; $q_V = \Delta E$).

6.4 • STOICHIOMETRY OF THERMOCHEMICAL EQUATIONS

A **thermochemical equation** is a balanced equation that includes the enthalpy change of the reaction (ΔH). Keep in mind that a given ΔH refers only to the *amounts (mol) of substances* ***and*** *their states of matter in that equation.* The enthalpy change of any process has two aspects:

- *Sign.* The sign of ΔH depends on whether the reaction is exothermic (−) or endothermic (+). A forward reaction has the *opposite* sign of the reverse reaction.
  Decomposition of 2 mol of water to its elements (endothermic):

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = 572\text{ kJ}$$

Formation of 2 mol of water from its elements (exothermic):

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -572\ \text{kJ}$$

- *Magnitude.* The magnitude of ΔH is *proportional to the amount of substance.* Formation of 1 mol of water from its elements (half the preceding amount):

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

Two key points to understand about thermochemical equations are as follows:

1. *Balancing coefficients.* When necessary, we use fractional coefficients to balance an equation, because we are specifying the magnitude of ΔH for a *particular amount* (often 1 mol) *of substance,* say gaseous SO_2:

$$\tfrac{1}{8}S_8(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -296.8\ \text{kJ}$$

2. *Thermochemical equivalence.* For a *particular reaction,* a certain amount of substance is thermochemically equivalent to a certain quantity of energy. Some examples from the previous two reactions are

286 kJ is thermochemically equivalent to $\tfrac{1}{2}$ mol of $O_2(g)$
286 kJ is thermochemically equivalent to 1 mol of $H_2O(l)$
296.8 kJ is thermochemically equivalent to $\tfrac{1}{8}$ mol of $S_8(s)$

Just as we use stoichiometrically equivalent molar ratios to find amounts of substances, we use thermochemically equivalent quantities to find the ΔH of a reaction for a given amount of substance. Also, just as we use molar mass (in g/mol) to convert an amount (mol) of a substance to mass (g), we use the ΔH (in kJ/mol) to convert an amount of a substance to an equivalent quantity of heat (in kJ). Figure 6.9 shows this new relationship, and Sample Problem 6.7 applies it.

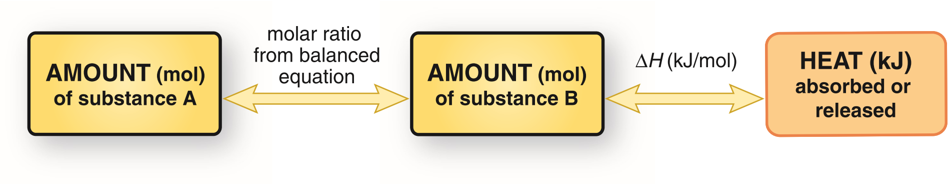


Figure 6.9 The relationship between amount (mol) of substance and the energy (kJ) transferred as heat during a reaction.

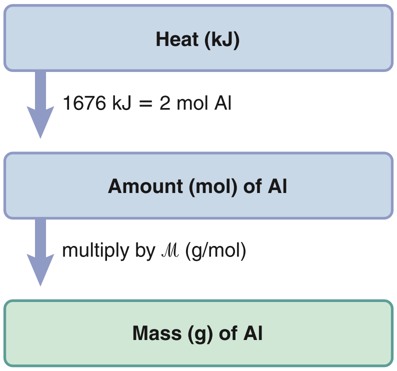
Sample Problem 6.7 Using the Enthalpy Change of a Reaction (ΔH) to Find Amounts of Substance

Problem The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be written as

$$Al_2O_3(s) \xrightarrow{\Delta} 2Al(s) + \tfrac{3}{2}O_2(g) \qquad \Delta H = 1676\ \text{kJ}$$

If aluminum is produced this way (see Comment), how many grams of aluminum can form when 1.000×10^3 kJ of heat is transferred?

Road Map



Plan From the balanced equation and the enthalpy change, we see that 1676 kJ of heat is thermochemically equivalent to 2 mol of Al. We convert the given number of kJ to amount (mol) formed and then to mass (g).

Solution Combining steps to convert from heat transferred to mass of Al:

$$\text{Mass (g) of Al} = (1.000\times10^3\ \text{kJ}) \times \frac{2\ \text{mol Al}}{1676\ \text{kJ}} \times \frac{26.98\ \text{g Al}}{1\ \text{mol Al}} = \boxed{32.20\ \text{g Al}}$$

Check The mass of aluminum seems correct: ~1700 kJ forms about 2 mol of Al (54 g), so 1000 kJ should form a bit more than half that amount (27 g).

Comment In practice, aluminum is not obtained by heating bauxite but by supplying electrical energy (as you'll see in Chapter 22). Because H is a state function, however, the total energy required for the change, ΔH, is the same no matter how it occurs.

FOLLOW-UP PROBLEM 6.7 Hydrogenation reactions, in which H_2 and an "unsaturated" organic compound combine, are used in the food, fuel, and polymer industries. In the simplest case, ethene (C_2H_4) and H_2 form ethane (C_2H_6). If 137 kJ is given off per mole of C_2H_4 reacting, how much heat is released when 15.0 kg of C_2H_6 forms?

Summary of Section 6.4

- A thermochemical equation shows a balanced reaction *and* its ΔH value. The sign of ΔH for a forward reaction is opposite that for the reverse reaction. The magnitude of ΔH is specific for the given equation.
- The amount of a substance and the quantity of heat specified by the balanced equation are thermochemically equivalent and act as conversion factors to find the quantity of heat transferred when any amount of the substance reacts.

6.5 • HESS'S LAW: FINDING ΔH OF ANY REACTION

In some cases, a reaction is difficult, even impossible, to carry out individually: it may be part of a complex biochemical process, or take place under extreme conditions, or require a change in conditions to occur. Even if we can't run a reaction in the lab, we can still find its enthalpy change. In fact, the state-function property of enthalpy (H) allows us to find ΔH of *any* reaction for which we can write an equation.

This application is based on **Hess's law:** *the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps:*

$$\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \cdots + \Delta H_n \qquad \textbf{(6.8)}$$

This law follows from the fact that ΔH for a process depends only on the difference between the final and initial states. We apply Hess's law by

- Imagining that an overall reaction occurs through a series of individual reaction steps, whether or not it actually does. Adding the steps must give the overall reaction.
- Choosing individual reaction steps that each has a known ΔH.
- Adding the known ΔH values for the steps to get the unknown ΔH of the overall reaction. We can also find an unknown ΔH of one of the steps by subtraction, if we know the ΔH values for the overall reaction and all the other steps.

Let's apply Hess's law to the oxidation of sulfur to sulfur trioxide, the key change in the industrial production of sulfuric acid and in the formation of acid rain. (To introduce this approach, we'll use S as the formula for sulfur, rather than the more correct S_8.) When we burn S in an excess of O_2, sulfur dioxide (SO_2) forms, *not* sulfur trioxide (SO_3) (equation 1). After a change in conditions, we add more O_2 and oxidize SO_2 to SO_3 (equation 2). Thus, we cannot put S and O_2 in a calorimeter and find ΔH for the overall reaction of S to SO_3 (equation 3). But, we *can* find it with Hess's law. The three equations are

$$\begin{array}{lrcll}
\text{Equation 1:} & S(s) + O_2(g) & \longrightarrow & SO_2(g) & \Delta H_1 = -296.8\text{ kJ} \\
\text{Equation 2:} & 2SO_2(g) + O_2(g) & \longrightarrow & 2SO_3(g) & \Delta H_2 = -198.4\text{ kJ} \\
\text{Equation 3:} & S(s) + \tfrac{3}{2}O_2(g) & \longrightarrow & SO_3(g) & \Delta H_3 = ?
\end{array}$$

If we can manipulate equation 1 and/or equation 2, *along with their* ΔH *value(s),* so the equations add up to equation 3, their ΔH values will add up to the unknown ΔH_3.

First, we identify our "target" equation, the one whose ΔH we want to find, and note the amount (mol) of each reactant and product; our "target" is equation 3. Then, we manipulate equations 1 and/or 2 to make them add up to equation 3:

- Equations 3 and 1 have the same amount of S, so we don't change equation 1.
- Equation 3 has half as much SO_3 as equation 2, so we multiply equation 2, ***and*** $\boldsymbol{\Delta H_2}$**,** by $\frac{1}{2}$; that is, we always treat the equation and its ΔH value the same.
- With the targeted amounts of reactants and products present, we add equation 1 to the halved equation 2 and cancel terms that appear on both sides:

$$\begin{array}{lrcll}
\text{Equation 1:} & S(s) + O_2(g) & \longrightarrow & SO_2(g) & \Delta H_1 = -296.8\text{ kJ} \\
\tfrac{1}{2}(\text{Equation 2}): & SO_2(g) + \tfrac{1}{2}O_2(g) & \longrightarrow & SO_3(g) & \tfrac{1}{2}(\Delta H_2) = -99.2\text{ kJ} \\
\hline
\text{Equation 3:} & S(s) + O_2(g) + \cancel{SO_2(g)} + \tfrac{1}{2}O_2(g) & \longrightarrow & \cancel{SO_2(g)} + SO_3(g) & \\
\text{or,} & S(s) + \tfrac{3}{2}O_2(g) & \longrightarrow & SO_3(g) & \Delta H_3 = -396.0\text{ kJ}
\end{array}$$

Because ΔH depends only on the difference between H_{final} and H_{initial}, Hess's law tells us that the difference between the enthalpies of the reactants (1 mol of S and $\frac{3}{2}$ mol of O_2) and the product (1 mol of SO_3) is the same, whether S is oxidized directly to SO_3 (impossible) or through the intermediate formation of SO_2 (actual).

To summarize, calculating an unknown ΔH involves three steps:

1. Identify the target equation, the step whose ΔH is unknown, and note the amount (mol) of each reactant and product.
2. Manipulate each equation with known ΔH values so that the target amount (mol) of each substance is on the correct side of the equation. Remember to:
    - Change the sign of ΔH when you reverse an equation.
    - Multiply amount (mol) and ΔH by the same factor.
3. Add the manipulated equations and their resulting ΔH values to get the target equation and its ΔH. All substances except those in the target equation must cancel.

Sample Problem 6.8 Using Hess's Law to Calculate an Unknown ΔH

Problem Two pollutants that form in auto exhaust are CO and NO. An environmental chemist must convert these pollutants to less harmful gases through the following:

$$CO(g) + NO(g) \longrightarrow CO_2(g) + \tfrac{1}{2}N_2(g) \qquad \Delta H = ?$$

Given the following information, calculate the unknown ΔH:

$$\begin{array}{lrcll} \text{Equation A:} & CO(g) + \frac{1}{2}O_2(g) & \longrightarrow & CO_2(g) & \Delta H = -283.0\ \text{kJ} \\ \text{Equation B:} & N_2(g) + O_2(g) & \longrightarrow & 2NO(g) & \Delta H = 180.6\ \text{kJ} \end{array}$$

Plan We note the amount (mol) of each substance and on which side each appears in the target equation. We manipulate equations A and/or B *and* their ΔH values as needed and add them together to obtain the target equation and the unknown ΔH.

Solution Noting substances in the target equation: For reactants, there are 1 mol of CO and 1 mol of NO; for products, there are 1 mol of CO_2 and $\frac{1}{2}$ mol of N_2.
Manipulating the given equations:

- Equation A has the same amounts of CO and CO_2 on the same sides of the arrow as in the target, so we leave it as written.
- Equation B has twice as much N_2 and NO as the target, and they are on the opposite sides in the target. Thus, we reverse equation B, change the sign of its ΔH, and multiply both by $\frac{1}{2}$:

$$\begin{array}{lll} & \frac{1}{2}[2NO(g) \longrightarrow N_2(g) + O_2(g)] & \Delta H = -\frac{1}{2}(\Delta H) = -\frac{1}{2}(180.6\ \text{kJ}) \\ \text{or} & NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) & \Delta H = -90.3\ \text{kJ} \end{array}$$

Adding the manipulated equations to obtain the target equation:

$$\begin{array}{lrcll} \text{Equation A:} & CO(g) + \cancel{\frac{1}{2}O_2(g)} & \longrightarrow & CO_2(g) & \Delta H = -283.0\ \text{kJ} \\ \frac{1}{2}\text{(Equation B reversed)} & NO(g) & \longrightarrow & \frac{1}{2}N_2(g) + \cancel{\frac{1}{2}O_2(g)} & \Delta H = {-90.3}\ \text{kJ} \\ \hline \text{Target equation:} & CO(g) + NO(g) & \longrightarrow & CO_2(g) + \frac{1}{2}N_2(g) & \boxed{\Delta H = -373.3\ \text{kJ}} \end{array}$$

Check Obtaining the desired target equation is a sufficient check. Be sure to remember to change the *sign* of ΔH for any equation you reverse.

FOLLOW-UP PROBLEM 6.8 Nitrogen oxides undergo many reactions in the environment and in industry. Given the following information, calculate ΔH for the overall equation, $2NO_2(g) + \frac{1}{2}O_2(g) \longrightarrow N_2O_5(s)$:

$$\begin{array}{rcll} N_2O_5(s) & \longrightarrow & 2NO(g) + \frac{3}{2}O_2(g) & \Delta H = 223.7\ \text{kJ} \\ NO(g) + \frac{1}{2}O_2(g) & \longrightarrow & NO_2(g) & \Delta H = -57.1\ \text{kJ} \end{array}$$

Summary of Section 6.5

- Because H is a state function, we can use Hess's law to determine ΔH of any reaction by assuming that it is the sum of other reactions.
- After manipulating the equations of those reactions and their ΔH values to match the substances in the target equation, we add the manipulated ΔH values to find the unknown ΔH.

6.6 • STANDARD ENTHALPIES OF REACTION ($\Delta H^\circ_{\text{rxn}}$)

In this section, we see how Hess's law allows us to determine the ΔH values of an enormous number of reactions. Thermodynamic variables, such as ΔH, vary somewhat with conditions. Therefore, in order to study and compare reactions, chemists have established a set of specific conditions called **standard states:**

- For a *gas,* the standard state is 1 atm* and ideal behavior.
- For a substance in *aqueous solution,* the standard state is 1 *M* concentration.
- For a *pure substance* (element or compound), the standard state is usually the most stable form of the substance at 1 atm and the temperature of interest. In this text (and in most thermodynamic tables), that temperature is usually 25°C (298 K).

The standard-state symbol (shown as a degree sign) indicates that the variable has been measured with *all the substances in their standard states*. For example, when the enthalpy change of a reaction is measured at the standard state, it is the **standard enthalpy of reaction, $\Delta H^\circ_{\text{rxn}}$** (also called *standard heat of reaction*).

Formation Equations and Their Standard Enthalpy Changes

In a **formation equation,** 1 mol of a compound forms from its elements. The **standard enthalpy of formation** (**ΔH°_f;** or *standard heat of formation*) is the enthalpy change for the formation equation when all the substances are in their standard states. For instance, the formation equation for methane (CH_4) is

$$\text{C(graphite)} + 2\text{H}_2(g) \longrightarrow \text{CH}_4(g) \quad \Delta H^\circ_f = -74.9 \text{ kJ}$$

Fractional coefficients are often used with reactants to obtain 1 mol of the product:

$$\text{Na}(s) + \tfrac{1}{2}\text{Cl}_2(g) \longrightarrow \text{NaCl}(s) \qquad \Delta H^\circ_f = -411.1 \text{ kJ}$$

$$2\text{C(graphite)} + 3\text{H}_2(g) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) \quad \Delta H^\circ_f = -277.6 \text{ kJ}$$

Standard enthalpies of formation have been tabulated for many substances. Table 6.3 shows several, and a much more extensive table appears in Appendix B. The values in Table 6.3 make two points:

1. *For an element in its standard state, $\Delta H^\circ_f = 0$.*
   - The standard state for sodium is the solid ($\Delta H^\circ_f = 0$); it takes 107.8 kJ of heat to form 1 mol of gaseous Na ($\Delta H^\circ_f = 107.8$ kJ/mol).
   - The standard state for molecular elements, such as the halogens, is the molecular form, not separate atoms: for Cl_2, $\Delta H^\circ_f = 0$, but for Cl, $\Delta H^\circ_f = 121.0$ kJ/mol.
   - Some elements exist in different forms (called *allotropes;* Chapter 14), but only one is the standard state. The standard state of carbon is graphite ($\Delta H^\circ_f = 0$), not diamond ($\Delta H^\circ_f = 1.9$ kJ/mol), the standard state of oxygen is O_2 ($\Delta H^\circ_f = 0$), not ozone (O_3; $\Delta H^\circ_f = 143$ kJ/mol), and the standard state of sulfur is S_8 in its rhombic crystal form ($\Delta H^\circ_f = 0$), not in its monoclinic form ($\Delta H^\circ_f = 0.3$ kJ/mol).
2. *Most compounds have a negative ΔH°_f.* That is, most compounds have exothermic formation reactions: *under standard conditions, heat is released when most compounds form from their elements.*

Table 6.3 Selected Standard Enthalpies of Formation at 25°C (298 K)

Formula	ΔH°_f (kJ/mol)
Calcium	
$Ca(s)$	0
$CaO(s)$	−635.1
$CaCO_3(s)$	−1206.9
Carbon	
C(graphite)	0
C(diamond)	1.9
$CO(g)$	−110.5
$CO_2(g)$	−393.5
$CH_4(g)$	−74.9
$CH_3OH(l)$	−238.6
$HCN(g)$	135
$CS_2(l)$	87.9
Chlorine	
$Cl(g)$	121.0
$Cl_2(g)$	0
$HCl(g)$	−92.3
Hydrogen	
$H(g)$	218.0
$H_2(g)$	0
Nitrogen	
$N_2(g)$	0
$NH_3(g)$	−45.9
$NO(g)$	90.3
Oxygen	
$O_2(g)$	0
$O_3(g)$	143
$H_2O(g)$	−241.8
$H_2O(l)$	−285.8
Silver	
$Ag(s)$	0
$AgCl(s)$	−127.0
Sodium	
$Na(s)$	0
$Na(g)$	107.8
$NaCl(s)$	−411.1
Sulfur	
S_8(rhombic)	0
S_8(monoclinic)	0.3
$SO_2(g)$	−296.8
$SO_3(g)$	−396.0

Sample Problem 6.9 Writing Formation Equations

Problem Write a balanced formation equation for each of the following and include the value of ΔH°_f:
(a) $AgCl(s)$ **(b)** $CaCO_3(s)$ **(c)** $HCN(g)$

Plan We write the elements as the reactants and 1 mol of the compound as the product, being sure all substances are in their standard states. Then, we balance the equations and find the ΔH°_f values in Table 6.3 or Appendix B.

---

*The definition of the standard state for gases has been changed to 1 bar, a slightly lower pressure than the 1 atm standard on which the data in this book are based (1 atm = 101.3 kPa = 1.013 bar). Except for very precise experimental work, this makes very little difference in the standard enthalpy values.

Solution **(a)** $Ag(s) + \frac{1}{2}Cl_2(g) \longrightarrow AgCl(s) \quad \Delta H^\circ_f = -127.0\ kJ$

(b) $Ca(s) + C(graphite) + \frac{3}{2}O_2(g) \longrightarrow CaCO_3(s) \quad \Delta H^\circ_f = -1206.9\ kJ$

(c) $\frac{1}{2}H_2(g) + C(graphite) + \frac{1}{2}N_2(g) \longrightarrow HCN(g) \quad \Delta H^\circ_f = 135\ kJ$

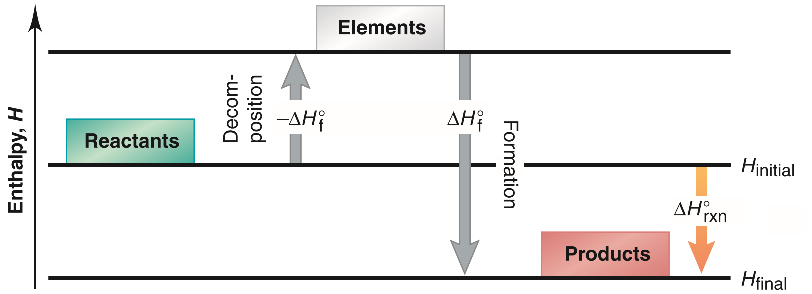
FOLLOW-UP PROBLEM 6.9 Write a balanced formation equation for each of the following and include its ΔH°_f: **(a)** $CH_3OH(l)$, **(b)** $CaO(s)$, **(c)** $CS_2(l)$.

Determining ΔH°_{rxn} from ΔH°_f Values for Reactants and Products

We can use ΔH°_f values to determine any ΔH°_{rxn}. Applying Hess's law, we imagine the reaction occurring in two steps (Figure 6.10):

Step 1. Each reactant decomposes to its elements. This is the *reverse* of the formation reaction for the *reactant,* so the standard enthalpy change is $-\Delta H^\circ_f$.

Step 2. Each product forms from its elements. This step *is* the formation reaction for the *product,* so the standard enthalpy change is ΔH°_f.



$$\Delta H^\circ_{rxn} = \Sigma m\Delta H^\circ_{f(products)} - \Sigma n\Delta H^\circ_{f(reactants)}$$

Figure 6.10 The two-step process for determining ΔH°_{rxn} from ΔH°_f values.

According to Hess's law, we add the enthalpy changes for these steps to obtain the overall enthalpy change for the reaction (ΔH°_{rxn}). Suppose we want ΔH°_{rxn} for

$$TiCl_4(l) + 2H_2O(g) \longrightarrow TiO_2(s) + 4HCl(g)$$

We write this equation as though it were the sum of four individual equations, one for each compound. The first two show step 1, the decomposition of the reactants to their elements (*reverse* of their formation); the second two show step 2, the formation of the products from their elements:

$$\begin{array}{rcll} TiCl_4(l) & \longrightarrow & Ti(s) + 2Cl_2(g) & -\Delta H^\circ_f[TiCl_4(l)] \\ 2H_2O(g) & \longrightarrow & 2H_2(g) + O_2(g) & -2\Delta H^\circ_f[H_2O(g)] \\ Ti(s) + O_2(g) & \longrightarrow & TiO_2(s) & \Delta H^\circ_f[TiO_2(s)] \\ 2H_2(g) + 2Cl_2(g) & \longrightarrow & 4HCl(g) & 4\Delta H^\circ_f[HCl(g)] \end{array}$$

$$TiCl_4(l) + 2H_2O(g) + \cancel{Ti(s)} + \cancel{O_2(g)} + \cancel{2H_2(g)} + \cancel{2Cl_2(g)} \longrightarrow$$
$$\cancel{Ti(s)} + \cancel{2Cl_2(g)} + \cancel{2H_2(g)} + \cancel{O_2(g)} + TiO_2(s) + 4HCl(g)$$

or $$TiCl_4(l) + 2H_2O(g) \longrightarrow TiO_2(s) + 4HCl(g)$$

It's important to realize that when titanium(IV) chloride and water react, the reactants don't *actually* decompose to their elements, which then recombine to form the products. But the great usefulness of Hess's law and the state-function concept is that ΔH°_{rxn} is the difference between two state functions, $H^\circ_{products}$ minus $H^\circ_{reactants}$, so it doesn't matter how the reaction *actually* occurs. We add the individual enthalpy changes to find ΔH°_{rxn}:

$$\begin{aligned} \Delta H^\circ_{rxn} &= \Delta H^\circ_f[TiO_2(s)] + 4\Delta H^\circ_f[HCl(g)] + \{-\Delta H^\circ_f[TiCl_4(l)]\} + \{-2\Delta H^\circ_f[H_2O(g)]\} \\ &= \underbrace{\{\Delta H^\circ_f[TiO_2(s)] + 4\Delta H^\circ_f[HCl(g)]\}}_{\text{Products}} - \underbrace{\{\Delta H^\circ_f[TiCl_4(l)] + 2\Delta H^\circ_f[H_2O(g)]\}}_{\text{Reactants}} \end{aligned}$$

The arithmetic in this case gives $\Delta H^\circ_{rxn} = -25.39$ kJ, but more importantly, when we generalize the pattern, we see that *the standard enthalpy of reaction is the sum of* *the standard enthalpies of formation of the* ***products*** *minus the sum of the standard enthalpies of formation of the* ***reactants*** (see Figure 6.10):

$$\Delta H^\circ_{\text{rxn}} = \Sigma m\Delta H^\circ_{\text{f (products)}} - \Sigma n\Delta H^\circ_{\text{f (reactants)}} \tag{6.9}$$

where Σ means "sum of," and m and n are the amounts (mol) of the products and reactants given by the coefficients in the balanced equation.

Sample Problem 6.10 Calculating $\Delta H^\circ_{\text{rxn}}$ from $\Delta H^\circ_{\text{f}}$ Values

Problem Nitric acid is used to make many products, including fertilizers, dyes, and explosives. The first step in its production is the oxidation of ammonia:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

Calculate $\Delta H^\circ_{\text{rxn}}$ from $\Delta H^\circ_{\text{f}}$ values.

Plan We use values from Table 6.3 (or Appendix B) and apply Equation 6.9.

Solution Calculating $\Delta H^\circ_{\text{rxn}}$:

$$\begin{aligned}
\Delta H^\circ_{\text{rxn}} &= \Sigma m\Delta H^\circ_{\text{f (products)}} - \Sigma n\Delta H^\circ_{\text{f (reactants)}}\\
&= \{4\Delta H^\circ_{\text{f}}[NO(g)] + 6\Delta H^\circ_{\text{f}}[H_2O(g)]\} - \{4\Delta H^\circ_{\text{f}}[NH_3(g)] + 5\Delta H^\circ_{\text{f}}[O_2(g)]\}\\
&= (4\ \text{mol})(90.3\ \text{kJ/mol}) + (6\ \text{mol})(-241.8\ \text{kJ/mol})\\
&\quad - [(4\ \text{mol})(-45.9\ \text{kJ/mol}) + (5\ \text{mol})(0\ \text{kJ/mol})]\\
&= 361\ \text{kJ} - 1451\ \text{kJ} + 184\ \text{kJ} - 0\ \text{kJ} = -906\ \text{kJ}
\end{aligned}$$

Check We write formation equations, with $\Delta H^\circ_{\text{f}}$ values for the amounts of each compound, in the correct direction (forward for products and reverse for reactants) and find the sum:

$$\begin{array}{rcl|rcrcr}
4NH_3(g) & \longrightarrow & \cancel{2N_2(g)} + \cancel{6H_2(g)} & -4\Delta H^\circ_{\text{f}} & = & -4(-45.9\ \text{kJ}) & = & 184\ \text{kJ}\\
\cancel{2N_2(g)} + 2O_2(g) & \longrightarrow & 4NO(g) & 4\Delta H^\circ_{\text{f}} & = & 4(90.3\ \text{kJ}) & = & 361\ \text{kJ}\\
\cancel{6H_2(g)} + 3O_2(g) & \longrightarrow & 6H_2O(g) & 6\Delta H^\circ_{\text{f}} & = & 6(-241.8\ \text{kJ}) & = & -1451\ \text{kJ}\\
\hline
4NH_3(g) + 5O_2(g) & \longrightarrow & 4NO(g) + 6H_2O(g) & & & \Delta H^\circ_{\text{rxn}} & = & -906\ \text{kJ}
\end{array}$$

Comment In this problem, we know the individual $\Delta H^\circ_{\text{f}}$ values and find the sum, $\Delta H^\circ_{\text{rxn}}$. In the follow-up problem, we know the sum and want to find one of the $\Delta H^\circ_{\text{f}}$ values.

FOLLOW-UP PROBLEM 6.10 Use the following to find $\Delta H^\circ_{\text{f}}$ of methanol [$CH_3OH(l)$]:

$$CH_3OH(l) + \tfrac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H^\circ_{\text{rxn}} = -638.5\ \text{kJ}$$

$$\Delta H^\circ_{\text{f}}\ \text{of}\ CO_2(g) = -393.5\ \text{kJ/mol}$$

$$\Delta H^\circ_{\text{f}}\ \text{of}\ H_2O(g) = -241.8\ \text{kJ/mol}$$

Fossil Fuels and Climate Change

Out of necessity, the nations of the world are finally beginning to radically rethink the issue of energy use. No scientific challenge today is greater than reversing the climatic effects of our increasing dependence on the combustion of **fossil fuels**—coal, petroleum, and natural gas. Because these fuels form so much more slowly than we consume them, they are *nonrenewable*. In contrast, wood and other fuels derived from plant and animal matter are *renewable*.

All carbon-based fuels release CO_2 when burned, and in the past few decades it has become increasingly clear that our use of these fuels is changing Earth's climate. The ability of CO_2 to absorb heat plays a vital temperature-regulating role in the atmosphere. Much of the sunlight that shines on Earth is absorbed by the land and oceans and converted to heat. Like the glass of a greenhouse, atmospheric CO_2 does not absorb visible light from the Sun, but it traps some of the heat (infrared light) radiating back from Earth's surface and, thus, helps warm the atmosphere. This process is called the natural *greenhouse effect* (Figure 6.11, *left; next page*).

Over several billion years, due largely to the spread of plant life, which uses CO_2 in photosynthesis, the amount of CO_2 originally present in Earth's atmosphere decreased to 0.028% by volume. However, today (mid-2011), as a result of the human use of fossil fuels for the past 200 years, and especially the past 65, this amount has

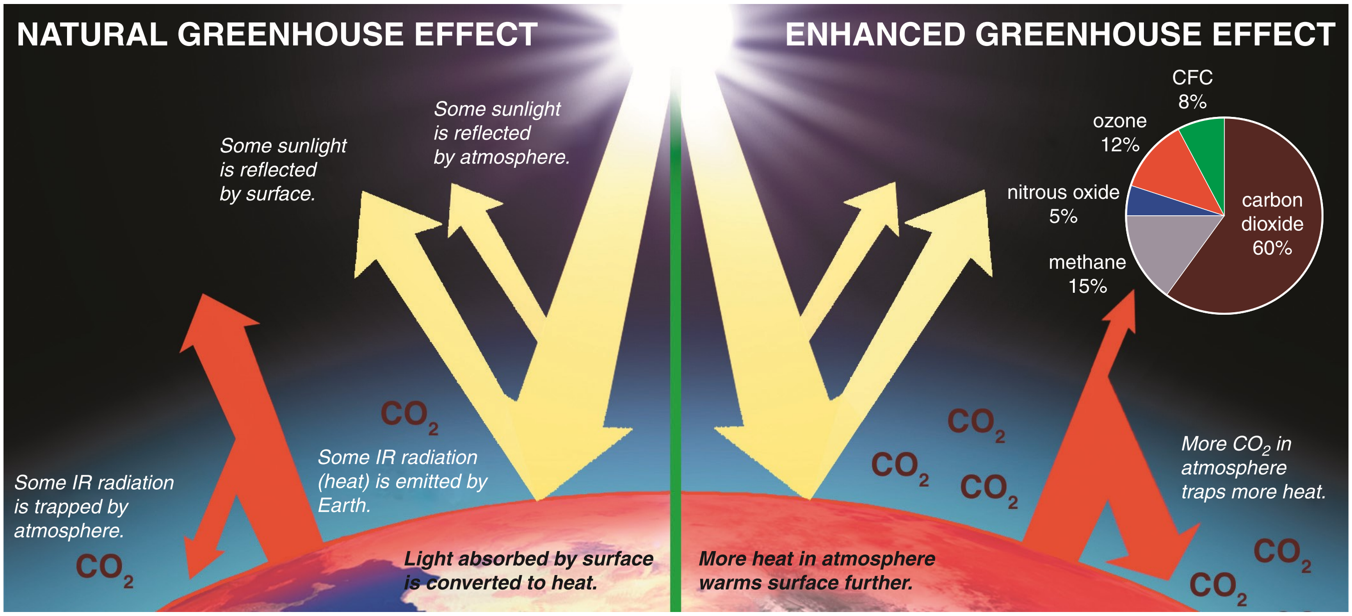


Figure 6.11 **The trapping of heat by the atmosphere.** Of the total sunlight reaching Earth, some is reflected and some is absorbed and converted to infrared (IR) radiation (heat). Some heat emitted by the surface is trapped by atmospheric CO_2, creating a *natural* greenhouse effect *(left)* that has been essential to life. But, largely as a result of human activity in the past 150 years, and especially the past several decades, the buildup of CO_2 and several other greenhouse gases *(pie chart)* has created an *enhanced* greenhouse effect *(right)*.

increased to slightly over 0.039%. Thus, although the same amount of solar energy passes through the atmosphere, more is trapped as heat, which has created an *enhanced* greenhouse effect that is changing the climate through *global warming* (Figure 6.11, *right*). Based on current trends in fossil fuel use, various estimates show that the CO_2 concentration will increase to between 0.049% and 0.126% by 2100.

Computer-based models that simulate the climate's behavior are used to predict how much the temperature will rise. Despite several complicating factors, the best models predicted a net warming of the atmosphere, and for the past several years, scientists have documented the predicted effects. The average temperature has increased by 0.6 ± 0.2°C since the late 19th century, of which 0.2–0.3°C has occurred over just the past 25 years. Globally, the decade from 2001 to 2010 was the warmest ever recorded. Snow cover and glacier extent in the Northern Hemisphere and floating ice in the Arctic Ocean have decreased dramatically. Globally, sea level has risen an average of 17 cm (6.7 in) over the past century, and flooding and other extreme weather events have increased worldwide.

Today, the models predict a future temperature rise more than 50% higher than the 1.0–3.5°C rise predicted only 10 years ago. Such increases would significantly alter rainfall patterns and crop yields throughout the world and could increase sea level as much as 1 meter, thereby flooding low-lying regions, such as the Netherlands, half of Florida, much of southern Asia, and many Pacific island nations. To make matters worse, as we burn fossil fuels that *release* CO_2, we cut down the forests that *absorb* it.

In addition to developing alternative energy sources to reduce fossil-fuel consumption, some researchers are studying *carbon capture and sequestration (CCS),* accomplished by large-scale tree planting and by liquefying CO_2 released from coal-fired power plants and burying it underground or injecting it deep into the oceans. But, CCS has not been effective, and most other scientists are pressing for more efficient usage and conserving current supplies.

In 1997, the United Nations Conference on Climate Change in Kyoto, Japan, created an international treaty that set legally binding limits on release of greenhouse gases. It was ratified by 189 countries, but not by the largest emitter of CO_2, the United States. The 2005 conference in Montreal, Canada, presented overwhelming scientific evidence that confirmed the human impact on climate change, but the 2009 conference in Copenhagen, Denmark, which was attended by representatives from 192 nations, failed to produce a legally binding agreement on emission targets. In late 2010, however, the conference in Cancun, Mexico, resulted in some financial commitments to help developing countries rely on alternative energy sources.

Summary of Section 6.6

- Standard states are a set of specific conditions used for determining thermodynamic variables for all substances.
- When 1 mol of a compound forms from its elements with all substances in their standard states, the enthalpy change is the standard enthalpy of formation, $\Delta H^\circ_\mathrm{f}$.
- Hess's law allows us to picture a reaction as the decomposition of the reactants to their elements followed by the formation of the products from their elements.
- We use tabulated $\Delta H^\circ_\mathrm{f}$ values to find $\Delta H^\circ_\mathrm{rxn}$ or use known $\Delta H^\circ_\mathrm{rxn}$ and $\Delta H^\circ_\mathrm{f}$ values to find an unknown $\Delta H^\circ_\mathrm{f}$.
- Because of major concerns about climate change, nations are beginning to develop alternative means of producing energy.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills to review after studying this chapter.

Related section (§), sample problem (SP), and end-of-chapter problem (EP) numbers are listed in parentheses.

1. Interconvert energy units; understand that ΔE of a system appears as the total heat and/or work transferred to or from its surroundings; understand the meaning of a state function (§6.1) (SP 6.1) (EPs 6.1–6.9)
2. Understand the meaning of H, why we measure ΔH, and the distinction between exothermic and endothermic reactions; draw enthalpy diagrams for chemical and physical changes (§6.2) (SP 6.2) (EPs 6.10–6.19)
3. Understand the relation between specific heat capacity and heat transferred in both constant-pressure (coffee-cup) and constant-volume (bomb) calorimeters (§6.3) (SPs 6.3–6.6) (EPs 6.20–6.32)
4. Understand the relation between heat of reaction and amount of substance (§6.4) (SP 6.7) (EPs 6.33–6.42)
5. Explain the importance of Hess's law and use it to find an unknown ΔH (§6.5) (SP 6.8) (EPs 6.43–6.48)
6. View a reaction as the decomposition of reactants followed by the formation of products; understand formation equations and how to use $\Delta H^\circ_\mathrm{f}$ values to find $\Delta H^\circ_\mathrm{rxn}$ (§6.6) (SPs 6.9, 6.10) (EPs 6.49–6.58)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

thermodynamics (189)
thermochemistry (189)

Section 6.1
system (189)
surroundings (189)
internal energy (E) (190)
heat (q) (190)
work (w) (190)
law of conservation of energy (first law of thermodynamics) (193)
joule (J) (193)
calorie (cal) (193)
state function (194)

Section 6.2
pressure-volume work (PV work) (195)
enthalpy (H) (195)
change in enthalpy (ΔH) (195)
exothermic process (196)
enthalpy diagram (196)
endothermic process (196)

Section 6.3
heat capacity (197)
specific heat capacity (c) (197)
molar heat capacity (C) (198)
calorimeter (198)

Section 6.4
thermochemical equation (201)

Section 6.5
Hess's law (203)

Section 6.6
standard state (205)
standard enthalpy of reaction ($\Delta H^\circ_\mathrm{rxn}$) (205)
formation equation (205)
standard enthalpy of formation ($\Delta H^\circ_\mathrm{f}$) (205)
fossil fuel (207)

Key Equations and Relationships

Numbered and screened concepts are listed for you to refer to or memorize.

6.1 Defining the change in internal energy (190):

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}}$$

6.2 Expressing the change in internal energy in terms of heat and work (190):

$$\Delta E = q + w$$

6.3 Stating the first law of thermodynamics (law of conservation of energy) (193):

$$\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$$

6.4 Determining the work due to a change in volume at constant pressure (*PV* work) (195):

$$w = -P\Delta V$$

6.5 Relating the enthalpy change to the internal energy change at constant pressure (195):

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

6.6 Identifying the enthalpy change with the heat absorbed or released at constant pressure (196):

$$q_P = \Delta E + P\Delta V = \Delta H$$

6.7 Calculating the heat absorbed or released when a substance undergoes a temperature change or a reaction occurs (197):

$$q = c \times \text{mass} \times \Delta T$$

6.8 Calculating the overall enthalpy change of a reaction (Hess's law) (203):

$$\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \cdots + \Delta H_n$$

6.9 Calculating the standard enthalpy of reaction (207):

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

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS

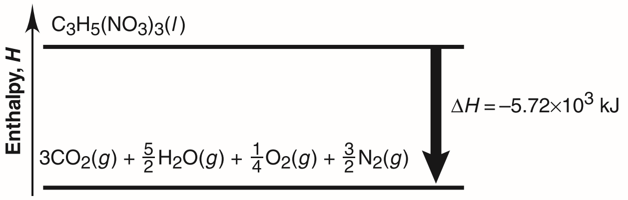
Compare your own solutions to these calculation steps and answers.

6.1 $\Delta E = q + w$

$$= \left(-26.0\ \text{kcal} \times \frac{4.184\ \text{kJ}}{1\ \text{kcal}}\right) + \left(15.0\ \text{Btu} \times \frac{1.055\ \text{kJ}}{1\ \text{Btu}}\right)$$

$$= -93\ \text{kJ}$$

6.2 The reaction is exothermic.



6.3 $\Delta T = 25.0°\text{C} - 37.0°\text{C} = -12.0°\text{C} = -12.0\ \text{K}$

$$\text{Mass (g)} = 1.11\ \text{g/mL} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times 5.50\ \text{L} = 6.10\times10^3\ \text{g}$$

$$q = c \times \text{mass} \times \Delta T$$

$$= (2.42\ \text{J/g·K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)(6.10\times10^3\ \text{g})(-12.0\ \text{K}) = -177\ \text{kJ}$$

6.4 $$c_{\text{solid}} = -\frac{4.184\ \text{J/g·K} \times 25.00\ \text{g} \times 1.70\ \text{K}}{12.18\ \text{g} \times (-37.75\ \text{K})} = 0.387\ \text{J/g·K}$$

From Table 6.2, the metal is copper.

6.5 $2HCl(aq) + Ba(OH)_2(aq) \longrightarrow 2H_2O(l) + BaCl_2(aq)$

Amount (mol) of HCl = 0.500 mol HCl/L × 0.0500 L
= 0.0250 mol HCl

Similarly, we have 0.0250 mol $BaCl_2$.
Finding the limiting reactant from the balanced equation:

$$\text{Amount (mol) of } H_2O = 0.0250\ \text{mol HCl} \times \frac{2\ \text{mol } H_2O}{2\ \text{mol HCl}}$$

$$= 0.0250\ \text{mol } H_2O$$

$$\text{Amount (mol) of } H_2O = 0.0250\ \text{mol } Ba(OH)_2 \times \frac{2\ \text{mol } H_2O}{1\ \text{mol } Ba(OH)_2}$$

$$= 0.0500\ \text{mol } H_2O$$

Thus, HCl is limiting.

$$\Delta H\ (\text{kJ/mol } H_2O) = \frac{q_{\text{rxn}}}{\text{mol } H_2O} = \frac{-1.386\ \text{kJ}}{0.0250\ \text{mol } H_2O}$$

$$= -55.4\ \text{kJ/mol } H_2O$$

6.6 $$-q_{\text{sample}} = q_{\text{calorimeter}}$$

$$-(0.8650\ \text{g C})\left(\frac{1\ \text{mol C}}{12.01\ \text{g C}}\right)(-393.5\ \text{kJ/mol C}) = (2.613\ \text{K})x$$

x = heat capacity of calorimeter = 10.85 kJ/K

6.7 $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g) + 137\ \text{kJ}$

$$\text{Heat (kJ)} = 15.0\ \text{kg} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{mol } C_2H_6}{30.07\ \text{g } C_2H_6} \times \frac{137\ \text{kJ}}{1\ \text{mol}}$$

$$= 6.83\times10^4\ \text{kJ}$$

6.8

$$2NO(g) + \tfrac{3}{2}O_2(g) \longrightarrow N_2O_5(s) \qquad \Delta H = -223.7\ \text{kJ}$$

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g) \qquad \Delta H = 114.2\ \text{kJ}$$

$$\cancel{2NO(g)} + \tfrac{1}{2}\,\cancel{\tfrac{3}{2}}O_2(g) + 2NO_2(g) \longrightarrow N_2O_5(s) + \cancel{2NO(g)} + \cancel{O_2(g)}$$

$$2NO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow N_2O_5(s) \qquad \Delta H = -109.5\ \text{kJ}$$

6.9 (a) $C(\text{graphite}) + 2H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3OH(l)$ $\quad \Delta H^\circ_f = -238.6\ \text{kJ}$

(b) $Ca(s) + \tfrac{1}{2}O_2(g) \longrightarrow CaO(s) \quad \Delta H^\circ_f = -635.1\ \text{kJ}$

(c) $C(\text{graphite}) + \tfrac{1}{4}S_8(\text{rhombic}) \longrightarrow CS_2(l) \quad \Delta H^\circ_f = 87.9\ \text{kJ}$

6.10 ΔH°_f of $CH_3OH(l)$

$$= -\Delta H^\circ_{\text{rxn}} + 2\Delta H^\circ_f[H_2O(g)] + \Delta H^\circ_f[CO_2(g)]$$

$$= 638.5\ \text{kJ} + (2\ \text{mol})(-241.8\ \text{kJ/mol}) + (1\ \text{mol})(-393.5\ \text{kJ/mol})$$

$$= -238.6\ \text{kJ}$$

PROBLEMS

Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

Forms of Energy and Their Interconversion

(Sample Problem 6.1)

6.1 If you feel warm after exercising, have you increased the internal energy of your body? Explain.

6.2 An *adiabatic* process is one that involves no heat transfer. What is the relationship between work and the change in internal energy in an adiabatic process?

6.3 Name a common device used to accomplish each change:
(a) Electrical energy to thermal energy
(b) Electrical energy to sound energy
(c) Electrical energy to light energy
(d) Mechanical energy to electrical energy
(e) Chemical energy to electrical energy

6.4 You lift your textbook and drop it onto a desk. Describe the energy transformations (from one form to another) that occur, moving backward in time from a moment after impact.

6.5 A system receives 425 J of heat from and delivers 425 J of work to its surroundings. What is the change in internal energy of the system (in J)?

6.6 A system releases 255 cal of heat to the surroundings and delivers 428 cal of work. What is the change in internal energy of the system (in cal)?

6.7 Complete combustion of 2.0 metric tons of coal to gaseous carbon dioxide releases 6.6×10^{10} J of heat. Convert this energy to (a) kilojoules; (b) kilocalories; (c) British thermal units.

6.8 Thermal decomposition of 5.0 metric tons of limestone to lime and carbon dioxide absorbs 9.0×10^{6} kJ of heat. Convert this energy to (a) joules; (b) calories; (c) British thermal units.

6.9 The nutritional calorie (Calorie) is equivalent to 1 kcal. One pound of body fat is equivalent to about 4.1×10^{3} Calories. Express this quantity of energy in joules and kilojoules.

Enthalpy: Chemical Change at Constant Pressure

(Sample Problem 6.2)

6.10 Classify the following processes as exothermic or endothermic: (a) freezing of water; (b) boiling of water; (c) digestion of food; (d) a person running; (e) a person growing; (f) wood being chopped; (g) heating with a furnace.

6.11 Why can we measure only *changes* in enthalpy, not absolute enthalpy values?

6.12 Draw an enthalpy diagram for a general exothermic reaction; label the axis, reactants, products, and ΔH with its sign.

6.13 Draw an enthalpy diagram for a general endothermic reaction; label the axis, reactants, products, and ΔH with its sign.

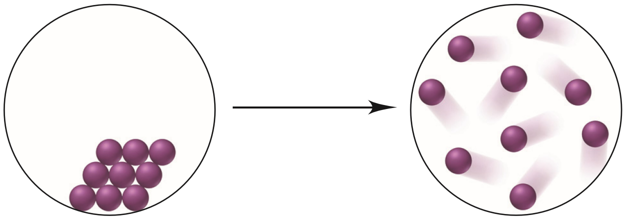
6.14 Write a balanced equation and draw an approximate enthalpy diagram for: (a) combustion of 1 mol of ethane; (b) freezing of liquid water.

6.15 Write a balanced equation and draw an approximate enthalpy diagram for (a) formation of 1 mol of sodium chloride from its elements (heat is released); (b) vaporization of liquid benzene.

6.16 Write a balanced equation and draw an approximate enthalpy diagram for (a) combustion of 1 mol of liquid methanol (CH_3OH); (b) formation of 1 mol of NO_2 from its elements (heat is absorbed).

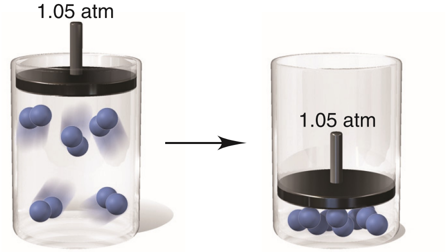
6.17 Write a balanced equation and draw an approximate enthalpy diagram for (a) sublimation of dry ice [conversion of $CO_2(s)$ directly to $CO_2(g)$]; (b) reaction of 1 mol of SO_2 with O_2.

6.18 The circles represent a phase change at constant temperature:



Is the value of each of the following positive (+), negative (−), or zero: (a) q_{sys}; (b) ΔE_{sys}; (c) ΔE_{univ}?

6.19 The scenes below represent a physical change taking place in a piston-cylinder assembly:



(a) Is w_{sys} +, −, or 0? (b) Is ΔH_{sys} +, −, or 0? (c) Can you determine whether ΔE_{surr} is +, −, or 0? Explain.

Calorimetry: Measuring the Heat of a Chemical or Physical Change

(Sample Problems 6.3 to 6.6)

6.20 What data do you need to determine the specific heat capacity of a substance?

6.21 Is the specific heat capacity of a substance an intensive or extensive property? Explain.

6.22 Find q when 22.0 g of water is heated from 25.0°C to 100.°C.

6.23 Calculate q when 0.10 g of ice is cooled from 10.°C to −75°C (c_{ice} = 2.087 J/g·K).

6.24 A 295-g aluminum engine part at an initial temperature of 13.00°C absorbs 75.0 kJ of heat. What is the final temperature of the part (c of Al = 0.900 J/g·K)?

6.25 A 27.7-g sample of the radiator coolant ethylene glycol releases 688 J of heat. What was the initial temperature of the sample if the final temperature is 32.5°C (c of ethylene glycol = 2.42 J/g·K)?

6.26 Two iron bolts of equal mass—one at 100.°C, the other at 55°C—are placed in an insulated container. Assuming the heat capacity of the container is negligible, what is the final temperature inside the container (c of iron = 0.450 J/g·K)?

6.27 One piece of copper jewelry at 105°C has twice the mass of another piece at 45°C. Both are placed in a calorimeter of negligible heat capacity. What is the final temperature inside the calorimeter (c of copper = 0.387 J/g·K)?

6.28 When 155 mL of water at 26°C is mixed with 75 mL of water at 85°C, what is the final temperature? (Assume that no heat is released to the surroundings; d of water is 1.00 g/mL.)

6.29 An unknown volume of water at 18.2°C is added to 24.4 mL of water at 35.0°C. If the final temperature is 23.5°C, what was the unknown volume? (Assume that no heat is released to the surroundings; d of water is 1.00 g/mL.)

6.30 High-purity benzoic acid (C_6H_5COOH; ΔH for combustion = −3227 kJ/mol) is used to calibrate bomb calorimeters. A 1.221-g sample burns in a calorimeter (heat capacity = 1365 J/°C) that contains 1.200 kg of water. What is the temperature change?

6.31 Two aircraft rivets, one iron and the other copper, are placed in a calorimeter that has an initial temperature of 20.°C. The data for the rivets are as follows:

	Iron	Copper
Mass (g)	30.0	20.0
Initial T (°C)	0.0	100.0
c (J/g·K)	0.450	0.387

(a) Will heat flow from Fe to Cu or from Cu to Fe?
(b) What other information is needed to correct any measurements in an actual experiment?
(c) What is the maximum final temperature of the system (assuming the heat capacity of the calorimeter is negligible)?

6.32 When 25.0 mL of 0.500 M H_2SO_4 is added to 25.0 mL of 1.00 M KOH in a coffee-cup calorimeter at 23.50°C, the temperature rises to 30.17°C. Calculate ΔH of this reaction. (Assume the total volume is the sum of the volumes and the density and specific heat capacity of the solution are the same as for water.)

Stoichiometry of Thermochemical Equations

(Sample Problem 6.7)

6.33 Would you expect $O_2(g) \longrightarrow 2O(g)$ to have a positive or a negative ΔH? Explain.

6.34 Is ΔH positive or negative when 1 mol of water vapor condenses to liquid water? Why? How does this value compare with ΔH for the vaporization of 2 mol of liquid water to water vapor?

6.35 Consider the following balanced thermochemical equation for a reaction sometimes used for H_2S production:

$$\tfrac{1}{8}S_8(s) + H_2(g) \longrightarrow H_2S(g) \quad \Delta H = -20.2\ \text{kJ}$$

(a) Is this an exothermic or endothermic reaction?
(b) What is ΔH for the reverse reaction?
(c) What is ΔH when 2.6 mol of S_8 reacts?
(d) What is ΔH when 25.0 g of S_8 reacts?

6.36 Consider the following balanced thermochemical equation for the decomposition of the mineral magnesite:

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g) \quad \Delta H = 117.3\ \text{kJ}$$

(a) Is heat absorbed or released in the reaction?
(b) What is ΔH for the reverse reaction?
(c) What is ΔH when 5.35 mol of CO_2 reacts with excess MgO?
(d) What is ΔH when 35.5 g of CO_2 reacts with excess MgO?

6.37 When 1 mol of NO(g) forms from its elements, 90.29 kJ of heat is absorbed. (a) Write a balanced thermochemical equation. (b) What is ΔH when 3.50 g of NO decomposes to its elements?

6.38 When 1 mol of KBr(s) decomposes to its elements, 394 kJ of heat is absorbed. (a) Write a balanced thermochemical equation. (b) What is ΔH when 10.0 kg of KBr forms from its elements?

6.39 Liquid hydrogen peroxide, an oxidizing agent in many rocket fuel mixtures, releases oxygen gas on decomposition:

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g) \quad \Delta H = -196.1\ \text{kJ}$$

How much heat is released when 652 kg of H_2O_2 decomposes?

6.40 Compounds of boron and hydrogen are remarkable for their unusual bonding (described in Section 14.5) and also for their reactivity. With the more reactive halogens, for example, diborane (B_2H_6) forms trihalides even at low temperatures:

$$B_2H_6(g) + 6Cl_2(g) \longrightarrow 2BCl_3(g) + 6HCl(g) \qquad \Delta H = -755.4\ \text{kJ}$$

What is ΔH per kilogram of diborane that reacts?

6.41 Most ethylene (C_2H_4), the starting material for producing polyethylene, comes from petroleum processing. It also occurs naturally as a fruit-ripening hormone and as a component of natural gas. (a) The heat transferred during combustion of C_2H_4 is −1411 kJ/mol. Write a balanced thermochemical equation. (b) How many grams of C_2H_4 must burn to give 70.0 kJ of heat?

6.42 Sucrose ($C_{12}H_{22}O_{11}$, table sugar) is oxidized in the body by O_2 via a complex set of reactions that produces $CO_2(g)$ and $H_2O(g)$ and releases 5.64×10^3 kJ/mol of sucrose. (a) Write a balanced thermochemical equation for the overall process. (b) How much heat is released per gram of sucrose oxidized?

Hess's Law: Finding ΔH of Any Reaction

(Sample Problem 6.8)

6.43 Express Hess's law in your own words.

6.44 Calculate ΔH for

$$Ca(s) + \tfrac{1}{2}O_2(g) + CO_2(g) \longrightarrow CaCO_3(s)$$

given the following reactions:

$$Ca(s) + \tfrac{1}{2}O_2(g) \longrightarrow CaO(s) \qquad \Delta H = -635.1\ \text{kJ}$$
$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H = 178.3\ \text{kJ}$$

6.45 Calculate ΔH for

$$2NOCl(g) \longrightarrow N_2(g) + O_2(g) + Cl_2(g)$$

given the following reactions:

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO(g) \qquad \Delta H = 90.3\ \text{kJ}$$
$$NO(g) + \tfrac{1}{2}Cl_2(g) \longrightarrow NOCl(g) \qquad \Delta H = -38.6\ \text{kJ}$$

6.46 Write the balanced overall equation (equation 3) for the following process, calculate $\Delta H_{\text{overall}}$, and match the number of each equation with the letter of the appropriate arrow in Figure P6.46 *(facing page)*:

(1) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\qquad \Delta H = 180.6$ kJ
(2) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\qquad \Delta H = -114.2$ kJ
(3) $\qquad \Delta H_{\text{overall}} = ?$

6.47 Write the balanced overall equation (equation 3) for the following process, calculate $\Delta H_{\text{overall}}$, and match the number of each equation with the letter of the appropriate arrow in Figure P6.47:

(1) $P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(g)$ $\quad \Delta H = -1148$ kJ

(2) $4PCl_3(g) + 4Cl_2(g) \longrightarrow 4PCl_5(g)$ $\quad \Delta H = -460$ kJ

(3) $\quad \Delta H_{\text{overall}} = ?$

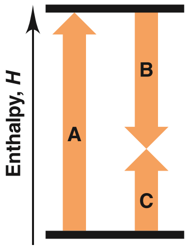


Figure P6.46

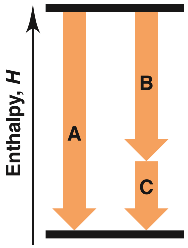


Figure P6.47

6.48 Diamond and graphite are two crystalline forms of carbon. At 1 atm and 25°C, diamond changes to graphite so slowly that the enthalpy change of the process must be obtained indirectly. Using equations from the numbered list below, determine ΔH for

$$C(\text{diamond}) \longrightarrow C(\text{graphite})$$

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

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

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

(4) $2CO(g) \longrightarrow C(\text{graphite}) + CO_2(g)$ $\quad \Delta H = -172.5$ kJ

Standard Enthalpies of Reaction ($\Delta H^\circ_{\text{rxn}}$)

(Sample Problems 6.9 and 6.10)

6.49 What is the difference between the standard enthalpy of formation and the standard enthalpy of reaction?

6.50 Make any changes needed in each of the following equations to make the enthalpy change equal to ΔH°_f for the compound:

(a) $Cl(g) + Na(s) \longrightarrow NaCl(s)$

(b) $H_2O(g) \longrightarrow 2H(g) + \frac{1}{2}O_2(g)$

(c) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

6.51 Use Table 6.3 or Appendix B to write a balanced formation equation at standard conditions for each of the following compounds: (a) $CaCl_2$; (b) $NaHCO_3$; (c) CCl_4; (d) HNO_3.

6.52 Use Table 6.3 or Appendix B to write a balanced formation equation at standard conditions for each of the following compounds: (a) HI; (b) SiF_4; (c) O_3; (d) $Ca_3(PO_4)_2$.

6.53 Calculate $\Delta H^\circ_{\text{rxn}}$ for each of the following:

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

(b) $CH_4(g) + Cl_2(g) \longrightarrow CCl_4(l) + HCl(g)$ [unbalanced]

6.54 Calculate $\Delta H^\circ_{\text{rxn}}$ for each of the following:

(a) $SiO_2(s) + 4HF(g) \longrightarrow SiF_4(g) + 2H_2O(l)$

(b) $C_2H_6(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$ [unbalanced]

6.55 Copper(I) oxide can be oxidized to copper(II) oxide:

$$Cu_2O(s) + \tfrac{1}{2}O_2(g) \longrightarrow 2CuO(s) \quad \Delta H^\circ_{\text{rxn}} = -146.0 \text{ kJ}$$

Given ΔH°_f of $Cu_2O(s) = -168.6$ kJ/mol, find ΔH°_f of $CuO(s)$.

6.56 Acetylene burns in air by the following equation:

$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(g) \quad \Delta H^\circ_{\text{rxn}} = -1255.8 \text{ kJ}$$

Given ΔH°_f of $CO_2(g) = -393.5$ kJ/mol and ΔH°_f of $H_2O(g) = -241.8$ kJ/mol, find ΔH°_f of $C_2H_2(g)$.

6.57 Nitroglycerine, $C_3H_5(NO_3)_3(l)$, a powerful explosive used in mining, detonates to produce a hot gaseous mixture of nitrogen, water, carbon dioxide, and oxygen.

(a) Write a balanced equation for this reaction using the smallest whole-number coefficients.

(b) If $\Delta H^\circ_{\text{rxn}} = -2.29 \times 10^4$ kJ for the equation as written in part (a), calculate ΔH°_f of nitroglycerine.

6.58 The common lead-acid car battery produces a large burst of current, even at low temperatures, and is rechargeable. The reaction that occurs while recharging a "dead" battery is

$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(l)$$

(a) Use ΔH°_f values from Appendix B to calculate $\Delta H^\circ_{\text{rxn}}$.

(b) Use the following equations to check your answer to part (a):

(1) $Pb(s) + PbO_2(s) + 2SO_3(g) \longrightarrow 2PbSO_4(s)$ $\quad \Delta H^\circ_{\text{rxn}} = -768$ kJ

(2) $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$ $\quad \Delta H^\circ_{\text{rxn}} = -132$ kJ

Comprehensive Problems

6.59 Stearic acid ($C_{18}H_{36}O_2$) is a fatty acid, a molecule with a long hydrocarbon chain and an organic acid group (COOH) at the end. It is used to make cosmetics, ointments, soaps, and candles and is found in animal tissue as part of many saturated fats. In fact, when you eat meat, you are ingesting some fats containing stearic acid. (a) Write a balanced equation for the combustion of stearic acid to gaseous products. (b) Calculate $\Delta H^\circ_{\text{rxn}}$ for this combustion (ΔH°_f of $C_{18}H_{36}O_2 = -948$ kJ/mol). (c) Calculate the heat (q) released in kJ and kcal when 1.00 g of stearic acid is burned completely. (d) A candy bar contains 11.0 g of fat and 100. Cal from fat; is this consistent with your answer for part (c)?

6.60 A balloonist begins a trip in a helium-filled balloon in early morning when the temperature is 15°C. By mid-afternoon, the temperature is 30.°C. Assuming the pressure remains at 1.00 atm, for each mole of helium, calculate the following:

(a) The initial and final volumes

(b) The change in internal energy, ΔE (*Hint:* Helium behaves like an ideal gas, so $E = \frac{3}{2}nRT$. Be sure the units of R are consistent with those of E.)

(c) The work (w) done by the helium (in J)

(d) The heat (q) transferred (in J)

(e) ΔH for the process (in J)

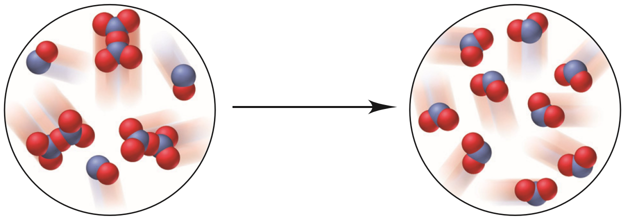
(f) Explain the relationship between the answers to parts (d) and (e).

6.61 In winemaking, the sugars in grapes undergo *fermentation* by yeast to yield CH_3CH_2OH and CO_2. During cellular *respiration* (combustion), sugar and ethanol yield water vapor and CO_2.

(a) Using $C_6H_{12}O_6$ for sugar, calculate $\Delta H^\circ_{\text{rxn}}$ of fermentation and of respiration.

(b) Write a combustion reaction for ethanol. Which has a higher $\Delta H^\circ_{\text{rxn}}$ for combustion per mole of C, sugar or ethanol?

6.62 The following scenes represent a gaseous reaction between compounds of nitrogen (blue) and oxygen (red) at 298 K:

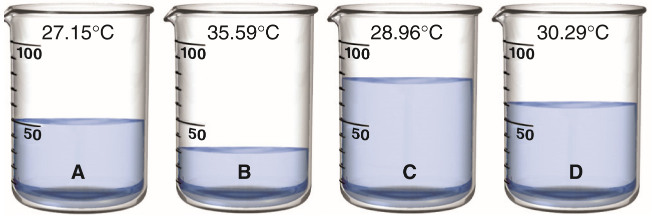


(a) Write a balanced equation and use Appendix B to calculate ΔH°_{rxn}.
(b) If each molecule of product represents 1.50×10^{-2} mol, what quantity of heat (in J) is released or absorbed?

6.63 Iron metal is produced in a blast furnace through a complex series of reactions that involve reduction of iron(III) oxide with carbon monoxide.
(a) Write a balanced overall equation for the process, including the other product.
(b) Use the equations below to calculate ΔH°_{rxn} for the overall equation:
(1) $3Fe_2O_3(s) + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g)$ $\Delta H^\circ = -48.5$ kJ
(2) $Fe(s) + CO_2(g) \longrightarrow FeO(s) + CO(g)$ $\Delta H^\circ = -11.0$ kJ
(3) $Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g)$ $\Delta H^\circ = 22$ kJ

6.64 Pure liquid octane (C_8H_{18}; $d = 0.702$ g/mL) is used as the fuel in a test of a new automobile drive train.
(a) How much energy (in kJ) is released by complete combustion of the octane in a 20.4-gal fuel tank to gases ($\Delta H^\circ_{rxn} = -5.45\times10^3$ kJ/mol)?
(b) The energy delivered to the wheels at 65 mph is 5.5×10^4 kJ/h. Assuming all the energy is transferred to the wheels, what is the cruising range (in km) of the car on a full tank?
(c) If the actual cruising range is 455 miles, explain your answer to part (b).

6.65 Four 50.-g samples of different liquids are placed in separate beakers at $T_{initial} = 25.00$°C. Each liquid is heated until 450. J of heat has been absorbed; T_{final} is shown on each beaker below. Rank the liquids in order of increasing specific heat capacity.



6.66 When simple sugars, called *monosaccharides,* link together, they form a variety of complex sugars and, ultimately, *polysaccharides,* such as starch, glycogen, and cellulose. Glucose and fructose have the same molecular formula, $C_6H_{12}O_6$, but different arrangements of atoms. A molecule of glucose links with one of fructose to form a molecule of sucrose (table sugar) and a molecule of liquid water. The ΔH°_f values for glucose, fructose, and sucrose are -1273 kJ/mol, -1266 kJ/mol, and -2226 kJ/mol, respectively. Write a balanced equation for this reaction and calculate ΔH°_{rxn}.

6.67 Reaction of gaseous ClF with F_2 yields liquid ClF_3, an important fluorinating agent. Use the following thermochemical equations to calculate ΔH°_{rxn} for this reaction:
(1) $2ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g)$ $\Delta H^\circ_{rxn} = 167.5$ kJ
(2) $2F_2(g) + O_2(g) \longrightarrow 2OF_2(g)$ $\Delta H^\circ_{rxn} = -43.5$ kJ
(3) $2ClF_3(l) + 2O_2(g) \longrightarrow Cl_2O(g) + 3OF_2(g)$ $\Delta H^\circ_{rxn} = 394.1$ kJ

6.68 Silver bromide is used to coat ordinary black-and-white photographic film, while high-speed film uses silver iodide.
(a) When 50.0 mL of 5.0 g/L $AgNO_3$ is added to a coffee-cup calorimeter containing 50.0 mL of 5.0 g/L NaI, with both solutions at 25°C, what mass of AgI forms?
(b) Use Appendix B to find ΔH°_{rxn}.
(c) What is ΔT_{soln} (assuming the volumes are additive and the solution has the density and specific heat capacity of water)?

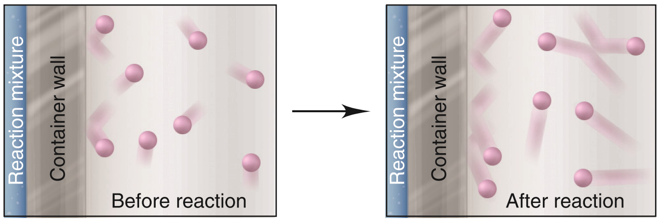
6.69 When organic matter decomposes under oxygen-free (anaerobic) conditions, methane is one of the products. Thus, enormous deposits of natural gas, which is almost entirely methane, serve as a major source of fuel for home and industry.
(a) Known deposits of natural gas can produce 5600 EJ of energy (1 EJ = 10^{18} J). Current total global energy usage is 4.0×10^2 EJ per year. Find the mass (in kg) of known deposits of natural gas (ΔH°_{rxn} for the combustion of $CH_4 = -802$ kJ/mol).
(b) At current rates of usage, for how many years could these deposits supply the world's total energy needs?
(c) What volume (in ft^3) of natural gas, measured at STP, is required to heat 1.00 qt of water from 25.0°C to 100.0°C (d of $H_2O = 1.00$ g/mL; d of CH_4 at STP = 0.72 g/L)?
(d) The fission of 1 mol of uranium (about 4×10^{-4} ft^3) in a nuclear reactor produces 2×10^{13} J. What volume (in ft^3) of natural gas would produce the same amount of energy?

6.70 The heat of atomization (ΔH°_{atom}) is the heat needed to form separated gaseous atoms from a substance in its standard state. The equation for the atomization of graphite is

$$C(graphite) \longrightarrow C(g)$$

Use Hess's law to calculate ΔH°_{atom} of graphite from these data:
(1) ΔH°_f of $CH_4 = -74.9$ kJ/mol
(2) ΔH°_{atom} of $CH_4 = 1660$ kJ/mol
(3) ΔH°_{atom} of $H_2 = 432$ kJ/mol

6.71 A reaction takes place in a steel vessel within a chamber filled with argon gas. Shown below are molecular views of the argon adjacent to the surface of the reaction vessel before and after the reaction. Was the reaction exothermic or endothermic? Explain.



6.72 Benzene (C_6H_6) and acetylene (C_2H_2) have the same empirical formula, CH. Which releases more energy per mole of CH (ΔH°_f of gaseous $C_6H_6 = 82.9$ kJ/mol)?

6.73 An aqueous waste stream with a maximum concentration of 0.50 *M* H_2SO_4 ($d = 1.030$ g/mL at 25°C) is neutralized by controlled addition of 40% NaOH ($d = 1.430$ g/L) before it goes to the process sewer and then to the chemical plant waste treatment facility. A safety review finds that the waste stream could meet a small stream of an immiscible organic compound, which could form a flammable vapor in air at 40.°C. The maximum temperature reached by the NaOH solution and the waste stream is 31°C. Could the temperature increase due to the heat transferred by the neutralization cause the organic vapor to explode? Assume the specific heat capacity of each solution is 4.184 J/g·K.

6.74 Kerosene, a common space-heater fuel, is a mixture of hydrocarbons whose "average" formula is $C_{12}H_{26}$.
(a) Write a balanced equation, using the simplest whole-number coefficients, for the complete combustion of kerosene to gases.
(b) If $\Delta H^\circ_{rxn} = -1.50\times10^4$ kJ for the combustion equation as written in part (a), determine ΔH°_f of kerosene.
(c) Calculate the heat released by combustion of 0.50 gal of kerosene (d of kerosene = 0.749 g/mL).

(d) How many gallons of kerosene must be burned for a kerosene furnace to produce 1250. Btu (1 Btu = 1.055 kJ)?

6.75 Coal gasification is a multistep process to convert coal into cleaner-burning gaseous fuels. In one step, a certain coal sample reacts with superheated steam:

$$\mathrm{C(coal)} + \mathrm{H_2O}(g) \longrightarrow \mathrm{CO}(g) + \mathrm{H_2}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = 129.7\ \mathrm{kJ}$$

(a) Combine this reaction with the following two to write an overall reaction for the production of methane:

$$\mathrm{CO}(g) + \mathrm{H_2O}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{H_2}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -41\ \mathrm{kJ}$$
$$\mathrm{CO}(g) + 3\mathrm{H_2}(g) \longrightarrow \mathrm{CH_4}(g) + \mathrm{H_2O}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -206\ \mathrm{kJ}$$

(b) Calculate $\Delta H^\circ_{\mathrm{rxn}}$ for this overall change.
(c) Using the value in (b) and calculating the $\Delta H^\circ_{\mathrm{rxn}}$ for combustion of methane, find the total heat for gasifying 1.00 kg of coal and burning the methane formed (assume water forms as a gas and $\mathcal{M}$ of coal = 12.00 g/mol).

6.76 Phosphorus pentachloride is used in the industrial preparation of organic phosphorus compounds. Equation 1 shows its preparation from $\mathrm{PCl_3}$ and $\mathrm{Cl_2}$:

$$(1)\ \mathrm{PCl_3}(l) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{PCl_5}(s)$$

Use equations 2 and 3 to calculate ΔH_{rxn} for equation 1:

$$(2)\ \mathrm{P_4}(s) + 6\mathrm{Cl_2}(g) \longrightarrow 4\mathrm{PCl_3}(l) \qquad \Delta H = -1280\ \mathrm{kJ}$$
$$(3)\ \mathrm{P_4}(s) + 10\mathrm{Cl_2}(g) \longrightarrow 4\mathrm{PCl_5}(s) \qquad \Delta H = -1774\ \mathrm{kJ}$$

6.77 A typical candy bar weighs about 2 oz (1.00 oz = 28.4 g).
(a) Assuming that a candy bar is 100% sugar and that 1.0 g of sugar is equivalent to about 4.0 Calories of energy, calculate the energy (in kJ) contained in a typical candy bar.
(b) Assuming that your mass is 58 kg and you convert chemical potential energy to work with 100% efficiency, how high would you have to climb to work off the energy in a candy bar? (Potential energy = mass × g × height, where $g = 9.8\ \mathrm{m/s^2}$.)
(c) Why is your actual conversion of potential energy to work less than 100% efficient?

6.78 Silicon tetrachloride is produced annually on the multikiloton scale and used in making transistor-grade silicon. It can be produced directly from the elements (reaction 1) or, more cheaply, by heating sand and graphite with chlorine gas (reaction 2). If water is present in reaction 2, some tetrachloride may be lost in an unwanted side reaction (reaction 3):

$$(1)\ \mathrm{Si}(s) + 2\mathrm{Cl_2}(g) \longrightarrow \mathrm{SiCl_4}(g)$$
$$(2)\ \mathrm{SiO_2}(s) + 2\mathrm{C(graphite)} + 2\mathrm{Cl_2}(g) \longrightarrow \mathrm{SiCl_4}(g) + 2\mathrm{CO}(g)$$
$$(3)\ \mathrm{SiCl_4}(g) + 2\mathrm{H_2O}(g) \longrightarrow \mathrm{SiO_2}(s) + 4\mathrm{HCl}(g)$$
$$\Delta H^\circ_{\mathrm{rxn}} = -139.5\ \mathrm{kJ}$$

(a) Use reaction 3 to calculate the standard enthalpies of reaction of reactions 1 and 2. (b) What is the standard enthalpy of reaction for a fourth reaction that is the sum of reactions 2 and 3?

6.79 Use the following information to find $\Delta H^\circ_{\mathrm{f}}$ of gaseous HCl:

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -91.8\ \mathrm{kJ}$$
$$\mathrm{N_2}(g) + 4\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\mathrm{NH_4Cl}(s) \qquad \Delta H^\circ_{\mathrm{rxn}} = -628.8\ \mathrm{kJ}$$
$$\mathrm{NH_3}(g) + \mathrm{HCl}(g) \longrightarrow \mathrm{NH_4Cl}(s) \qquad \Delta H^\circ_{\mathrm{rxn}} = -176.2\ \mathrm{kJ}$$

6.80 You want to determine ΔH° for the reaction

$$\mathrm{Zn}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g)$$

(a) To do so, you first determine the heat capacity of a calorimeter using the following reaction, whose ΔH is known:

$$\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \qquad \Delta H^\circ = -57.32\ \mathrm{kJ}$$

Calculate the heat capacity of the calorimeter from these data:

Amounts used: 50.0 mL of 2.00 *M* HCl and
50.0 mL of 2.00 *M* NaOH
Initial *T* of both solutions: 16.9°C
Maximum *T* recorded during reaction: 30.4°C
Density of resulting NaCl solution: 1.04 g/mL
c of 1.00 *M* NaCl(*aq*) = 3.93 J/g·K

(b) Use the result from part (a) and the following data to determine $\Delta H^\circ_{\mathrm{rxn}}$ for the reaction between zinc and HCl(*aq*):

Amounts used: 100.0 mL of 1.00 *M* HCl and 1.3078 g of Zn
Initial *T* of HCl solution and Zn: 16.8°C
Maximum *T* recorded during reaction: 24.1°C
Density of 1.0 *M* HCl solution = 1.015 g/mL
c of resulting $\mathrm{ZnCl_2}(aq)$ = 3.95 J/g·K

(c) Given the values below, what is the error in your experiment?

$$\Delta H^\circ_{\mathrm{f}}\ \text{of}\ \mathrm{HCl}(aq) = -1.652\times10^2\ \mathrm{kJ/mol}$$
$$\Delta H^\circ_{\mathrm{f}}\ \text{of}\ \mathrm{ZnCl_2}(aq) = -4.822\times10^2\ \mathrm{kJ/mol}$$

6.81 One mole of nitrogen gas confined within a cylinder by a piston is heated from 0°C to 819°C at 1.00 atm.
(a) Calculate the work done by the expanding gas in joules ($1\ \mathrm{J} = 9.87\times10^{-3}\ \mathrm{atm{\cdot}L}$). Assume all the energy is used to do work.
(b) What would be the temperature change if the gas were heated using the same amount of energy in a container of fixed volume? (Assume the specific heat capacity of $\mathrm{N_2}$ is 1.00 J/g·K.)

6.82 The chemistry of nitrogen oxides is very versatile. Given the following reactions and their standard enthalpy changes,

$$(1)\ \mathrm{NO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{N_2O_3}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -39.8\ \mathrm{kJ}$$
$$(2)\ \mathrm{NO}(g) + \mathrm{NO_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{N_2O_5}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -112.5\ \mathrm{kJ}$$
$$(3)\ 2\mathrm{NO_2}(g) \longrightarrow \mathrm{N_2O_4}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -57.2\ \mathrm{kJ}$$
$$(4)\ 2\mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{NO_2}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -114.2\ \mathrm{kJ}$$
$$(5)\ \mathrm{N_2O_5}(s) \longrightarrow \mathrm{N_2O_5}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = 54.1\ \mathrm{kJ}$$

calculate the standard enthalpy of reaction for

$$\mathrm{N_2O_3}(g) + \mathrm{N_2O_5}(s) \longrightarrow 2\mathrm{N_2O_4}(g)$$

6.83 Liquid methanol ($\mathrm{CH_3OH}$) can be used as an alternative fuel in pickup and SUV engines. An industrial method for preparing it involves the catalytic hydrogenation of carbon monoxide:

$$\mathrm{CO}(g) + 2\mathrm{H_2}(g) \xrightarrow{\text{catalyst}} \mathrm{CH_3OH}(l)$$

How much heat (in kJ) is released when 15.0 L of CO at 85°C and 112 kPa reacts with 18.5 L of $\mathrm{H_2}$ at 75°C and 744 torr?

6.84 (a) How much heat is released when 25.0 g of methane burns in excess $\mathrm{O_2}$ to form gaseous $\mathrm{CO_2}$ and $\mathrm{H_2O}$?
(b) Calculate the temperature of the product mixture if the methane and air are both at an initial temperature of 0.0°C. Assume a stoichiometric ratio of methane to oxygen from the air, with air being 21% $\mathrm{O_2}$ by volume (*c* of $\mathrm{CO_2}$ = 57.2 J/mol·K; *c* of $\mathrm{H_2O}(g)$ = 36.0 J/mol·K; *c* of $\mathrm{N_2}$ = 30.5 J/mol·K).